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OPTICALLY ACTIVE POLYPYRAZOLYLBORATE MOLYBDENUM COMPLEXES WITH AMINOPHOSPHINES AS CHIRAL LIGANDS

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Summary

The prochiral polypyrazolylborate complexes $[R-B(3,5\text{-}X_2\text{-}pz)_3]Mo(CO)_2(NO)$ ($R = pz$, $X = H$; $R = H$, $X = CH_3$), react with the optically active aminophosphines $L = (C_6H_5)_2PNR'CH(CH_3)(C_6H_5)$ ($R' = H$, CH_3), to give the monosubstitution products $[R-B(3,5\text{-}X_2\text{-}pz)_3]Mo(CO)(NO)L$, in which the metal atom is a new chiral center. The separation of the diastereoisomers, differing only in the Mo configuration, by preparative liquid chromatography and fractional crystallization is described, their CD and ^1H NMR spectra and their reactivities are discussed and compared with those of the cyclopentadienyl analogues.

Introduction

The polypyrazolylborate ligands are uninegative chelating ligands of general structure $[R_nB(pz)_{4-n}]^-$ were R is a noncoordinating substituent, pz is a 1-pyrazolyl group and n may be 0, 1 or 2 [1]. The tris(pyrazolyl)borate ions are unique in forming a number of complexes analogous to their well-known cyclopentadienyl counterparts. Although structurally similar, the tris(pyrazolyl)borate complexes are generally more stable than the cyclopentadienyl compounds [2,3].

Continuing interest in organometallic stereochemistry and asymmetric catalysis leads to a steady increase in the study of optically active organometallic complexes. Most of the chiral complexes described with asymmetric metal atoms contain a cyclopentadienyl ligand [4]. As there is no report on optically active polypyrazolylborate complexes we tried to synthesize such species. We choose the polypyrazolylborate–Mo(CO)(NO)–aminophosphine system, because the corresponding optically active cyclopentadienyl–Mo(CO)(NO)–aminophosphine derivatives [5,6] are

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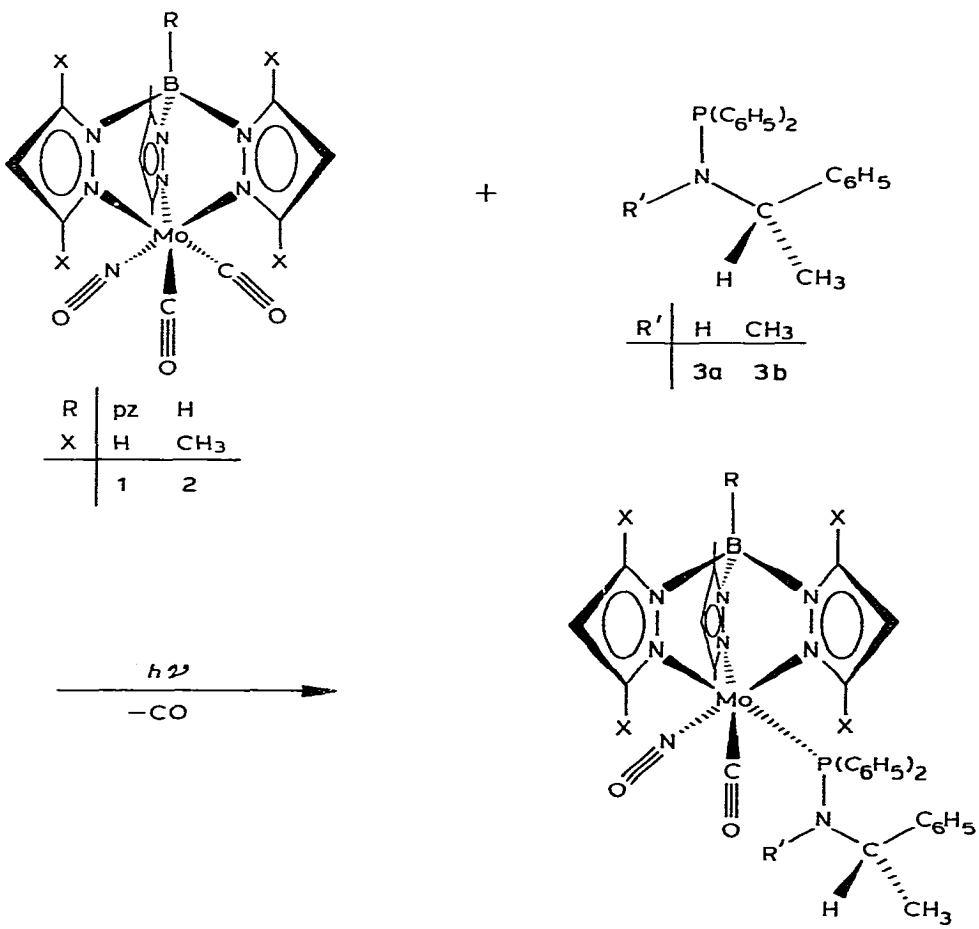
well known. So a comparison with respect to diastereoisomer separation, configurational stability, chiroptical properties and NMR differentiability of diastereoisomers could be carried out.

Preparation of the complexes

Triphenylphosphine quantitatively replaces a CO ligand in $C_5H_5Mo(CO)_2NO$ in boiling benzene [7], whereas in boiling DMF the corresponding monosubstitution occurs only to the extent of 80% in **1** and to 40% in **2** [8]. Ligands **3a** and **3b** react with $C_5H_5Mo(CO)_2NO$ only under more vigorous conditions. Heating of $C_5H_5Mo(CO)_2NO$ with **3a** and **3b**, respectively, without a solvent yields 75% of the monosubstitution products [6]. However, **1** and **2** do not react with **3a** and **3b** in boiling DMF, diglyme or without a solvent prior to decomposition.

The irradiation of solutions of **1** with **3a**, **3b** and of **2** with **3a** in toluene gives the corresponding monosubstitution products **1-3a**, **1-3b**, and **2-3a** in yields of about 10% according to Scheme 1. For the sake of clarity substituents X on the rear pyrazolyl ring are ommitted.



SCHEME 1

TABLE 1

ANALYTICAL DATA, YIELDS, AND PROPERTIES OF THE NEW MONOSUBSTITUTION PRODUCTS

	Formula Mol. weight	Analysis: Found (calcd.) (%)			Yield (%)	Colour	M.p. (°C)
		C	H	N			
1-3a	$C_{33}H_{32}BMoN_{10}O_2P$ 738.1	53.73 (53.70)	4.34 (4.37)	18.89 (18.98)	11	brick-red	143 [a]
1-3b	$C_{34}H_{34}BMoN_{10}O_2P$ 752.4	54.27 (54.27)	4.41 (4.55)	18.58 (18.62)	9	dark-red	177 [a] 221 [b]
2-3a	$C_{36}H_{42}BMoN_8O_2P$ 756.5	57.18 (57.16)	5.84 (5.60)	15.33 (14.81)	11	light-red	188 [a]
$PH(C_6H_5)_2$-derivative	$C_{28}H_{33}BMoN_7O_2P$ 637.3	52.76 (52.81)	5.15 (5.15)	15.18 (15.38)	12	brick-red	198

[a] Diastereoisomer mixture. [b] Optically pure diastereoisomer (−)**1-3b**.

Attempts to synthesize the monosubstitution products by photochemical generation of the cyclooctene or THF derivatives of complexes **1** and **2** [9,10], followed by a dark reaction with phosphines **3a** and **3b** were unsuccessful due to complete decarbonylation and denitrosylation. Similar results were obtained by increasing the light intensity or by extending the irradiation time in the direct photochemical reaction.

Results different from those shown in Scheme 1 were obtained in the photochemical reaction of **2** with **3b**. The monosubstitution product, isolated as in the other cases, turned out to be the compound $HB[3,5\text{-}(CH_3)_2\text{-}pz]_3Mo(CO)(NO)PH(C_6H_5)_2$, in which the $PH(C_6H_5)_2$-ligand is a degradation product of phosphine **3b**.

After column chromatography on silica gel the complexes are analytically pure. Their analytical data, properties and yields are summarized in Table 1. In the solid state all the compounds are air-stable. In solution complexes **2-3a** and $HB[3,5\text{-}(CH_3)_2\text{-}pz]_3Mo(CO)(NO)PH(C_6H_5)_2$ are also air stable, whereas the solutions of complexes **1-3a** and **1-3b** decompose slowly on exposure to air.

The observed stabilities and reactivities of the Mo(CO)(NO)L complexes in the series cyclopentadienyl, $RB(pz)_3$ and $HB[3,5\text{-}(CH_3)_2\text{-}pz]_3$ can be related to the steric requirements of the ligands. In analogy to the phosphines [11] the available structural data [12–14] can be used to determine the following cone angles: C_5H_5Mo 100°, $RB(pz)_3Mo$ 180° and $HB[3,5\text{-}(CH_3)_2\text{-}pz]_3Fe$ 225°. It is well known that the additional methyl substituents in the 3,5-dimethylpyrazolylborate ligand change the reactivities of the complexes compared to those of the unsubstituted derivatives [15–18]. Some consequences of the increased steric shielding of the metal atom by the methyl substituents in the $HB[3,5\text{-}(CH_3)_2\text{-}pz_3]$ complexes in the present work are the reduced air-sensitivity of **2-3a** and the corresponding $PH(C_6H_5)_2$ derivative, as well as the degradation of the aminophosphine **3b** in the reaction with **2** which would give the sterically most congested product. Side reactions to form $PH(C_6H_5)_2$-complexes are not observed in the reaction of **1** with **3a** and **3b** and in the reaction of **2** with **3a**.

Diastereoisomer separation and configurational stability

For the preparation of complexes **1-3a**, **1-3b**, and **2-3a**, according to Scheme 1 the optically pure (*S*)-aminophosphines **3a** [6] and **3b** [19] were used. In each case a pair of diastereoisomers is formed, the components of which differ only in the metal configuration. Only one of the two possible diastereoisomers is shown in Scheme 1. Whereas the corresponding diastereoisomers of the C_5H_5 analogues can be easily separated [6] by fractional crystallization and by preparative liquid chromatography with Merck Lobar columns, the separation of the diastereoisomers of **1-3a**, **1-3b**, and **2-3a** is more difficult. Preparative liquid chromatography with toluene/petrolether or methylene chloride/methanol in all three cases leads to broad bands, in which the faster and the slower migrating diastereoisomers are enriched in the first and the last fractions. The middle fractions, containing most of the material, do not show appreciable optical activity (Table 2).

Diastereoisomer separation by fractional crystallization works best with **1-3b**. Less soluble (−)**1-3b** can be obtained optically pure by repeated crystallization from methylene chloride/methanol. From the mother liquor of the first crystallization (+)**1-3b** is isolated in an enrichment of 92/8. Table 2 summarizes the optical rotations of the stereoisomers obtained.

The configuration at the Mo atom of optically pure (−)**1-3b** in the solid state is stable at room temperature. Solutions of (−)**1-3b** in toluene, CH_2Cl_2 and THF do not show a drop in optical rotation after standing 24 h at room temperature. A ^1H NMR investigation demonstrates that (−)**1-3b** and (+)**2-3a** in C_6D_6 in sealed NMR tubes neither epimerize nor decompose during 48 h at 70°C. Furthermore, in C_6D_6 solution there is no phosphine exchange when **1-3b** is treated with an excess of triphenylphosphine.

Spectra

In the IR spectra of all the monosubstitution products described the CO frequencies are in the range 1890–1920 cm^{-1} and the NO frequencies in the range

TABLE 2

SPECIFIC OPTICAL ROTATIONS (3×10^{-3} *M* solutions in toluene), polarimeter Perkin–Elmer 241

λ (nm)		$[\alpha]_\lambda^{25}$ (°)		$[\alpha]_\lambda^{25}$ (°)
546	(−)**1-3a** [b,c,e]	+13		
436	52/48 [d]	−28		
546	(−)**1-3b** [a,c,e]	+330	(+)**1-3b** [a,e]	−355
436	opt. pure [d]	−1275	92/8 [d]	+1265
546	(−)**2-3a** [b,e]	+17	(+)**2-3a** [b,c,e]	−25
436	53/47 [d]	−32	56/44 [d]	+44

[a] Enriched by fractional crystallization. [b] Enriched by preparative liquid chromatography. [c] Faster migrating diastereoisomer. [d] Diastereoisomer ratios determined by planimetry of suitable expanded ^1H NMR signals. [e] Prefix (−) or (+) in front of compound number refers to sign of optical rotation at λ 436 nm throughout the paper.

1600–1640 cm^{-1} (KBr and toluene solution). It is noteworthy that the complexes **1-3a** and **2-3a** containing the NH-aminophosphine **3a** exhibit 2 CO and 2 NO bands in agreement with observations on C_5H_5Fe complexes of the same aminophosphine **3a** [20].

Figure 1 shows the CD spectra of optically pure (−)**1-3b** and (+)**1-3b**, the latter enriched to the extent of 92/8. As usual for diastereoisomers differing only in the metal configuration, the CD spectra are almost mirror images [4].

Figure 2, the ^1H NMR spectrum of (+)**2-3a** (enrichment 56/44), and the spectra of all the other monosubstitution products (Table 3) clearly show that the poly-pyrazolylborate ligand is fixed in a definite position and does not rotate freely in the complexes. For each diastereoisomer of **1-3a** and **1-3b**, four triplets arising from the 4-H pyrazolyl signals (ratio 1/1/1/1) are observed, and for each diastereoisomer of **2-3a** and for $HB[3,5\text{-}(CH_3)_2\text{-}pz]_3Mo(CO)(NO)PH(C_6H_5)_2$ six singlets of equal intensity for the 3,5-methyl groups of the pyrazoles. Free rotation would require in the first case two 4-H signals for coordinated and uncoordinated pyrazolyl rings (ratio 3/1) and in the second case two signals for the 3,5-methyl groups (ratio 1/1).

For complexes **1-3a** and **1-3b** the signals of the 3.5-protons of the pyrazolyl rings coincide with the phenyl signals and only the signals of the 4-protons can be observed. The diastereoisomers of **1-3a** in C_6D_6 solution do not differ in the chemical shifts of their 4-H pyrazolylborate signals. However, a diastereoisomer differentiation is possible for **1-3b**, because only two of the four triplets of each diastereoisomer coincide in $CDCl_3$ solution (Table 3).

For each of the two diastereoisomers of complex **2-3a**, six signals for the different

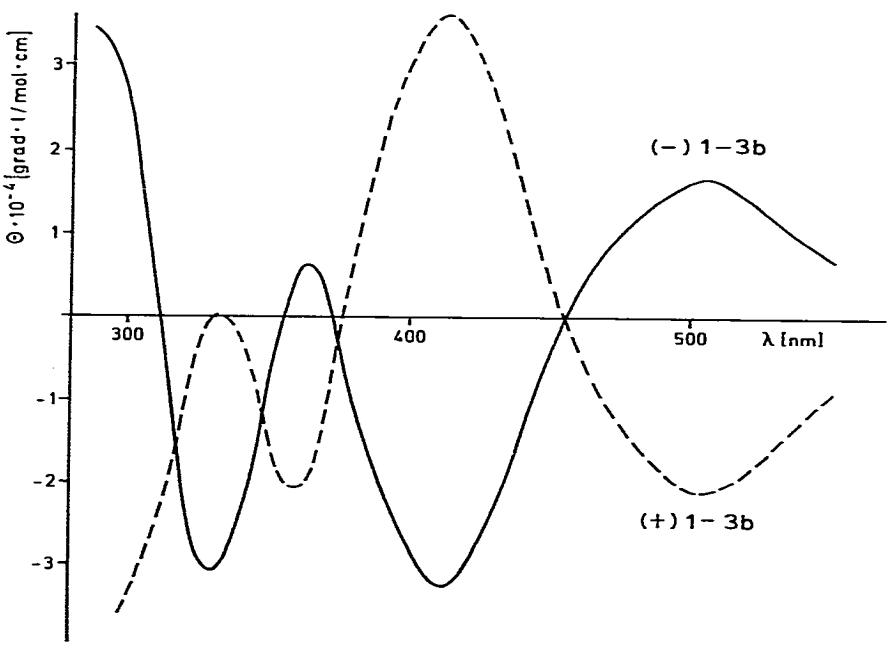


Fig. 1. CD spectra of (−)**1-3b** (optically pure) and (+)**1-3b** (enrichment 92/8), 3×10^{-3} *M* solution in toluene, Jasco 40A.

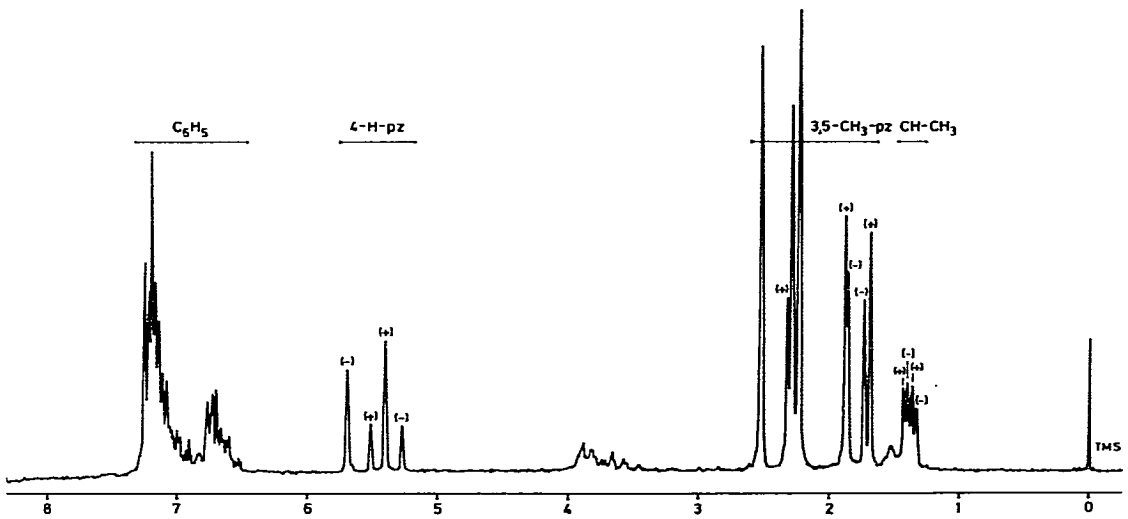


Fig. 2. ^{1}H NMR spectrum of a (+)2-3a/(−)2-3a mixture of 56/44 in $CDCl_3$ solution (i-TMS). Bruker WH 90.

3- and 5-methyl groups are expected. As Fig. 2 shows, there are 8 methyl signals present. The three more intense signals of the 5-methyl groups pointing away from the metal do not show diastereoisomer splitting, whilst the resonances of the 3-methyl groups close to the metal are well resolved for both diastereoisomers, the sixth signal coinciding with one of the 5-methyl signals. The trend in the diastereoisomer splitting of 0.08, 0.05 and 0.02 ppm probably reflects the varying distance to the chiral aminophosphine. For **2-3a** the 4-H pyrazolyl signals are especially well separated for the two diastereoisomers (+)**2-3a** and (−)**2-3a** (Fig. 2).

Thus, in the ^{1}H NMR spectra of complexes **1-3a** and **2-3a** the pyrazolylborate ligand exhibits signals sufficiently separated for both diastereoisomers to allow determination of the diastereomer ratio. In addition, in all cases the separation of the N-methyl and/or C-methyl doublets of the amine part (Fig. 2, Table 3) is large enough for both diastereoisomers to permit the estimation of the diastereoisomeric purity.

Experimental

All operations were carried out under nitrogen with anhydrous solvents. Starting materials: (S)-(−)-diphenyl(1-phenylethylamino)phosphine, **3a** [6], (S)-(+)-methyl(1-phenylethylamino)diphenylphosphine, **3b** [19], dicarbonylnitrosyl(tetra-1-pyrazolylborate)molybdenum, **1** [21], dicarbonylnitrosyl(hydrotris-3,5-dimethyl-1-pyrazolylborate)molybdenum, **2** [21].

*Preparation of complexes **1-3a, 1-3b, 2-3a***

A solution of 0.010 mol of the dicarbonylnitrosyl Mo complex **1**, **2** and 0.011 mol of the aminophosphine **3a**, **3b** in 300 ml toluene is prepared, and 50 ml portions of it are irradiated in a Pyrex apparatus with a 150 W mercury lamp for 30 min. The 6

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	C*H*-CH_3	3,5-Me-pz	NH N-CH_3	CH-C*H*$_3$	P-H
(+)**1-3a** [d]	6.61–7.91m	6.24t (2.0), 5.74t (2.0) 5.63t (2.0), 5.24t (2.2)	3.91m		1.32 [c]	1.07d (6.8)	
(−)**1-3a** [d]	6.61–7.91m	6.24t (2.0), 5.74t (2.0) 5.55t (2.0), 5.36t (2.2)	3.91m		1.32 [c]	1.20d (6.6)	
(+)**1-3b** [d]	6.60–8.01m	6.29t (2.0), 5.74t (2.0) 5.57t (2.2), 5.27t (2.0)	3.15m		12.12d (7.4)	1.79d (7.0)	
(−)**1-3b** [d]	6.60–8.01m	identical to (+)**1-3b**	3.15m		2.17d (7.2)	1.72d (7.0)	
(+)**2-3a** [e]	6.63–7.29m	5.54s, 5.43s	3.82m	2.53s, 2.32s 2.29s, 2.24s 1.88s, 1.69s	1.69 [c]	1.40d (6.09)	
(−)**2-3a** [e]	6.63–7.29m	5.73s, 5.29s	3.82m	2.53s, 2.29s 2.24s, 1.86s 1.74s	1.69 [c]	1.37d (6.47)	
$PH(C_6H_5)_2$ [e] derivative	7.08–7.32	5.77s, 5.65s, 5.60s		2.50s, 2.41s 2.38s, 2.32s 1.97s, 1.94s			6.98d (327.4)

[a] Bruker-Spectrometer WH 90, m, multiplet; t, triplet; s, singlet; d, doublet. [b] Intergrals in agreement with proposed structures. [c] Broad NH-signal. [d] C_6D_6 (i-TMS). [e] $CDCl_3$ (i-TMS).

portions are combined and concentrated. The resulting black solution is transferred to a chromatography column (*l* 60 cm, *d* 3 cm, silica gel). Elution with toluene/petroleum ether (1/1) gives a yellow band of unreacted starting material. Elution with toluene than gives the red band of complexes **1-3a**, **1-3b**, **2-3a** and $HB[3,5\text{-}(CH_3)_2\text{-}pz]_3Mo(CO)(NO)PH(C_6H_5)_2$. After evaporation of the solvent the residue is dissolved in several ml of toluene. A fivefold quantity of petroleum ether is added and the solution is allowed to crystallize at −25°C.

$(-)_{436}$-Carbonylnitrosyl(tetrakis-1-pyrazolylborate)(S)-[methyl(1-phenylethyl)amino]diphenylphosphine}molybdenum (-)1-3b by fractional crystallization

To the solution of 1.2 g **1-3b** in 18 ml CH_2Cl_2 are added 36 ml CH_3OH and the mixture is allowed to crystallize at room temperature. Red crystals are formed. After one day the supernatant solution, enriched in (+)**1-3b**, is decanted. The crystals are washed with petroleumether (40–60°C) and dried. After six crystallizations from CH_2Cl_2/CH_3OH (1/2), with the volume of solvent reduced in proportion to the decreasing amount of material, (−)**1-3b** is obtained optically pure in about 10% yield.

The mother liquor from the first crystallization is passed through three Merck Lobar columns, type B, (toluene/ petrolether 1/4) as described below, giving (+)**1-3b** (enrichment 92/8).

Diastereoisomer separation by preparative liquid chromatography

For the chromatographic separation of the diastereoisomers of **1-3a**, **1-3b**, and **2-3a**, approximately 0.5 g of material in 5 ml solvent and prepacked Merck Lobar columns type B were used. The set-up has been described previously [5,6]. For the chromatography of **1-3a** and **1-3b** toluene/petrolether (1/1) and for **2-3a** toluene/petroleumether (1/4) were used as solvent. After passage through three columns the broad red band was collected in 8 equal fractions. Only the first and the last fraction exhibited appreciable optical activity, as indicated in Table 2.

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