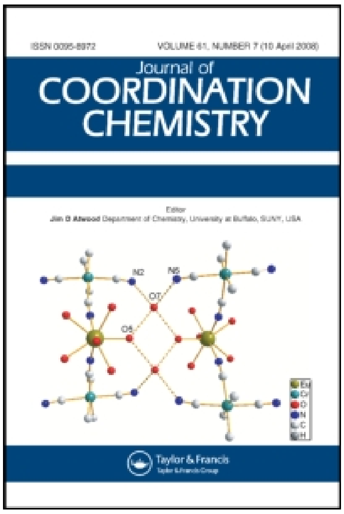

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R. B. King[a]; P. R. Heckley[a]
[a] Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

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ISOCYANIDE-METAL COMPLEXES. V. OCTAHEDRAL METAL CARBONYL COMPLEXES OF THE OPTICALLY PURE ENANTIOMERS OF α-METHYLBENZYLISOCYANIDE[1]

R. B. KING and P. R. HECKLEY

Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

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Octahedral metal complexes of the types $LMo(CO)_5$, cis-$L_2M(CO)_4$, and fac-$L_3M(CO)_3$ (M = Cr, Mo, and W) containing the optically pure enantiomers of α-methylbenzylisocyanide (L) as ligand have been prepared by conventional methods. The specific $[\alpha]_D^{25}$ and molar $[\phi]_D^{25}$ rotations of the resulting optically active metal carbonyl complexes have been measured. The molar rotations $[\phi]_D^{25}$ of the $LMo(CO)_5$ (+58°) and cis-$L_2M(CO)_4$ (± 118–126°) complexes increase incrementally with the number of optically active ligands (L) in the complex. The fac-$L_3M(CO)_3$ complexes do not exhibit a regular incremental increase in their molar rotation (± 148–163°) when compared with the other complexes in the series.

INTRODUCTION

One of the most readily available optically active strong π-acceptor ligands is α-methylbenzylisocyanide, $C_6H_5CH(CH_3)NC$. Each enantiomer can be readily prepared in good yield from the commercially available and inexpensive enantiomers of α-methylbenzylamine ("phenethylamine").[2] This optically active isocyanide has been used previously as a ligand in cyclopentadienyliron[3] and in cyclopentadienylcobalt[4] chemistry. This paper describes the use of the optically pure enantiomers of α-methylbenzylisocyanide for the preparation of optically active octahedral metal carbonyl derivatives using previously established methods.[5–7] This work demonstrates how ligand substitution reactions can be used to introduce systematically multiple chiral sites into octahedral metal carbonyl complexes.

EXPERIMENTAL SECTION

Microanalyses (Table I) were performed by Atlantic Microanalytical Laboratory, Atlanta, Georgia. Infrared spectra (Table I) were obtained in hexane or dichloromethane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Optical rotation measurements (Table I) were done on 0.01 M dichloromethane solutions at 25°C using the sodium D line (589 nm) on a Perkin-Elmer Model 141 automatic polarimeter. The values of $[\alpha]_D^{25}$ and $[\phi]_D^{25}$ were calculated from the measured rotations α_D by standard methods. Melting points (Table I) were taken in capillaries and are uncorrected.

The pure enantiomers (+)-and (–)-α-methylbenzylisocyanide were prepared from the commercially available pure enantiomers (+)- and (–)-α-methylbenzylamine, respectively via the formamide using $POCl_3$ in pyridine for the dehydration of the formamide.[2] Commercial samples of the metal hexacarbonyls (Pressure Chemical Company, Pittsburgh, Pennsylvania) were converted to the corresponding norbornadiene-metal tetracarbonyls,[8] cycloheptatriene-metal tricarbonyls,[8] and acetonitrile-tungsten carbonyls[9] using the cited published procedures. All reactions were carried out under nitrogen,

Preparation of cis-[$C_6H_5CH(CH_3)NC]_2M(CO)_4$ Derivatives (M = Cr and Mo)

A solution of 3.5 mmoles of the norbornadiene-metal tetracarbonyl in 75 to 100 ml. of degassed hexane was stirred overnight with 1.3 to 1.4 ml. (excess) of the appropriate α-methylbenzylisocyanide enantiomer. The reaction mixture was filtered and the filtrate concentrated to ~25 to 30 ml. at 25 mm. Analytically pure cis-$[C_6H_5CH(CH_3)NC]_2M(CO)_4$ precipitated as white needles and was isolated by filtration in >80% yield. The product was dried at ~25°/0.5 mm for 16 hr. Additional product was isolated by cooling the filtrate.

The cis-$[C_6H_5CH(CH_3)NC]_2M(CO)_4$ derivatives can be purified further by crystallization either from

TABLE I

Octahedral metal carbonyl complexes of the enantiomers of the optically active isocyanide $C_6H_5CH(CH_3)NC$

					Analyses, [a]%			Infrared spectrum, cm^{-1}		Optical rotation	
Compound Type	Enantiomer	Yield %	Color	M.P. °C	C	H	N	ν(CO)	ν(CN)	$[\alpha]_D^{25}$	$[\phi]_D^{25}$
$LMo(CO)_5$					C 45.8	2.5	3.8				
	+	35	white	61–63	F 46.3	2.5	3.9	2072s, 1957vs, 1928m	2152m	+15.8°	+58°
cis-$L_2Cr(CO)_4$					C 62.0	4.2	6.6				
	+	93	white	81–82	F 61.8	4.2	6.5	2019s, 1942s, 1929vs	2156m, 2110s	+29.6°	+126°
	–	90	white	80–82	F 61.8	4.2	6.7	2020s, 1943s, 1926vs	2157m, 2117s	–28.4°	–121°
cis-$L_2Mo(CO)_4$					C 56.2	3.8	6.0				
	+	80	white	98–99	F 56.0	4.0	5.9	2022s, 1942s, 1930vs	2158m, 2118s	+25.1°	+118°
	–	80	white	98–99	F 56.0	3.9	5.9	2026s, 1946s, 1931vs	2158m, 2118s	–25.7°	–121°
cis-$L_2W(CO)_4$					C 47.3	3.2	5.0				
	+	85	cream	95–98	F 47.6	3.3	5.2	2019s, 1939s, 1923vs	2152m, 2106s	+21.9°	+122°
	–	80	cream	93–96	F 47.4	3.4	5.2	2018s, 1932s, 1918vs	2154m, 2123s	–21.7°	–121°
fac-$L_3Cr(CO)_3$					C 68.1	5.1	7.9				
	+	87	white	61–63	F 68.1	5.1	8.0	1937s, 1875s, br	2150w, 2112m	+29.9°	+158°
	–	90	white	62–63	F 68.2	5.1	7.9	1940s, 1878s, br	2160w, 2115m	–28.1°	–149°
fac-$L_3Mo(CO)_3$					C 62.8	4.7	7.3				
	+	85	white	78–79	F 62.8	4.8	7.4	1939s, 1847s, br	2160w, 2118m	+27.2°	+156°
	–	80	white	77–79	F 62.9	4.7	7.4	1940s, 1972s, br	2160w, 2120m	–25.8°	–148°
fac-$L_3W(CO)_3$					C 54.5	4.1	6.4				
	+	85	cream	85–87	F 54.6	4.1	6.4	1937s, 1967s, br	2159w, 2110m	+24.7°	+163°
	–	80	cream	84–86	F 54.6	4.2	6.4	1935s, 1869s, br	2160w, 2111m	–22.3°	–148°

[a] C = calculated, F = found

hot saturated hexane solutions upon cooling or from 1:1 dichloromethane-ethanol mixtures by spontaneous evaporation of the dichloromethane at room temperature.

Preparation of cis-$[C_6H_5CH(CH_3)NC]_2W(CO)_4$

A mixture of 7.3 mmoles of cis-$(CH_3CN)_2W(CO)_4$ in 65–75 ml. of degassed dichloromethane was stirred for 20 hr. with 2.2 ml. of the appropriate α-methylbenzylisocyanide enantiomer. Dichloromethane was removed from the reaction mixture at ~25°/25 mm. The oily residue was dissolved in boiling hexane, and filtered hot. The filtrate was concentrated to 30 to 40 ml. and cooled to 0° to give cream crystalline cis-$[C_6H_5CH(CH_3)NC]_2W(CO)_4$ in >80% yield. This product can be purified further by crystallization from hot saturated hexane solutions upon cooling or from a mixture of dichloromethane and ethanol.

Preparation of fac-$[C_6H_5CH(CH_3)NC]_3M(CO)_3$ *(M = Cr and Mo)*

A solution of 3.5 mmoles of the cycloheptatriene-metal tricarbonyl in 75 ml. of degassed hexane was stirred for 16 to 18 hr. at room temperature with 2.0 ml. (excess) of the appropriate α-methylbenzylisocyanide enantiomer. Solvent was then removed at ~25°/25 mm. The residue was dissolved in 50 ml. of dichloromethane and filtered. The filtered solution was treated with 30 to 40 ml. of ethanol. The dichloromethane was then allowed to evaporate spontaneously at room temperature to give >80% yields of analytically pure fac-$[C_6H_5CH(CH_3)NC]_3M(CO)_3$.

Preparation of fac-$[C_6H_5CH(CH_3)NC]_3W(CO)_3$

A solution of 5.4 mmoles of $(CH_3CN)_3W(CO)_3$, 3.0 ml. (excess) of the appropriate α-methylbenzylisocyanide enantiomer, and 100 ml. of freshly distilled tetrahydrofuran was stirred at room temperature for 16 to 18 hr. The solvent was then removed at 25°/25 mm. The residue was dissolved in 40 ml. of degassed dichloromethane. This solution was filtered and the filtrate was treated with 50 ml. of ethanol. Spontaneous evaporation of the dichloromethane gave cream solid fac-$[C_6H_5CH(CH_3)NC]_3W(CO)_3$ in >80% yield.

Preparation of $(+)$-$C_6H_5CH(CH_3)NCMo(CO)_5$

A solution of 2.2 mmoles of $[(C_2H_5)_4N][Mo(CO)_5I]$ in 100 ml. of degassed acetone was cooled at 0° and *while keeping at 0°* was treated with 0.8 ml. (excess) of $(+)$-$C_6H_5CH(CH_3)NC$. After stirring the reaction mixture at 0° for 3½ hr., the solvent was removed in vacuum. The oily residue was treated with 60 ml. of degassed hexane and filtered. The filtered hexane solution was evaporated at ~25°/25 mm. The liquid residue was carefully distilled evaporatively in vacuum over a period of 24 hr. to give a 35% yield of $(+)$-$C_6H_5CH(CH_3)NCMo(CO)_5$, b.p. 40–50°/0.02 to 0.05 mm. This material solidified to a white solid, m.p. 61–63°, upon cooling to −78° for 1 hr.

The temperature is very critical for this reaction. If the reaction is carried out at room temperature rather than 0° in tetrahydrofuran, dichloromethane, hexane, or acetone, then a mixture of $C_6H_5CH(CH_3)NCMo(CO)_5$ and cis-$[C_6H_5CH(CH_3)NC]_2Mo(CO)_4$ is obtained even with short reaction times. The amount of the latter complex relative to the former complex increases rapidly with increases in the reaction temperature and/or the reaction time. Similar results were obtained with the corresponding chromium and tungsten complexes although in these latter cases the $LM(CO)_5$ derivatives were not obtained analytically pure. Several attempted thermal reactions of α-methylbenzylisocyanide with the metal hexacarbonyls $Cr(CO)_6$ (boiling xylene or boiling cyclooctane), or $Mo(CO)_6$ (boiling hexane) did not give the corresponding $LM(CO)_5$ derivatives. Possibly the required reaction temperatures are above the decomposition temperatures of these compounds.

DISCUSSION

The methods for preparing the α-methylbenzylisocyanide complexes cis-$L_2M(CO)_4$ and fac-$L_3M(CO)_3$ involve displacement of coordinated norbornadiene, cycloheptatriene, or acetonitrile by the optically active isocyanide and are completely analogous to methods used[5-7] for the preparation of other isocyanide derivatives of the octahedral metal carbonyls. The preparations of the monosubstituted derivatives are considerably more difficult (see experimental section) but an analytically pure sample of $(+)$-$C_6H_5CH(CH_3)NCMo(CO)_5$ can be prepared by displacement of iodide from $Mo(CO)_5I^-$ by the isocyanide provided that conditions are kept mild enough to prevent further displacement of carbonyl groups.

The optical rotation data for the octahedral metal carbonyl complexes of the optically active isocyanide, α-methylbenzylisocyanide, prepared during this investigation are found in Table I.

The series of metal complexes $LMo(CO)_5$ and cis-

$L_2M(CO)_4$(M = Cr, Mo, and W) have molar rotations $[\phi]_D^{25}$ of + 58° and ± 118–126°, respectively. This gives a molar rotational increment of ± 58–63° for each optically active ligand (L) in the metal complex. This is in excellent agreement with the molar rotation of ± 60° found for a sample of free α-methylbenzylisocyanide. This observation and the observation that the metal does not influence the molar rotation of the metal complex suggests that the metal ion does not influence the chiral environment around the asymmetric carbon atom.

The series of complexes fac-$L_3M(CO)_3$ (M = Cr, Mo, and W) have molar rotations of ± 148–163°. The molar rotational increment per ligand (± 50–55°) is significantly less than that of the free isocyanide (± 60°). The reason for this change in the incremental value of the molar rotations in this series of complexes is not understood at this time. Changes in the incremental values of these molar rotations may possibly be attributable to small stereochemical deformations taking place around the asymmetric carbon atom owing to steric crowding of the three isocyanide ligands in facial positions of the coordination sphere of the metal ion. Also minor changes could arise from deviations in the absorptions of the metal complexes in the 589 nm region (sodium D line) where the optical rotation measurements were made. No attempts have been made to analyze these possibilities further.

This work illustrates how simple ligand substitution reactions on stable octahedral metal carbonyl complexes by appropriate chiral ligands can be used to introduce multiple chiral sites into a molecular in a systematic manner.

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