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ANIONIC METAL CARBONYL COMPLEXES OF THE TETRAPHENYLBORATE, CYANOTRIHYDROBORATE, AND CYANOTRIPHENYLBORATE LIGANDS

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Summary

Reactions of sodium cyanotrihydroborate with the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) in boiling glyme give the yellow anions $[H_3BCNM(CO)_5]^-$ in which the cyano group acts as an electron donor. Reactions of sodium tetraphenylborate with the metal hexacarbonyls $M(CO)_6$ (M = Cr and W) in boiling diglyme give the yellow anions $[(C_6H_5)_2B\{C_6H_5M(CO)_3\}_2]^-$ (M = Cr and W) in which two of the four phenyl rings are π-complexed to metal tricarbonyl moieties. Reactions of sodium cyanotriphenylborate with the metal hexacarbonyls $M(CO)_6$ (M = Mo and W) in boiling glyme result in complexation of the cyano group rather than the phenyl rings to give the yellow anions $[(C_6H_5)_3BCNM(CO)_5]^-$ (M = Mo and W). All of these new anionic metal carbonyl derivatives are isolated as their tetramethylammonium salts.

Introduction

Reactions of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with tetracoordinate boron anions containing appropriate donor groups bonded to the boron provide possible routes to novel anionic metal carbonyl derivatives. For example, the metal hexacarbonyls react with various polypyrazolylborates [1] to form anionic metal carbonyl complexes of the types $[R_2B(C_3H_3N_2)_2M(CO)_4]^-$ and $[RB(C_3H_3N_2)_3M(CO)_3]^-$ (R = H or alkyl, M = Cr, Mo, and W). This paper reports the reactions of the metal hexacarbonyls with the tetracoordinate boron anions cyanotrihydroborate, tetraphenylborate, and cyanotri-

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TABLE 1

NEW ANIONIC METAL CARBONYL DERIVATIVES PREPARED IN THIS WORK

Compound	Color	M.p. (°C) [a]	Reaction conditions			Analyses [c] found (calcd.) (%)		
			Mole ratio $R_4B^-/M(CO)_6$	Time (h)	Yield (%) [b]	C	H	N
$[Me_4N][H_3BCNCr(CO)_5]$	Yellow	Dec. > 170	1.9	48	64	39.1 (39.2)	4.7 (4.9)	9.1 (9.2)
$[Me_4N][H_3BCNMo(CO)_5]$	Yellow	Dec. [d]	6.0	90	34	34.6 (34.3)	4.4 (4.3)	8.1 (8.0)
$[Me_4N][H_3BCNW(CO)_5]$	Yellow	Dec. [d]	5.7	90	68	27.6 (27.4)	3.5 (3.4)	6.3 (6.4)
$[Me_4N][Ph_2B\{PhCr(CO)_3\}_2]$	Yellow	Dec. 111–112	1.3	24	28	61.2 (61.4)	4.9 (4.8)	2.2 (2.1)
$[Me_4N][Ph_2B\{PhW(CO)_3\}_2]$	Yellow	Dec. 102–104	0.35	44	58	44.1 (43.9)	3.5 (3.5)	1.6 (1.5)
$[Me_4N][Ph_3BCNMo(CO)_5]$	Pale yellow	160–162	0.9	24	66	58.2 (58.1)	4.8 (4.7)	4.8 (4.8)
$[Me_4N][Ph_3BCNW(CO)_5]$	Yellow	172–174	0.9	74	71	49.6 (50.5)	3.9 (4.1)	4.1 (4.2)

[a] Melting and decomposition points were determined in capillaries under nitrogen and sealed with grease and are uncorrected. [b] The reported yields were determined before crystallization. [c] Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. [d] The decomposition of this compound occurred very gradually over a broad range.

TABLE 2

SOME INFRARED SPECTRA OF THE NEW ANIONIC METAL CARBONYL DERIVATIVES

Compound	Infrared spectra [a] (cm^{-1})		
	ν(CO)	ν(CN)	ν(BH)
$[Me_4N][H_3BCNCr(CO)_5]$	2075 w, 1983 vw, 1937 s, 1887 m	2207 vw	2337 w (br), 2310 w (sh)
$[Me_4N][H_3BCNMo(CO)_5]$	2078 w, 1985 vw, 1935 s, 1885 m	2200 vw	2335 vw (br), 2290 vw (br)
$[Me_4N][H_3BCNW(CO)_5]$	2077 w, 1976 vw, 1928 s, 1882 m	2200 vw	2335 vw (br), 2312 vw (sh)
$[Me_4N][Ph_2B\{PhCr(CO)_3\}_2]$	1947 s, 1869 vs		
$[Me_4N][Ph_2B\{PhW(CO)_3\}_2]$	1944 s, 1855 vs		
$[Me_4N][Ph_3BCNMo(CO)_5]$	2074 w, 1986 vw, 1940 s (br)	2166 w	
$[Me_4N][Ph_3BCNW(CO)_5]$	2071 w, 1980 vw, 1933 s (br)	2171 w	

[a] Infrared spectra in the indicated regions were taken in CH_2Cl_2 solutions and recorded on a Perkin–Elmer Model 621 spectrometer with grating optics. The spectra were calibrated against the 1601 cm^{-1} band of polystyrene film.

phenylborate where cyano groups and/or phenyl rings are potential donor groups. Other types of transition metal complexes with cyanotrihydroborate [2,3,4,5] and with tetraphenylborate [6,7] anions have been reported.

Experimental

A nitrogen atmosphere was routinely provided for the following operations: *(a)* carrying out reactions; *(b)* filling evacuated vessels containing organometallic compounds; (*c*) handling solutions of organometallic compounds. Ethylene glycol dimethyl ether (glyme) and diethylene glycol dimethyl ether (diglyme) were freshly distilled under nitrogen over sodium benzophenone ketyl. Recrystallization solvents, aqueous tetramethylammonium chloride, and water were saturated with nitrogen before use.

The metal hexacarbonyls were purchased from Pressure Chemical Corporation, Pittsburgh, Pennsylvania. The sodium salts $Na[BH_3CN]$ (Alfa Inorganics), $Na[B(C_6H_5)_4]$ (Aldrich), and $Na[(C_6H_5)_3BCN]$ (Pfaltz and Bauer) were purchased from the indicated companies.

General procedure for the reactions of the metal hexacarbonyls with the tetracoordinate boron anions

The metal hexacarbonyl and the sodium salt of the tetracoordinate boron anion were boiled under reflux in glyme (for $Na[BH_3CN]$ or $Na[(C_6H_5)_3BCN]$) or diglyme (for $Na[B(C_6H_5)_4]$ for the period indicated in Table 1. About 0.9 to 3.5 g of the metal hexacarbonyl and about 25 ml of solvent for each gram of the metal hexacarbonyl were used. The mole ratios of the sodium salt of the tetracoordinate boron anion to the metal hexacarbonyl used for the preparations are given in Table 1. After the reaction period was over, the reaction mixture was cooled to room temperature and then filtered into excess aqueous tetramethylammonium chloride. The volume of this aqueous tetramethylammonium chloride was four to six times the volume of monoglyme or diglyme originally used. The yellow precipitate of the tetramethylammonium salt of the anionic metal carbonyl derivative was filtered, washed with water, and dried. The analytical samples were purified by dissolving the crude product in a minimum volume of dichloromethane. The dichloromethane solution was filtered into excess diethyl ether (for the tetraphenylborate and cyanotriphenylborate derivatives) or heptane (for the cyanotrihydroborate derivatives). The yellow precipitate of pure product was filtered and dried. Analytical data of the products are given in Table 1. Their infrared and NMR spectra are given in Tables 2 and 3, respectively.

The anionic metal carbonyl derivatives prepared in this work (Table 1) are readily soluble in dichloromethane and acetone and sparingly soluble in water, diethyl ether, and hydrocarbons. The compounds are less air-sensitive in the solid state than in solution. For a given type of complex the sequence of relative air stability both in the solid state and in solution is as follows: tungsten (most stable) > chromium (intermediate stability) > molybdenum (least stable).

TABLE 3

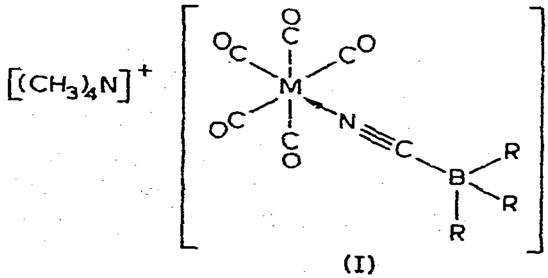
NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE NEW ANIONIC METAL CARBONYL DERIVATIVES AND RELATED COMPOUNDS

Compound	PMR Spectrum,[a, b] τ (ppm)			Boron-11 NMR spectrum[a,c]
	C_6H_5 protons		$(CH_3)_4N$ protons	
	uncomplexed	complexed		
$[Me_4N][H_3BCN]$ [d]				+ 41.8(q) (92)
$[Me_4N][H_3BCNCr(CO)_5]$				+ 42.1(q) (91)
$[Me_4N][H_3BCNMo(CO)_5]$				+ 42.6(q) (91)
$[Me_4N][H_3BCNW(CO)_5]$				+ 42.3(q) (91)
$[Me_4N][Ph_2B\{PhCr(CO)_3\}_2]$	2.59(m) 3.03(m)	4.18(d) (6) 4.44(t) (7) 4.60(t) (6) 4.74(t) (6)	6.72(s)	
$[Me_4N][Ph_2B\{PhW(CO)_3\}_2]$	2.62(br) 3.05(m)	4.0—4.6(m)	6.71(s)	
$[Me_4N][Ph_3BCNMo(CO)_5]$	2.67(m) 3.02(m)	None	6.76(s)	
$[Me_4N][Ph_3BCNW(CO)_5]$	2.67(m) 3.00(m)	None	6.78(s)	

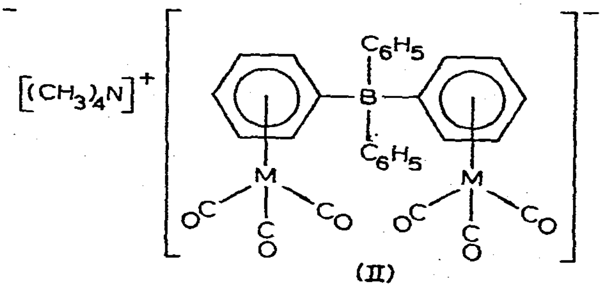
[a] The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet of uncertain multiplicity, br = broad. Coupling constants in Hz are given in parentheses. [b] PMR spectra were taken in acetone-d_6 solutions and recorded on a Varian HA-100 spectrometer at 100 MHz. [c] Boron-11 NMR spectra were taken in acetone solutions and recorded on a Varian HA-100 spectrometer at 32 MHz. Chemical shifts are given in ppm upfield from external $(C_2H_5)_2O \cdot BF_3$. [d] This $[Me_4N][H_3BCN]$ was precipitated upon metathesis of $Na[H_3BCN]$ with tetramethylammonium chloride in absolute ethanol.

Discussion

The properties of the complexes $[(CH_3)_4N][H_3BCNM(CO)_5]$ obtained from the metal hexacarbonyls and the cyanotrihydroborate anion are consistent with their formulation as (I) (R = H) in which the nitrogen of the cyano group of the BH_3CN^- ligand replaces one of the carbonyl groups in the metal hexacarbonyls. The infrared ν(CO) frequencies in the ranges 2076 ± 2, 1980 ± 5, 1933 ± 5 and 1885 ± 3 cm^{-1} may be assigned to the A_1, B_1, E, and A_1 modes, respectively, of an $LM(CO)_5$ molecule [8]. The A_1, E, and A_1 ν(CO) frequencies of the isoelectronic $CH_3CNCr(CO)_5$ [8] appear at 2080, 1954 and 1930 cm^{-1} indicating that substitution of H_3BCN^- for CH_3CN as a ligand lowers the ν(CO) frequencies in accord with the greater possibility for back bonding in an anionic relative to an isoelectronic neutral metal carbonyl deri-



(I)



(II)

vative. The infrared spectra of the complexes $[(CH_3)_4N][H_3BCNM(CO)_5\cdot]$ (Table 2) also exhibit relatively weak bands in the expected regions for the ν(BH) and ν(CN) frequencies. The ^{11}B NMR spectra of the complexes $[(CH_3)_4N]$ $[H_3BCNM(CO)_5]$ (Table 3) exhibit the expected quartets consistent with retention of an intact BH_3 group in the H_3BCN ligand.

The properties of the complexes $[(CH_3)_4N][(C_6H_5)_2B\{C_6H_5M(CO)_3\}_2]$ (M = Cr and W) obtained from the appropriate metal hexacarbonyls and sodium tetraphenylborate are consistent with their formulation as (II) in which two of the four phenyl groups of the tetraphenylborate ligand are π-bonded to $M(CO)_3$ moieties as in benzenetricarbonylchromium and related compounds [9]. The PMR spectra of these tetraphenylborate complexes exhibit two distinctly separated complex multiplets in the ranges τ 2.5 to 3.1 ppm and τ 4.0 to 4.8 ppm of equal relative intensities indicating an equal number of protons on uncomplexed and complexed phenyl rings in accord with structure (II). The infrared spectra of the complexes $[(CH_3)_4N][(C_6H_5)_2B\{C_6H_5M(CO)_3\}_2]$ (M = Cr and W) exhibit ν(CO) frequencies at 1945 ± 2 and 1862 ± 7 cm^{-1} in acoord with formulations as *cis*-$L_3M(CO)_3$ derivatives [8]. These ν(CO) frequencies for the tetraphenylborate complexes (II) are appreciably lower than those found for neutral (arene)$M(CO)_3$ derivatives (e.g. reported [10] ν(CO) for $C_6H_6Cr(CO)_3$: 1987 and 1917 cm^{-1}), again consistent with the greater possibility for back bonding in anionic relative to isoelectronic neutral metal carbonyl derivatives.

The reaction of sodium tetraphenylborate with $Mo(CO)_6$ in boiling diglyme followed by treatment of the reaction mixture with excess aqueous tetramethylammonium chloride gave a yellow solid of similar appearance to the products of structure (II) obtained by reactions of sodium tetraphenylborate with chromium and tungsten hexacarbonyls. However, the PMR spectrum of this tetraphenylborate—molybdenum carbonyl complex indicated an excess of coordinated phenyl protons relative to uncoordinated phenyl protons corresponding to a non-stoichiometric formula $[(CH_3)_4N][(C_6H_5)_{1.7}B\{C_6H_5Mo(CO)_3\}_{2.3}]$. The larger content of π-bonded $Mo(CO)_3$ groups in the molybdenum tricarbonyl than in the chromium and tungsten tricarbonyl complexes of tetraphenylborate is a reasonable consequence of the well-established [11] greater reactivity of $Mo(CO)_6$ relative to $Cr(CO)_6$ and $W(CO)_6$.

The cyanotriphenylborate anion $[(C_6H_5)_3BCN]^-$ has a cyano group which can bond to metal carbonyl residues like the cyanotrihydroborate anion $[H_3BCN]^-$ in the complexes (I) (R = H) and three phenyl rings which can bond to metal carbonyl residues like the tetraphenylborate anion $[(C_6H_5)_4B]^-$ in the complexes (II). Reactions of the cyanotriphenylborate anion with the hexacarbonyls of molybdenum and tungsten in boiling glyme followed by tetramethylammonium chloride treatment gave yellow products clearly indicated by their ν(CO) frequencies (Table 2) to be the pentacarbonyls $[(CH_3)_4N]$ $[(C_6H_5)_3BCNM(CO)_5]$ [(I): R = C_6H_5; M = Mo and W]. The corresponding reaction of the cyanotriphenylborate anion with $Cr(CO)_6$ followed by tetramethylammonium chloride treatment gave a similar yellow product but this product was not pure $[(CH_3)_4N][(C_6H_5)_3BCNCr(CO)_5]$ since its PMR spectrum indicated that 10% of the phenyl groups in the cyanotriphenylborate anion were π-bonded to $Cr(CO)_3$ moieties. This apparently greater ease of formation of (arene)Cr$(CO)_3$ derivatives relative to (arene)Mo$(CO)_3$ and (arene)W$(CO)_3$ derivatives is consistent with previous observations [12].

This work demonstrates that either cyano or phenyl groups bonded to anionic tetracoordinate boron can act as ligands in metal carbonyl chemistry similar to cyano or phenyl groups in normal organic compounds. The work with cyanotriphenylborate described in this paper indicates that when both cyano and phenyl groups are present in the same tetracoordinate boron anion, the cyano groups are generally the more reactive toward metal carbonyl systems. This observation can be a simple consequence of the fact that a cyano group needs to replace only one carbonyl group from a metal hexacarbonyl whereas a phenyl group needs to replace three carbonyl groups from a metal hexacarbonyl before stable ligand—metal bonds can be formed.

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