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resonances at τ 4.67 and 4.73 were strong and of equal intensity and new peaks of relative intensity 1:3 were observed at τ 6.35 and 6.90. The ^{19}F NMR spectrum of the solution showed a broad signal throughout the course of the reaction 6.74 ppm from C_6F_6 (BF_4).

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ (R = CH_3, C_2H_5) with $(C_2H_5)_3OPF_6$. A solution of 0.723 g (2.53 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ and 0.613 g (2.47 mmol) of $(C_2H_5)_3OPF_6$ in 35 mL of $CHCl_3$ was stirred for 6 h at 25 °C, during which time it changed color from yellow to brown. The volatiles were removed, the solid residue was extracted with 25 mL of CH_2Cl_2, and the extract was filtered. Addition of 25 mL of cyclohexane to the filtrate immediately induced the formation of yellow-brown, air-stable crystals. The volume of the solution was reduced to 30 mL, and the crystals were collected by filtration, 0.641 g (60% yield) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)_2]]PF_6$: ^1H NMR ($(CD_3)_2CO$) τ 4.08 (s, C_5H_5), 5.25–5.75 (m, $2CH_2$), 8.56 (t, J = 7 Hz, $2CH_3$); IR (hexachlorobutadiene) 3130 (m), 2960 (sh), 2925 (m), 2860 (m), 2085 (vs), 2050 (vs), 1420 (m) cm^{-1}; IR (Nujol) 1264 (m), 1224 (s), 1095 (w), 990 (s), 920 (s), 880 (s), 842–822 (s), 755 (m), 738 (m), 582 (m), 551 (s), 540 (sh) cm^{-1}; Λ_m (CH_3NO_2) 86.5 $\Omega^{-1}\,cm^2\,mol^{-1}$. Anal. Calcd for $C_{11}H_{15}F_6FeO_5PS$: C, 28.69; H, 3.29. Found: C, 29.09; H, 3.31.

In a strictly analogous manner, reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ with $(C_2H_5)_3OPF_6$ gave $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OCH_3]]PF_6$ as yellow, air-stable crystals in 59% yield: ^1H NMR ($(CD_3)_2CO$) τ 4.15 (s, C_5H_5), 5.2–5.7 (m, CH_2), 5.97 (s, OCH_3), 8.57 (t, J = 7 Hz, CCH_3); IR (hexachlorobutadiene) 3095 (m), 2085 (vs), 2050 (vs) cm^{-1}; IR (Nujol) 1260 (w), 1228 (s), 1152 (w), 1102 (w), 988 (m), 920 (s), 880 (s), 840–820 (s), 770 (m), 602 (sh), 588 (s) cm^{-1}; Λ_m (CH_3NO_2) 89.6 $\Omega^{-1}\,cm^2\,mol^{-1}$.

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)[S(O)_2CH_3]$ (L = CO, $P(C_6H_5)_3$) with $(C_2H_5)_3OPF_6$. Reaction between equimolar amounts of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2CH_3]$ and $(C_2H_5)_3OPF_6$ was conducted analogously to the foregoing syntheses to afford $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)CH_3]]PF_6$ as a yellow solid in 75% yield: ^1H NMR ($(CD_3)_2CO$) τ 4.33 (br, C_5H_5), 5.66 (br, CH_2), 6.36 (br, SCH_3), 8.56 (br, CCH_3); IR (KBr) (prominent absorptions) 2077 (vs), 2040 (vs), 1190 (s), 980 (s), 880 (s) cm^{-1}; Λ_m (CH_3NO_2) 85 $\Omega^{-1}\,cm^2\,mol^{-1}$. Anal. Calcd for $C_{10}H_{13}F_6FeO_4PS$: C, 27.93; H, 3.05. Found: C, 27.86; H, 3.00.

In a similar manner, $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)(OC_2H_5)CH_3]]PF_6$ was prepared in 70% yield from $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)_2CH_3]$ and $(C_2H_5)_3OPF_6$: ^1H NMR ($(CD_3)_2CO$) τ 2.38 (m, $3C_6H_5$), 4.76 (s, C_5H_5), 6.00 (br, CH_2), 6.55 (br, SCH_3), 8.92 (br, CCH_3); IR (KBr) (prominent absorptions) 1990 (vs), 1435 (s), 1188 (s), 1100 (s), 1008 (m), 968 (s), 888 (s), 850 (s), 842 (s) cm^{-1}; Λ_m (CH_3NO_2) 80 $\Omega^{-1}\,cm^2\,mol^{-1}$. Anal. Calcd for $C_{27}H_{28}F_6FeO_3P_2S$: C, 48.81; H, 4.25. Found: C, 48.98; H, 4.45.

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Registry No. $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$, 75111-95-4; $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$, 75111-96-5; $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_3H_7\text{-}1]$, 75111-97-6; $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_3H_7\text{-}2]$, 75111-98-7; $(+)_{589}\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$, 75172-30-4; $Mn(CO)_3(bpy)[S(O)_2OCH_3]$, 75111-99-8; $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$, 69526-44-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OD]$, 75112-00-4; $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$, 69363-96-8; $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2N(CH_3)_2]$, 75112-01-5; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OCH_3]]PF_6$, 75112-03-7; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)_2]]PF_6$, 75112-30-0; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)CH_3]]PF_6$, 75112-32-2; $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)(OC_2H_5)CH_3]]PF_6$, 75112-34-4; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]_2$, 58657-88-8; $(CH_3)_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$, 75112-35-5; $(C_2H_5)_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$, 75112-36-6; $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)_2CH_3]$, 31811-87-7; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]$, 65669-26-3; $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, 12078-28-3; $Mn(CO)_3(bpy)Cl$, 14881-43-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, 12107-04-9; $1\text{-}C_3H_7OH$, 71-23-8; $2\text{-}C_3H_7OH$, 67-63-0; C_2H_5OH, 64-17-5; $(CH_3)_3OPF_6$, 12116-05-1; CH_3OH, 67-56-1; $(+)_{589}\text{-}2\text{-}C_8H_{17}OH$, 6169-06-8; $(C_2H_5)_3OPF_6$, 17950-40-2; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$, 62077-08-1; $ClS(O)_2N(CH_3)_2$, 13360-57-1; CH_3OSO_2F, 421-20-5.

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Cationic Cyclopentadienylchromium–Nitrosyl Complexes: Synthesis and Reactions[1]

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Reaction of $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$ with $AgPF_6$ in CH_3CN or of $\eta^5\text{-}C_5H_5Cr(NO)_2CH_3$ with $HPF_6\cdot(C_2H_5)_2O$, also in CH_3CN, affords $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ in high yield. However, when the latter reaction takes place in ether, the organochromium product is $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$. The complexes $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ and $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$ yield a series of cationic cyclopentadienylchromium dinitrosyls, $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$, when treated with L (L = an aromatic amine, pyridine, and organic cyanide or isocyanide) in CH_3NO_2 at 25 °C. Treatment of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ with 2,2′-bipyridine and with 1,10-phenanthroline (L–L) in CH_3NO_2 at reflux affords 17-electron complexes, $[\eta^5\text{-}C_5H_5Cr(NO)(L\text{–}L)]PF_6$. The isocyanide complex $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ reacts with NaOR (R = CH_3, C_2H_5) to give the relatively unstable $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OR)NCH_3]$ complexes, which on protonation with $HPF_6\cdot(C_2H_5)_2O$ yield the corresponding carbene complexes $\{\eta^5\text{-}C_5H_5Cr(NO)_2[C(OR)NHCH_3]\}PF_6$. In a similar reaction, $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ was converted by action of KOH to the carbamoyl complex $\eta^5\text{-}C_5H_5Cr(NO)_2[C(O)NHCH_3]$, which on treatment with $HPF_6\cdot(C_3H_5)_2O$ furnished known $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$. The characterization of all new complexes is described.

Introduction

The paucity of well-characterized cationic complexes $[\eta^5\text{-}C_5H_5Cr(NO)_2L]X$ (L = neutral monodentate ligand, X = uninegative ion)[2,3] presents a striking contrast with the abundance of their isoelectronic analogues, $[\eta^5\text{-}C_5H_5Fe(CO)_2L]X$.[4,5] This is further surprising in view of the existence of corresponding molybdenum and tungsten complexes, $[\eta^5\text{-}C_5H_5M(NO)_2L]X$ (M = Mo, W), for a variety of ligands L.[6] To fill this void we set out to develop general synthetic routes to $[\eta^5\text{-}C_5H_5Cr(NO)_2L]X$. Reported here are our results

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on preparation and reaction chemistry of such cationic chromium complexes.

Results and Discussion

Synthesis and Characterization of [η^5-$C_5H_5Cr(NO)_2L$]PF_6. Reaction of η^5-$C_5H_5Cr(NO)_2Cl$ with an equimolar amount of $TlNO_3$ in acetone at 25 °C for 24 h resulted in the precipitation of TlCl and formation of neutral η^5-$C_5H_5Cr(NO)_2ONO_2$ (eq 1). The same complex was obtained from

$$\eta^5\text{-}C_5H_5Cr(NO)_2Cl + MNO_3 \rightarrow \eta^5\text{-}C_5H_5Cr(NO)_2ONO_2 + MCl \quad (1)$$
$$M = Tl, Ag$$

η^5-$C_5H_5Cr(NO)_2Cl$ and $AgNO_3$ in CH_3CN under comparable conditions. The nature of the organochromium product was ascertained from its very low conductance in acetone (1.0 Ω^{-1} cm^2 mol^{-1}) and from the position of its C_5H_5 proton resonance at τ 4.12 (in acetone solution) and of its infrared ν(NO) bands at 1814 and 1709 cm^{-1} (in CH_3CN solution), all of which fall in the range observed for neutral complexes, η^5-$C_5H_5Cr(NO)_2X$ (X = uninegative monodentate ligand) (vide infra).

By way of contrast, reaction between η^5-$C_5H_5Cr(NO)_2Cl$ and $AgPF_6$ in CH_3CN at room temperature afforded the cationic complex [η^5-$C_5H_5Cr(NO)_2(CH_3CN)$]PF_6 (eq 2).

$$\eta^5\text{-}C_5H_5Cr(NO)_2Cl + AgPF_6 + CH_3CN \rightarrow [\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6 + AgCl \quad (2)$$

The same compound was obtained, in comparable yield, by treatment of η^5-$C_5H_5Cr(NO)_2CH_3$ in CH_3CN with $HPF_6\cdot(C_2H_5)_2O$ (eq 3). However, when the latter reaction was

$$\eta^5\text{-}C_5H_5Cr(NO)_2CH_3 + HPF_6\cdot(C_2H_5)_2O + CH_3CN \rightarrow [\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6 + CH_4 + (C_2H_5)_2O \quad (3)$$

carried out in ether, a complex η^5-$C_5H_5Cr(NO)_2FPF_5$, in which one fluorine probably bonds weakly to chromium, precipitated from solution (eq 4). Although this product could

$$\eta^5\text{-}C_5H_5Cr(NO)_2CH_3 + HPF_6\cdot(C_2H_5)O \rightarrow \eta^5\text{-}C_5H_5Cr(NO)_2FPF_5 + CH_4 + (C_2H_5)_2O \quad (4)$$

not be characterized through elemental analysis because of low stability, the proposed formulation receives support from ^{1}H NMR and infrared spectral data, which reveal the absence of ether. The C_5H_5 proton resonance at τ 4.02 and the infrared ν(NO) bands at 1841 and 1741 cm^{-1} are, as shown in Table I, close to the corresponding values found for cationic complexes, [η^5-$C_5H_5Cr(NO)_2L$]X. This may be attributed to poor electron-donating ability of PF_6^-, compared to other anionic ligands, which would place considerable positive charge on chromium. The ^{19}F NMR spectrum of η^5-$C_5H_5Cr(NO)_2FPF_5$ shows a doublet resonance (J_{P-F} = 750 Hz) at 4.50 ppm from CF_3CO_2H, characteristic of the PF_6^- ion.[7] Essentially the same spectrum was obtained for [η^5-$C_5H_5Cr(NO)_2(CH_3CN)$]PF_6, suggesting a very labile Cr–FPF_5 bond in η^5-$C_5H_5Cr(NO)_2FPF_5$ and a rapid rotation of PF_6^- on the NMR time scale. Compounds similar to η^5-$C_5H_5Cr(NO)_2FPF_5$, including $Re(CO)_5FPF_5$ and η^5-$C_5H_5M(CO)_3FPF_5$ (M = Mo, W), were recently reported by Beck.[8]

The CH_3CN ligand in [η^5-$C_5H_5Cr(NO)_2(CH_3CN)$]PF_6 shows considerable lability in solution at 25 °C as demonstrated by ^{1}H NMR spectroscopy. Thus, the spectrum of [η^5-$C_5H_5Cr(NO)_2(CH_3CN)$]PF_6 in CD_3CN shows two signals: that of C_5H_5 at τ 3.84 and of free CH_3CN at τ 7.80, indicating complete conversion to [η^5-$C_5H_5Cr(NO)_2$-

Table I. Properties of New Cyclopentadienylchromium–Nitrosyl Complexes

complex	% C		% H		infrared, cm^{-1}		^{1}H NMR, τ^c		Λ_m, Ω^{-1} cm^2 mol^{-1} ^{a}	other measurements
	calcd	found	calcd	found	$\nu(NO)^a$	other^b	C_5H_5	CH_3, CH_2, NH		
η^5-$C_5H_5Cr(NO)_2FPF_5$					1841, 1741		4.02 (s)^g			^{19}F NMR^g δ 4.50 from CF_3CO_2H (J_{P-F} = 750 Hz)
[η^5-$C_5H_5Cr(NO)_2(CH_3CN)$]PF_6	23.15	23.41	2.22	2.48	1862, 1757	ν(CN) 2312	4.03 (s)^g	7.60 (s, CH_3)	101	
[η^5-$C_5H_5Cr(NO)_2(C_6H_5CN)$]PF_6	33.90	33.67	2.37	2.43	1851, 1745	ν(CN) 2278	3.90 (s)^g		83	
[η^5-$C_5H_5Cr(NO)_2(C_6H_5NH_2)$]$PF_6$	31.82	31.96	2.91	2.91	1834, 1736	$\nu(NH_2)$ 3290, 3240 ($\nu(ND_2)$ 2479, 2401)	3.90 (s)		88	
[η^5-$C_5H_5Cr(NO)_2$(p-$CH_3C_6H_4NH_2$)]PF_6	33.58	33.78	3.29	3.29	1831, 1731	$\nu(NH_2)$ 3301, 3267 ($\nu(ND_2)$ 2490, 2412)	3.87 (s)	7.70 (s, CH_3)	93	
[η^5-$C_5H_5Cr(NO)_2$(p-$ClC_6H_4NH_2$)]PF_6	29.38	29.10	2.47	2.48	1836, 1734	$\nu(NH_2)$ 3312, 3268 ($\nu(ND_2)$ 2468, 2390)	3.87 (s)		89	
[η^5-$C_5H_5Cr(NO)_2(C_5H_5N)$]PF_6	29.94	29.94	2.51	2.57	1840, 1740		3.84 (s)		97	
[η^5-$C_5H_5Cr(NO)_2(4\text{-}CH_3C_5H_4N)$]$PF_6$	31.82	31.70	2.91	3.03	1834, 1734		3.80 (s)	7.50 (s, CH_3)	85	
[η^5-$C_5H_5Cr(NO)_2(CH_3NC)$]PF_6	23.15	23.15	2.22	2.17	1856, 1756	ν(CN) 2278	3.82 (s)	6.23 (t, CH_3, J_{N-H} = 2.2 Hz)	87	
[η^5-$C_5H_5Cr(NO)_2(C_6H_{11}NC)$]$PF_6$	33.42	33.16	3.74	3.74	1856, 1756^e	ν(CN) 2240	4.03 (s)^h		95	
[η^5-$C_5H_5Cr(NO)(phen)$]PF_6	43.23	43.29	2.77	2.80	1690				67	μ_{eff} = 1.96 μ_B
[η^5-$C_5H_5Cr(NO)(bpy)$]PF_6	40.19	40.38	2.92	2.92	1690				72	μ_{eff} = 1.83 μ_B
η^5-$C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$					1795, 1690^f		4.30 (s)	6.43 (s, OCH_3), 7.10 (s, NCH_3)		
{η^5-$C_5H_5Cr(NO)_2[C(OCH_3)NHCH_3]$}$PF_6$	24.32	24.40	3.06	2.92	1834, 1734^f	ν(NH) 3384	3.90 (s)	5.90 (s, OCH_3), 6.77 (s, NCH_3)	76	
{η^5-$C_5H_5Cr(NO)_2[C(OC_2H_5)NHCH_3]$}$PF_6$					1845, 1740^f		3.93 (s)	5.60 (q, CH_2, J_{H-H} = 6.7 Hz), 6.73 (s, NCH_3), 8.57 (t, CCH_3, J_{H-H} = 6.7 Hz)		
η^5-$C_5H_5Cr(NO)_2[C(O)NHCH_3]$					1790, 1684^f	ν(C=O) 1657^f	4.47 (s)	4.73 (s, NH), 7.20 (s, CH_3)		
[η^5-$C_5H_5Cr(NO)_2(CO)$]PF_6^{d}					1867, 1778	ν(CO) 2134^a	3.83 (s)^g			

[a] CH_3NO_2 solution except as noted. [b] KBr pellet except as noted. [c] Acetone-d_6 solution except as noted. Abbreviations: s, singlet; t, triplet; q, quartet. [d] Compound reported previously.[2] [e] $CHCl_3$ solution. [f] CH_2Cl_2 solution. [g] CD_3NO_2 solution. [h] $CDCl_3$ solution.

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$(CD_3CN)]PF_6$. The spectrum in acetone-d_6 consists of four resonances which are assigned to C_5H_5 (τ 3.84) and CH_3CN (τ 7.40) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$, C_5H_5 (τ 3.80) of $\{\eta^5\text{-}C_5H_5Cr(NO)_2[(CD_3)_2CO]\}PF_6$, and free CH_3CN (τ 7.93). The equilibrium mixture of the two cationic species contains more than 60% of the CH_3CN complex. Finally, the spectrum of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ in CD_3NO_2 shows only the two resonances of the dissolved complex (Table I), indicating that no ligand exchange has occurred.

The complex $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ serves as a convenient precursor of a variety of cationic complexes, $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$. These conversions are accomplished in 70–85% yield by stirring a solution of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ and excess L in CH_3NO_2 at 25 °C (eq 5).

$$[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6 + L \xrightarrow{CH_3NO_2} [\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6 + CH_3CN \quad (5)$$

Successfully prepared in this fashion were the complexes incorporating L = an aromatic amine ($C_6H_5NH_2$, $p\text{-}CH_3C_6H_4NH_2$, $p\text{-}ClC_6H_4NH_2$), pyridine (C_5H_5N, $4\text{-}CH_3C_5H_4N$), and organic isocyanide (CH_3NC). However, attempts at introducing L = $P(C_6H_5)_3$ and $P(C_2H_5)_3$ under comparable reaction conditions resulted in complete decomposition of the $\eta^5\text{-}C_5H_5Cr(NO)_2$ moiety.

Another synthetic route to $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$ utilizes $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$ in conjunction with L, also in CH_3NO_2 at 25 °C (eq 6). Compared to the first-mentioned method,

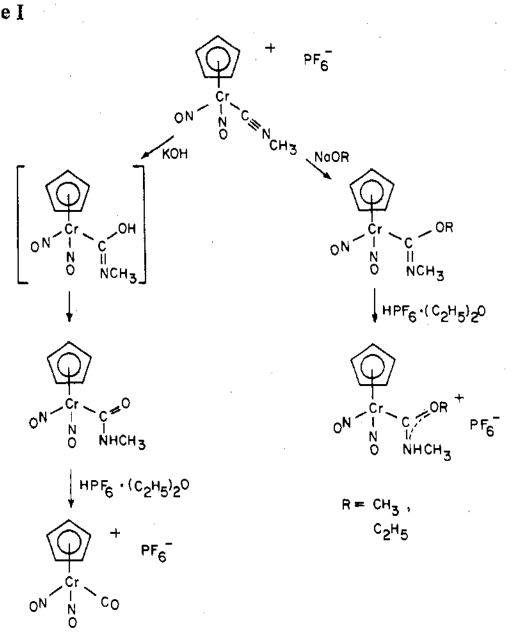
$$\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5 + L \xrightarrow{CH_3NO_2} [\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6 \quad (6)$$

$$L = C_6H_5CN,\ p\text{-}CH_3C_6H_4NH_2,\ C_6H_{11}NC$$

it suffers from the somewhat lower yields of 50–60% but has the advantage of cleanly affording the cationic complexes containing ligands of a wider range of basicity, including lower than or comparable to that of CH_3CN, viz., $[\eta^5\text{-}C_5H_5Cr(NO)_2(C_6H_5CN)]PF_6$. However, the very weak bases CO and styrene failed to react with $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$ under similar conditions.

The new complexes $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$ are stable to air in the solid state and moderately stable in solution. They were characterized by elemental analysis, molar conductance, and infrared and ^1H NMR spectroscopy, as shown in Table I. The values of Λ_m in CH_3NO_2 solution fall in the range 85–101 Ω^{-1} cm^2 mol^{-1}, being consistent with the presence of 1:1 electrolytes.[9] The infrared ν(NO) absorptions at 1862–1831 and 1757–1731 cm^{-1} are, as expected for cations $[\eta^5\text{-}C_5H_5Cr(NO)_2L]^+$, somewhat higher than those of the neutral species $\eta^5\text{-}C_5H_5Cr(NO)_2X$ (X = Cl, Br, I, NCS, NO_2, NO_3), the latter occurring at 1827–1810 and 1723–1695 cm^{-1}.[6,10–12] The resonance of the C_5H_5 protons in $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$ at τ 3.80–4.03 experiences the usual downfield shift when compared with the corresponding signal of the above-listed neutral $\eta^5\text{-}C_5H_5Cr(NO)_2X$, which occurs in the range τ 4.12–4.28.[11,12] A noteworthy feature in the ^1H NMR spectrum of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ is the occurrence of the CH_3 signal as a triplet (J_{N-H} = 2.2 Hz). This value agrees well with those reported in the literature for some transition metal–CH_3NC complexes.[13–15]

Scheme I



Interestingly, the amine complexes $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$, where L = $C_6H_5NH_2$, $p\text{-}CH_3C_6H_4NH_2$, and $p\text{-}ClC_6H_4NH_2$, readily exchange their NH_2 protons for deuterium during storage in acetone-d_6 solution at 25 °C for 12 h. This exchange was readily ascertained by noting that the infrared $\nu(NH_2)$ bands of the dissolved complex disappeared and the corresponding $\nu(ND_2)$ bands appeared in the complex isolated from acetone-d_6. The appropriate data are provided in Table I.

Synthesis and Characterization of $[\eta^5\text{-}C_5H_5Cr(NO)(L\text{-}L)]PF_6$. The complex $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ undergoes substitution reaction with bidentate N-donor ligands, bpy and phen (L–L), in CH_3NO_2 at reflux to afford the 17-electron products $[\eta^5\text{-}C_5H_5Cr(NO)(L\text{-}L)]PF_6$ in 70–75% yield (eq 7). These red-brown solids are air stable. Consistent with

$$[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6 + L\text{-}L \xrightarrow{CH_3NO_2} [\eta^5\text{-}C_5H_5Cr(NO)(L\text{-}L)]PF_6 + NO + CH_3CN \quad (7)$$

the proposed formulations, they exhibit magnetic moments that show the presence of one unpaired electron and molar conductance that is typical of 1:1 electrolytes.[9] In their infrared spectra, a single ν(NO) absorption occurs at 1690 cm^{-1}. The position of this band relates well to that at 1669 cm^{-1} for the previously synthesized 17-electron neutral complexes $\eta^5\text{-}C_5H_5Cr(NO)(L)Cl$, where L = C_5H_5N and $4\text{-}CH_3C_5H_4N$.[16] However, it surprisingly occurs at a considerably lower frequency than the corresponding absorption at 1748–1749 cm^{-1} (in CH_2Cl_2 solution) of the 18-electron $[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(L\text{-}L)]PF_6$ (L–L = bpy, phen).[17] The opposite would be predicted if the 18th electron resides in an orbital that is involved in π back-bonding with the nitrosyl ligand. For the same oxidation state of the metal, a d^6 system (i.e., Mn(I), with the nitrosyl as NO^+) should π back-bond more effectively than the corresponding d^5 system (i.e., Cr(I)). Thus the former should exhibit more extensive M–NO π bonding and consequently a lower value of ν(NO) than the latter.

Reactions of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ with Nucleophiles. Reactions of the title compound with several "hard" nucleophiles were carried out to establish whether attack would occur at NO or at CH_3NC. Both ligands are known to engage in such reactions, especially when present in a cationic complex.[18,19]

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Scheme I summarizes our results. Treatment of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ with $NaOCH_3$ in CH_3OH resulted in the formation of $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$. This neutral product could not be induced to crystallize and, because of its thermal instability, was characterized only spectroscopically. The position of the infrared ν(NO) bands and the ^1H NMR spectrum, both given in Table I, support the proposed structure that derives from attack of methoxide at the isocyanide carbon.

Protonation with $HPF_6\cdot(C_2H_5)_2O$ of $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$ in CH_2Cl_2 solution occurred at the NCH_3 nitrogen to yield $\{\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NHCH_3]\}PF_6$ as a stable, crystalline solid. This methoxy(methylamino)carbene complex also resulted from reaction of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ with CH_3OH in the presence of trace amounts of $NaOCH_3$. However, no reaction occurred in the absence of $NaOCH_3$. Thus, methoxide must be the reactive nucleophile, and the resulting neutral complex $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$ then undergoes protonation by the CH_3OH solvent.

The protonated product was characterized by elemental analysis, molar conductance, which shows it to be a 1:1 electrolyte,[9] and infrared and ^1H NMR spectroscopy. The infrared spectrum shows a ν(NH) band at 3384 cm^{-1} and two ν(NO) absorptions in the range appropriate for these cationic dinitrosyl complexes. In the ^1H NMR spectrum, the resonances of the C_5H_5, OCH_3, and NCH_3 groups are, as expected, downfield from the corresponding signals of neutral $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$.

Similarly prepared, by using $NaOC_2H_5$ in C_2H_5OH followed by protonation, was the ethoxy analogue of the aforementioned carbene complex. Obtained as an oil, $\{\eta^5\text{-}C_5H_5Cr(NO)_2[C(OC_2H_5)NHCH_3]\}PF_6$ could not be induced to crystallize and was characterized only spectroscopically (Table I).

Treatment of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ with KOH in CH_3CN at 25 °C afforded unstable $\eta^5\text{-}C_5H_5Cr(NO)_2[C(O)NHCH_3]$, which was characterized spectroscopically in solution. This carbamoyl complex results from attack of hydroxide at the isocyanide carbon, followed by a tautomeric proton shift to the more basic nitrogen. The proposed formulation receives support from the infrared ν(NO) absorptions at 1790 and 1684 cm^{-1} and the ν(C=O) band at 1657 cm^{-1}. The ^1H NMR spectrum shows all of the hydrogens at the expected positions and with the appropriate intensities.

Addition of $HPF_6\cdot(C_2H_5)_2O$ to a solution of the carbamoyl complex in CH_3NO_2 resulted in the formation of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$, which had previously been prepared, via a different route, by Fischer.[2] The infrared spectroscopic data in Table I match well with the literature values.

The carbonyl ligand in $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$ undergoes substitution by CH_3CN to yield $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$. Accordingly, a solution of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$ and a 12-fold excess of CH_3CN in CD_3NO_2 in a capped ^1H NMR tube showed a higher than 80% conversion to $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ in 84 h. By comparison, the corresponding $[\eta^5\text{-}C_5H_5M(NO)_2(CO)]PF_6$ (M = Mo, W) complexes react very rapidly with CH_3CN at room temperature also to give $[\eta^5\text{-}C_5H_5M(NO)_2(CH_3CN)]PF_6$.[6]

The foregoing reactions (Scheme I) parallel closely those reported for cationic square-planar platinum(II) isocyanide complexes, $[Pt(PR_3)_2(CH_3NC)_2]X_2$.[20,21] However, the platinum compounds also undergo similar nucleophilic attack by SH^- and $C_6H_5NH^-$. Attempts at reaction of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ with NaHS in CH_3CN and $KNHC_6H_5$ in THF at 25 °C resulted in complete destruction of the $\eta^5\text{-}C_5H_5Cr(NO)_2$ moiety. A similar decomposition occurred when $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ was treated with $(CH_3)_2NH$ in CH_3CN at room temperature. It is not known whether these decomposition reactions proceed by attack of the nucleophile at ligated NO or CH_3NC.

Experimental Section

General Procedures and Measurements. All reactions and manipulations were routinely carried out under purified nitrogen. Analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

^1H and ^{19}F NMR spectra were recorded on a Varian Associates EM360L spectrometer using Me_4Si as an internal reference for the former and CF_3CO_2H as an external reference for the latter. Infrared spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. Molar conductance was measured on ca. 10^{-3} M solutions by using a Lab-Line No. 11200 beaker-type conductivity cell in conjunction with an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge. Paramagnetic susceptibilities were determined by the method of Evans[22] on ca. 10^{-3} M solutions in CH_3NO_2. Mass spectra were recorded on a DuPont Instruments 21-490 spectrometer connected to a Perkin-Elmer 990 gas chromatograph.

Materials. All solvents were of reagent grade quality and were purified further by the methods described by Perrin et al.[23] prior to use. Commercially procured reagents were used as received except for $p\text{-}CH_3C_6H_4NH_2$ (30 °C), $p\text{-}ClC_6H_4NH_2$ (50 °C), 1,10-phenanthroline (phen) (50 °C), and 2,2′-bipyridine (bpy) (50 °C) which were sublimed in vacuo at the indicated temperatures, for $C_6H_5NH_2$ (65 °C/18 torr), C_5H_5N (115.6 °C/760 torr), and 4-$CH_3C_5H_4N$ (145 °C/760 torr) which were dried over KOH and distilled as indicated, and for C_6H_5CN which was dried over P_4O_{10} and distilled at 69 °C/10 torr.

Literature procedures were employed to synthesize CH_3NC,[24] $C_6H_{11}NC$,[25] $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$,[26] and $\eta^5\text{-}C_5H_5Cr(NO)_2CH_3$.[27]

Preparation of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$. A. By Reaction of $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$ with $AgPF_6$. A solution containing 1.67 g (6.6 mmol) of $AgPF_6$ in 75 mL of CH_3CN was treated with 1.40 g (6.6 mmol) of $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$, and the resulting mixture was stirred at 25 °C for 12 h. The green solution was filtered, the solvent was removed from the filtrate, the residual oil was extracted with 3 × 20 mL of $CHCl_3$, and the brown extracts were discarded. The residue was dried in vacuo and redissolved in CH_3CN, and this solution was filtered and concentrated to 5–7 mL. Chloroform was added, and the resulting solution was stored at −78 °C for 4 h. Crystalline $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ (1.85 g, 77% yield) was collected on a frit, washed with $CHCl_3$, and dried in vacuo.

B. By Reaction of $\eta^5C_5H_5Cr(NO)_2CH_3$ with $HPF_6\cdot(C_2H_5)_2O$ in CH_3CN. To a solution containing 0.50 g (2.6 mmol) of $\eta^5\text{-}C_5H_5Cr(NO)_2CH_3$ in 50 mL of CH_3CN was added 0.50 mL (3.0 mmol) of $HPF_6\cdot(C_2H_5)_2O$, and the resulting mixture was stirred at 25 °C for 20 min. A mass spectrometric analysis of collected gases showed the presence of CH_4. The green solution was filtered, concentrated to 1–2 mL by rotary evaporation, and treated with 20 mL of $CHCl_3$. Storage at −78 °C for 4 h induced crystallization of 0.75 g (80% yield) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$, which was collected on a frit, washed with liberal portions of $CHCl_3$, and dried in vacuo.

Preparation of $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$. A solution containing 0.10 g (0.52 mmol) of $\eta^5\text{-}C_5H_5Cr(NO)_2CH_3$ in 25 mL of ether in a 100-mL round-bottom flask equipped with a nitrogen inlet and a Schlenk filter tube was treated with 0.10 mL (0.60 mmol) of $HPF_6\cdot(C_2H_5)_2O$. the reaction mixture was stirred at 25 °C for 6 h, during which time a green precipitate formed. This solid was collected on a frit, washed

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with liberal portions of ether, and dried in vacuo. A mass spectrometric analysis of gases above the reaction mixture showed the presence of CH_4.

Preparation of $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$. A. By Reaction of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ with L (L = $C_6H_5NH_2$, $p\text{-}CH_3C_6H_4NH_2$, $p\text{-}ClC_6H_4NH_2$, C_5H_5N, 4-$CH_3C_5H_4N$, CH_3NC). A solution of 0.2–1.0 g (0.55–2.7 mmol) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ and a twofold to threefold excess of L in 25–75 mL of CH_3NO_2 was stirred at 25 °C for ca. 12 h. Solvent was removed from the reaction mixture, the residue was dissolved in a minimum amount of acetone, and the resulting solution was filtered and treated with 20–30 mL of $CHCl_3$. Storage at −78 °C for 4–12 h afforded $[\eta^5\text{-}C_5H_5Cr(NO)_2L]PF_6$ as green crystals which were collected on a frit, washed with $CHCl_3$, and dried in vacuo. The yield was 70–85%.

B. By Reaction of $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$ with L (L = C_6H_5CN, $p\text{-}CH_3C_6H_4NH_2$, $C_6H_{11}NC$). Freshly prepared $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$ was dissolved in CH_3NO_2, and the resulting solution was treated with excess L and stirred at 25 °C for 12 h. The rest of the procedure was identical with that of method A. The yield was 50–60%.

Preparation of $[\eta^5\text{-}C_5H_5Cr(NO)(L\text{–}L)]PF_6$ (L–L = phen, bpy). A solution of 0.30 g (0.82 mmol) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$ and a slight excess of L–L in 30 mL of CH_3NO_2 was kept at reflux for 4 h, during which time it changed from green to red-brown. Solvent was removed at 25 °C, the residue was dissolved in acetone, and the resulting solution was filtered and concentrated to ca. 5 mL. Treatment with 20 mL of $CHCl_3$, followed by slow evaporation of the solvent, afforded a red-brown precipitate which was collected on a frit, washed with $CHCl_3$, and dried in vacuo. The yield was 70–75%.

Preparation of $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$. To a solution containing 0.20 g (0.55 mmol) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ in 20 mL of CH_3OH was added 1.0 mL of 1.0 M (1.0 mmol) $NaOCH_3$ in CH_3OH. The mixture was stirred at 25 °C for 12 h, during which time it changed from green to gold. Solvent was removed, and the residue was cooled to −78 °C to prevent decomposition. It was then extracted with 10-mL portions of CH_2Cl_2 at 25 °C until the extracts became colorless. The extracts were combined, filtered, and freed of solvent to afford the title complex as a gold oil. Attempts at crystallization at ambient temperatures proved unsuccessful, owing to thermal instability of the complex.

Preparation of $\{[\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NHCH_3]\}PF_6$. The filtered extracts containing $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$ from the preceding preparation were treated with 0.10 mL (0.60 mmol) of $HPF_6\cdot(C_2H_5)_2O$ as the color changed from gold to green. The resulting solution was filtered and concentrated, and cyclohexane was added to induce precipitation of a green solid. The crude product was recrystallized from acetone–ether. The yield was 0.18 g (83% on the basis of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$).

Preparation of $\{\eta^5\text{-}C_5H_5Cr(NO)_2[C(OC_2H_5)NHCH_3]\}PF_6$. This complex was prepared by a procedure strictly analogous to that for its OCH_3 analogue by using C_2H_5OH and $NaOC_2H_5$ in place of CH_3OH and $NaOCH_3$. The product was isolated as a green oil which could not be induced to crystallize.

Preparation of $\eta^5\text{-}C_5H_5Cr(NO)_2[C(O)NHCH_3]$. To a solution containing 0.20 g (0.55 mmol) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$ in 30 mL of CH_3CN was added 10 mL of aqueous 0.10 M (1.0 mmol) KOH. The mixture was stirred at 25 °C for 1 h, during which time it changed from green to red-brown. Solvent was removed, and the residue was cooled to −78 °C and extracted with CH_2Cl_2 at 25 °C until the extracts became colorless. The extracts were combined, filtered, and freed of solvent to yield a red-brown powder, which was spectroscopically characterized as the title complex. The product decomposed during attempts at crystallization at ambient temperatures.

Preparation of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$. The product from the preceding reaction was dissolved in 15 mL of CH_3NO_2, and the resulting solution was treated with 0.20 mL (1.2 mmol) of $HPF_6\cdot(C_2H_5)_2O$ and stirred at 25 °C for 1 h as the color changed from red to green. Solvent was removed, and the residue was washed with 15 mL of H_2O and dried in vacuo. The crude product was recrystallized from acetone–ether to yield 0.04 g (20% on the basis of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$) of $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$.

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Registry No. $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3CN)]PF_6$, 74924-59-7; $\eta^5\text{-}C_5H_5Cr(NO)_2FPF_5$, 74924-60-0; $[\eta^5\text{-}C_5H_5Cr(NO)_2(C_6H_5NH_2)]PF_6$, 74924-62-2; $[\eta^5\text{-}C_5H_5Cr(NO)_2(p\text{-}CH_3C_6H_4NH_2)]PF_6$, 74924-64-4; $[\eta^5\text{-}C_5H_5Cr(NO)_2(C_5H_5N)]PF_6$, 74858-44-9; $[\eta^5\text{-}C_5H_5Cr(NO)_2(4\text{-}CH_3C_5H_4N)]PF_6$, 74924-66-6; $[\eta^5\text{-}C_5H_5Cr(NO)_2(p\text{-}ClC_6H_4NH_2)]PF_6$, 74924-68-8; $\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NCH_3]$, 74924-69-9; $[\eta^5\text{-}C_5H_5Cr(NO)_2[C(OCH_3)NHCH_3]]PF_6$, 74924-71-3; $[\eta^5\text{-}C_5H_5Cr(NO)_2[C(OC_2H_5)NHCH_3]]PF_6$, 74924-73-5; $\eta^5\text{-}C_5H_5Cr(NO)_2[C(O)NHCH_3]$, 74924-74-6; $[\eta^5\text{-}C_5H_5Cr(NO)_2(CO)]PF_6$, 69439-82-3; $[\eta^5\text{-}C_5H_5Cr(NO)_2(C_6H_{11}NC)]PF_6$, 74924-76-8; $[\eta^5\text{-}C_5H_5Cr(NO)(phen)]PF_6$, 74924-78-0; $[\eta^5\text{-}C_5H_5Cr(NO)(bpy)]PF_6$, 74924-80-4; $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$, 12071-51-1; $\eta^5\text{-}C_5H_5Cr(NO)_2CH_3$, 53522-59-1; $[\eta^5\text{-}C_5H_5Cr(NO)_2(C_6H_5CN)]PF_6$, 74924-82-6; $[\eta^5\text{-}C_5H_5Cr(NO)_2(CH_3NC)]PF_6$, 74924-84-8.

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Crystal Structure of Europium(II) Bromoborate

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Needlelike single crystals of $Eu_2B_5O_9Br$ were grown from the molten sample containing a large excess of $EuBr_2$ as a flux. The crystal structure was determined from three-dimensional X-ray diffraction data ($R = 0.047$ for 1979 observed reflections, with anisotropic thermal parameters for Eu and Br atoms). The bromoborate $Eu_2B_5O_9Br$ is isostructural with the Ca analogue. The crystal belongs to the orthorhombic (pseudotetragonal) system, of space group *Pnn*2, with four formula units in a cell of dimensions $a = 11.503$ (3), $b = 11.382$ (3), and $c = 6.484$ (2) Å. The structure consists of a three-dimensional $(B_5O_9)_\infty$ network, in which B_5O_{12} groups of three BO_4 tetrahedra and two BO_3 triangles are linked together by sharing cornered oxygens. The Eu and Br atoms are located in tunnels of the $(B_5O_9)_\infty$ network extending along the *c* axis. Each Eu atom is surrounded by two Br atoms and seven O atoms with interatomic distances from 3.009 to 3.093 Å and from 2.526 to 3.061 Å, respectively.

Introduction

Divalent europium (Eu^{2+}) containing compounds have been investigated because of their magnetic[1–3] and spectroscopic[4] properties, which are closely related to the crystal structure, e.g., the distances between neighboring Eu^{2+} ions and the anion environment around the Eu^{2+} ion. The Eu^{2+}-activated alka-

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