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Bonding Patterns in Metallocene Pseudohalide Complexes

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The results of infrared, visible–ultraviolet, and mass spectral studies involving the metallocene pseudohalide complexes $(\pi\text{-}C_5H_5)_2M(NCS)_2$ [M = Ti(IV), Zr(IV), Hf(IV), and V(IV)], $(\pi\text{-}C_5H_5)_2Ti(NCSe)_2$, $(\pi\text{-}C_5H_5)_2M(OCN)_2$ [M = Ti(IV), Zr(IV), and Hf(IV)], $(\pi\text{-}C_5H_5)_2V(NCO)_2$, and $(\pi\text{-}C_5H_5)_2TiNCO$ indicate that many of the previously published structural conclusions regarding the bonding modes of the ambidentate pseudohalide groups in these complexes are incorrect. All of the thiocyanate and selenocyanate complexes are shown to contain N-bonded groups, as do the d^1 cyanate complexes of V(IV) and Ti(III). The d^0 cyanate complexes of Ti(IV), Zr(IV), and Hf(IV), however, are apparently O bonded and thus represent the first reported examples of this bonding mode for the cyanate ion in a coordination complex.

The synthesis and characterization of metallocene pseudohalide complexes of the type $(\pi\text{-}C_5H_5)_2ML_2$, where M = Ti(IV), Zr(IV), or V(IV), and $L^- = OCN^-$, SCN^-, or $SeCN^-$, have been the subject of several recent studies.[1-7] The differing conclusions expressed in these papers regarding the bonding modes employed by the ambidentate XCN^- ligands, especially the cyanate ion,[1,2,6,7] in these complexes have prompted this critique.

Experimental Section

Preparation of Complexes.—The titanium(IV),[3,7] vanadium(IV),[6] and titanium(III)[8] complexes shown in Table I were prepared by the methods given in the literature. The zirconium(IV) thiocyanate complex was prepared according to Giddings' method[3] for the preparation of the corresponding titanium(IV) complex. The zirconium(IV) cyanate complex was prepared in the same manner as the hafnium(IV) cyanate complex (*vide infra*). Satisfactory C, H, N, and, where applicable, S analyses were obtained for all of the $(\pi\text{-}C_5H_5)_2ML_2$ complexes.

$(\pi\text{-}C_5H_5)_2Hf(NCS)_2$.—Potassium thiocyanate (4.4 mmol) and $(\pi\text{-}C_5H_5)_2HfCl_2$ (2.0 mmol) were stirred in 20 ml of dichloromethane for 3 hr at room temperature. After filtering the reaction mixture, the filtrate obtained was concentrated under reduced pressure to *ca.* 10 ml and cooled at −10° for 3 hr. Yellow crystals, which were washed with ethyl ether and dried *in vacuo*, were obtained in 45% yield (dec pt 257–259°). *Anal.* Calcd for $C_{12}H_{10}N_2S_2Hf$: C, 33.93; H, 2.37; N, 6.59; S, 15.10. Found: C, 33.78; H, 2.90; N, 6.74; S, 15.24.

$(\pi\text{-}C_5H_5)_2Hf(OCN)_2$.—This white complex was obtained in 66% yield (mp 185°) by using silver cyanate in place of potassium thiocyanate in the foregoing procedure (reaction time 2 hr). *Anal.* Calcd for $C_{12}H_{10}N_2O_2Hf$: C, 36.70; H, 2.57; N, 7.13. Found: C, 36.73; H, 2.61; N, 6.97.

Analyses.—Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, Germany, M-H-W Laboratories, Garden City, Mich., and Micro-Analysis, Inc., Wilmington, Del.

Conductance Measurements.—Molar conductances, at 25°, of 10^{-3} *M* solutions of the $(\pi\text{-}C_5H_5)_2ML_2$ complexes in nitrobenzene were measured with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. All of the complexes function as nonelectrolytes in this solvent. The molar conductances ($\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$) of the titanium(IV) complexes have been reported earlier;[7] those of the other metallocenes are as follows: zirconium(IV) chloride 0.0; thiocyanate, 0.65; cyanate, 0.0; hafnium(IV) chloride, 0.14; thiocyanate, 2.0; cyanate, 0.18; vanadium(IV) chloride, 1.7; thiocyanate, 0.18; cyanate, 0.35.

Infrared Spectra.—The infrared spectra of all of the metallocene pseudohalide complexes and their parent chlorides were measured on Perkin-Elmer 337, 457, and 421 grating spectrophotometers as KBr disks, Nujol mulls, and, in the ν_{CN} region (2400–2000 cm^{-1}, with a fourfold wave number scale expansion), dichloromethane solutions, using matched 0.1-mm sodium chloride cells. The integrated absorption intensities of the ν_{CN} bands were determined by Ramsay's method of direct integration.[9] The results are shown in Table I. The infrared spectra of the metallocene cyanate complexes in the N- and O-bonded cyanate ν_{CO} frequency ranges are shown in Figures 1 and 2. Except for slight frequency shifts, the spectra were found to be independent of the method used for sample preparation. No evidence for bromide substitution was observed in the KBr-disk spectra.

Visible–Ultraviolet Spectra.—The visible–uv spectra of dichloromethane solutions of all of the chloride, cyanate, and thiocyanate complexes (except $(\pi\text{-}C_5H_5)_2TiNCO$, which tends to decompose in solution) were measured on a Cary 14 spectrophotometer, using matched 1-cm quartz cells. The results are shown in Table II. Plots of ν_{max}(pseudohalide) *vs.* ν_{max}(chloride) for each of the bands labeled I–III in Table II are shown in Figures 3–5.

Mass Spectra.—The mass spectra of all of the chloride and pseudohalide complexes listed in Table II were measured on a CEC 21-110B double-focusing mass spectrometer. The mass spectrum of $(\pi\text{-}C_5H_5)_2TiNCO$ has been measured by Coutts and Wailes.[8]

Discussion

The behavior of the infrared absorption bands of the thiocyanate and selenocyanate ions upon N or X coordination has been extensively documented.[10,11] Relative to the free-ion values, N coordination has been found to result in an increase in the integrated absorption intensity of ν_{CN}, an increase in the frequency of ν_{CX}, and a small increase in the frequency of δ_{NCX}, whereas, following X coordination, the integrated absorption intensity of ν_{CN} and the ν_{CX} and δ_{XCN} frequencies decrease.

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[1] E. Samuel, *Bull. Soc. Chim. France*, 3548 (1966).

[2] R. S. P. Coutts and P. C. Wailes, *Australian J. Chem.*, **19**, 2069 (1966).

[3] S. A. Giddings, *Inorg. Chem.*, **6**, 849 (1967).

[4] A. Jensen and E. Jørgensen, *J. Organometal. Chem.* (Amsterdam), **7**, 528 (1967).

[5] H. Köpf, B. Block, and M. Schmidt, *Z. Naturforsch.*, **22b**, 1077 (1967).

[6] G. Doyle and R. S. Tobias, *Inorg. Chem.*, **7**, 2479 (1968).

[7] J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *ibid.*, **8**, 170 (1969).

[8] R. Coutts and P. C. Wailes, *Inorg. Nucl. Chem. Letters*, **3**, 1 (1967).

[9] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[10] J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

[11] J. S. Thayer and R. West, *Advan. Organometal. Chem.*, **5**, 115 (1967).

TABLE I

INFRARED DATA FOR $(\pi\text{-}C_5H_5)_2ML_2$ COMPLEXES[n]

M(IV)	-L	ν_{CX},[a] cm^{-1}	δ_{NCX},[a] cm^{-1}	ν_{CN}[b] Freq, cm^{-1}	ν_{CN}[b] $10^{-4}A$,[c] M^{-1} cm^{-2}
Ti	-NCS	*d*	491 w	2058	11
				2017	20
Zr	-NCS	*d*	497 w	2041	11
				2003	21
Hf	-NCS	*d*	505 sh, 502 w	2049	12
				2011	20
V	-NCS	*d*	480 w	2092	8
				2066	13
KNCS		749[e]	486, 471[e]	2060[f]	4.4[f]
Ti	-NCSe	595 w	450 sh, 443 w	2050[g]	12[g]
				2015[g]	10[g]
KNCSe		558[h]	424, 416[h]	2069[f]	3.1[f]
Ti	-OCN	1132 m[i]	626 m, 593 m	2235	13
				2196	18
Zr	-OCN	1257 w, 1070 sh[i]	631 m, 607 m	2233	12
				2200	16
Hf	-OCN	1257 w, 1071 sh[i]	632 m, 606 m	2246	12
				2211	18
V	-NCO	1329 m–s	603 m, 592 m	2239	14
				2213	15
Ionic cyanate		1300, 1205[j]	636, 626[j]	2158[k]	8.4[k]
$[(\pi\text{-}C_5H_5)_2TiNCO]$		1302 m–s	599 m, 590 m	2216[l]	*m*

[a] Measured as KBr disk. [b] Dichloromethane solution. [c] Integrated absorption intensity, calculated per mole of coordinated pseudohalide for each band of the doublet. [d] No band in S-bonded range; N-bonded range obscured by cyclopentadienyl absorption. [e] L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956). [f] 2-Butanone solution; data taken from C. Pecile, *Inorg. Chem.*, **5**, 210 (1966). [g] Acetone solution, data taken from ref 7. [h] H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961). [i] See text and Figures 1 and 2. [j] As KNCO; data taken from T. C. Waddington, *J. Chem. Soc.*, 2499 (1959). [k] As $[(C_6H_5)_4As]NCO$–acetone solution; data taken from A. H. Norbury and A. I. P. Sinha, *ibid.*, *A*, 1598 (1968). [l] Acetone solution. [m] Could not be accurately determined, due to partial decomposition of complex in solution. [n] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

TABLE II

VISIBLE–ULTRAVIOLET SPECTRA OF $(\pi\text{-}C_5H_5)_2ML_2$ COMPLEXES[a]

M(IV)	L	ν_{max}, kK (ϵ, M^{-1} cm^{-1}) I	II	III	IV
Ti	Cl	39.2 (21,400)	32.3 sh (5610)	25.7 (2100)	19.1 (192)
	-OCN	39.5 (28,100)	35.8 (17,800)	26.5 (4670)	20.4 (295)
	-NCS	33.8 (13,700)	28.3 (10,100)	22.5 (14,000)	18.2 (304)
Zr	Cl	42.5 (5830)	34.4 (3010)		
	-OCN	43.5 (7460)	35.7 (5160)	29.8 sh (764)	
	-NCS	39.6 (30,900)	33.0 (5620)	29.5 (13,800)	
Hf	Cl	44.0 (4680)	37.6 (3460)	33.1 (1050)	
	−OCN	43.8 (6000)	38.0 (6480)	33.4 (1230)	
	-NCS	42.0 (5370)	35.0 (6060)	31.6 (21,900)	
V	Cl		35.4 (7880)	26.3 (2220)	
	-NCO	42.4 (14,700)	36.3 (12,770)	26.8 (4010)	
	-NCS	37.8 (11,400)	28.9 (5260)	25.0 (6120)	21.6 (5520)

[a] Dichloromethane solutions.

The situation regarding the determination of the bonding mode of the cyanate ion using criteria based on infrared spectral data is less straightforward. Complicating the issue is the fact that virtually all of the previously reported coordination compounds of the cyanate ion are believed to contain isocyanate (N bonded) groups.[12,13] The considerable amount of infrared data that has been reported for the isocyanate coordination complexes[12] (numbering approximately 50), organometallic isocyanates,[11] and organic isocyanates[14,15] may be summarized as follows: (1) all of the compounds exhibit ν_{CN} bands which are at higher frequencies, whether measured as mulls or in solution, than that of the free ion; (2) all of the compounds exhibit ν_{CO} bands which are at higher frequencies than the unperturbed[16] frequency (1254 cm^{-1}) of the free ion (the doublet actually observed (Table I) is due to Fermi resonance between the overtone of the NCO bending frequency and the fundamental CO stretching frequency); (3) the δ_{NCO} frequencies tend to be, in general, little changed from the free-ion values; (4) the integrated absorption intensities of the ν_{CN} bands, where measured, are larger than that of the free ion.

Except for the titanium(IV) complex discussed below,

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[12] See references cited in J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, **8**, 1546 (1969).

[13] S. M. Nelson and T. M. Shepherd, *J. Inorg. Nucl. Chem.*, **27**, 2123 (1965).

[14] R. P. Hirschmann, R. N. Kniseley, and V. A. Fassel, *Spectrochim. Acta*, **21**, 2125 (1965).

[15] N. S. Ham and J. B. Willis, *ibid.*, **16**, 279 (1960).

[16] A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959).

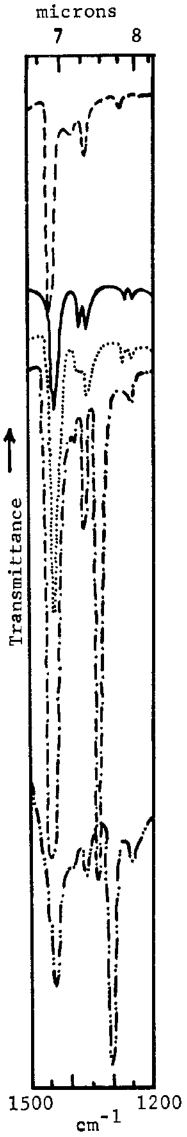

Figure 1.—Infrared spectra of metallocene cyanate complexes (pressed in KBr disks) in the N-bonded cyanate ν_{CO} frequency range: – – – –, $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$; ———, $(\pi\text{-}C_5H_5)_2Zr(OCN)_2$; ······, $(\pi\text{-}C_5H_5)_2Hf(OCN)_2$; —·—·—·, $(\pi\text{-}C_5H_5)_2V(NCO)_2$; ··—··, $(\pi\text{-}C_5H_5)_2TiNCO$.

only one report involving O-bonded cyanate coordination complexes [hexacyanates of Re(IV), Re(V), and Mo(III)] has appeared in the literature.[17] These complexes, as well as the O-bonded organic cyanates[18-20] (no O-bonded organometallic cyanates have been reported), exhibit ν_{CN} and δ_{NCO} bands in the same region as the isocyanates; however, their ν_{CO} frequencies are *lower* than that of the free ion.

The data shown in Table I clearly indicate that all of the metallocene thiocyanate and selenocyanate complexes contain N-bonded groups. The earlier structural conclusions expressed in the literature regarding the titanium(IV)[1-3] and zirconium(IV)[1,2] thiocyanate complexes are, therefore, for the most part, incorrect. Samuel[1] has indicated that both complexes contain S-bonded groups but did not offer any arguments in support of his conclusions. Giddings[3] concluded that the titanium(IV) complex is S bonded on the basis of the color of the complex and its lack of reactivity with butylamine. Coutts and Wailes[2] correctly surmised that both complexes are N bonded, albeit only on the basis of the absence of ν_{CS} bands in the S-bonded frequency range in their infrared spectra.

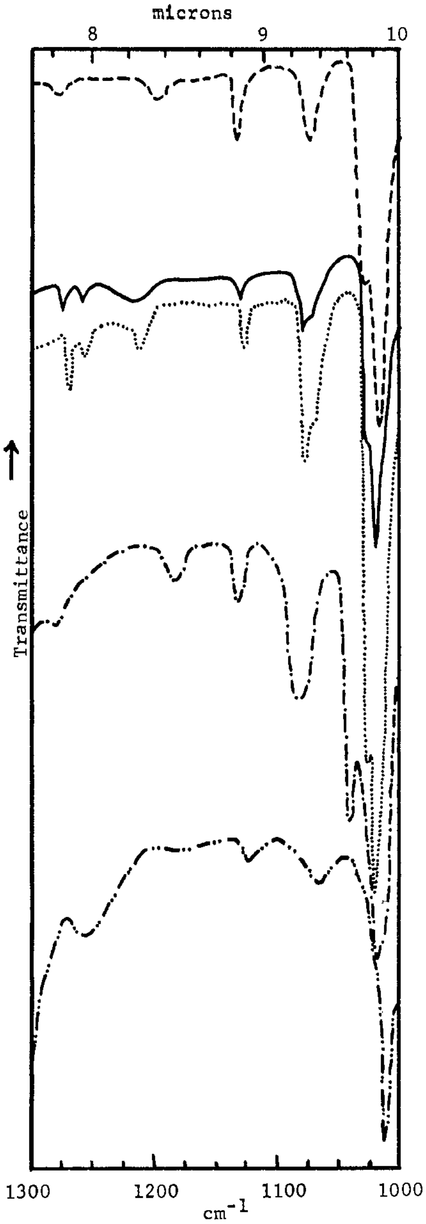

Figure 2.—Infrared spectra of metallocene cyanate complexes (pressed in KBr disks) in the O-bonded cyanate ν_{CO} frequency range: – – – –, $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$; ———, $(\pi\text{-}C_5H_5)_2Zr(OCN)_2$; ······, $(\pi\text{-}C_5H_5)_2Hf(OCN)_2$; —·—·—·, $(\pi\text{-}C_5H_5)_2V(NCO)_2$; —··—, $(\pi\text{-}C_5H_5)_2TiNCO$.

Likewise, Köpf, *et al.*,[5] correctly concluded that the titanium(IV) selenocyanate complex contains N-bonded groups, although their ν_{CSe} stretching frequency assignment (725, 695 cm^{-1}) is incorrect. Doyle and Tobias[6] did not reach any conclusion regarding the bonding mode of the thiocyanate groups in the vanadium(IV)

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(17) R. A. Bailey and S. L. Kozak, *J. Inorg. Nucl. Chem.*, **31**, 689 (1969).

(18) D. Martin, *Angew. Chem. Intern. Ed. Engl.*, **3**, 311 (1964).

(19) H. Hoyer, *Chem. Ber.*, **94**, 1042 (1961).

(20) N. Groving and A. Holm, *Acta Chem. Scand.*, **19**, 443 (1965).

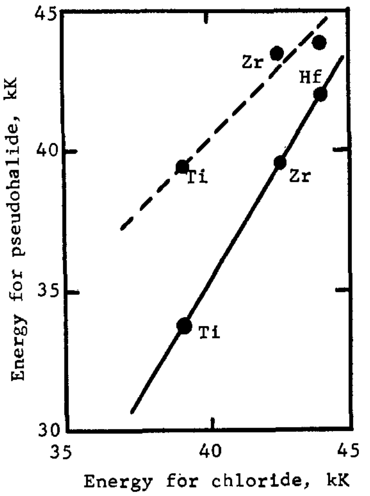

Figure 3.—Plots of metallocene pseudohalide *vs.* chloride energies for visible–uv absorption band I: ———, thiocyanates; – – – –, cyanates.

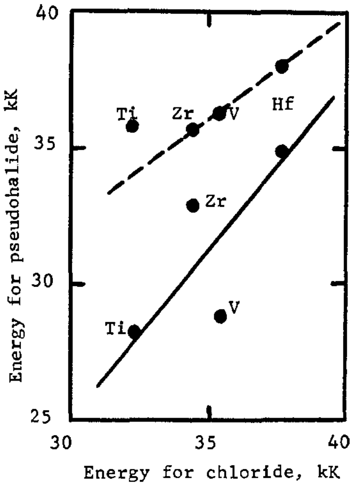

Figure 4.—Plots of metallocene pseudohalide *vs.* chloride energies for visible–uv absorption band II: ———, thiocyanates; – – – –, cyanates.

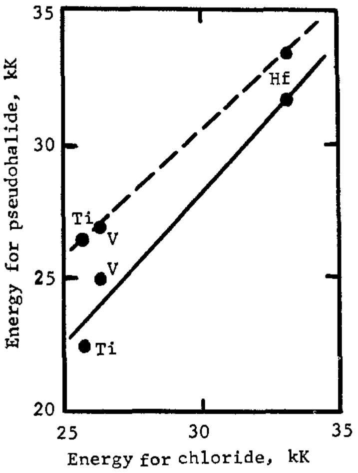

Figure 5.—Plots of metallocene pseudohalide *vs.* chloride energies for visible–uv absorption band III: ———, thiocyanates; – – – –, cyanates.

complex, although they did note the plausibility of the isothiocyanate structure in view of the stability of the corresponding azide and cyanate complexes.

The data for the $(\pi\text{-C}_5\text{H}_5)_2\text{V(NCO)}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{TiNCO}$ complexes fall into the ranges previously observed for metal, organometallic, and organic isocyanates and confirm the structural conclusions reached previously[6,8] on the basis of incomplete infrared spectral data. However, the data for the titanium(IV), zirconium(IV), and hafnium(IV) cyanate complexes differ in one very important respect—they do not exhibit ν_{CO} bands in the N-bonded range. This difference should not be taken lightly, for, except for the vanadium(IV) and titanium(III) cyanate complexes, *all* of the pseudohalide complexes, as well as *all* of the parent chlorides, exhibit spectra which are virtually identical in this region: a band of medium intensity at 1440–1430 cm^{-1}, assigned[21] to ν_{CC} or asymmetric ring breathing of the cyclopentadienyl rings, and a weak band, sometimes split, at 1370–1355 cm^{-1}. As shown in Figure 1, these bands are also present in the spectra of the vanadium(IV) and titanium(III) cyanate complexes. Reproductions of the infrared spectra of the $(\pi\text{-C}_5\text{H}_5)_2\text{TiL}_2$[7] ($\text{L}^-$ = Cl^-, -NCS^-, -NCSe^-, -OCN^-), $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(NCS)}_2$,[1] and $(\pi\text{-C}_5\text{H}_5)_2\text{VL}_2$[6] ($\text{L}^-$ = -CN^-, -NCO^-, -NCS^-, -NCSe^-, N_3^-) complexes are given in the literature. We would therefore conclude that the titanium(IV), zirconium(IV), and hafnium(IV) cyanate complexes contain O-bonded cyanate groups and that the titanium(IV) cyanate complex reported earlier[1,2,7] is actually the first example of this bonding mode for the cyanate ion.

It should be noted that Coutts and Wailes[2] also reported only two bands in this region in their KBr-disk spectra of the titanium (IV) and zirconium (IV) cyanate complexes [Ti(IV), 1370 and 1300 cm^{-1}; Zr(IV), 1370 and 1350 cm^{-1}]. They noted that both bands were of medium intensity and assigned them to ν_{CO} of an N-bonded cyanate and the first harmonic of δ_{NCO}. As shown in Figure 1, their frequency assignments are clearly in error. Furthermore, as noted above, these bands are characteristic, not of the cyanate group, but of $(\pi\text{-C}_5\text{H}_5)_2\text{ML}_2$ complexes in general. The spurious assignments of Coutts and Wailes may be attributed to the relatively low resolving capability of their infrared spectrophotometer (a Perkin-Elmer 137 Infracord). For example, they noted only singlet ν_{CN} bands for the titanium(IV) and zirconium(IV) cyanate (2250 and 2240 cm^{-1}, respectively) and thiocyanate (2090 and 2040 cm^{-1}, respectively) complexes, quite unlike the doublets with a frequency separation of *ca.* 35 cm^{-1} observed in this study, both in solution (Table I) and in the solid state.

All of the chloride and pseudohalide complexes exhibit spectra in the O-bonded cyanate ν_{CO} range which are remarkably similar, consisting, with the exceptions noted below, of five bands: 1280–1265 cm^{-1} (w), 1225–1180 cm^{-1} (w), 1135–1120 cm^{-1} (w) (C–H deformation[21]), 1085–1060 cm^{-1} (m), 1040–1010 cm^{-1} (doublet, s) (in-plane deformation[21]). The relative

[21] H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

intensities of the 1135–1120- and 1085–1060-cm^{-1} bands are reversed from those shown in the case of the chloride complexes, and the δ_{CH} band is not split in the case of $(\pi\text{-}C_5H_5)_2TiNCO$. However, the zirconium(IV) and hafnium(IV) cyanate complexes are unique in that they exhibit (Figure 2) two additional bands in this region: a weak band at 1257 cm^{-1} and a definite shoulder (1070 cm^{-1}) on the 1077-cm^{-1} band. This is precisely the same infrared behavior as that reported by Bailey and Kozak[17] for their O-bonded cyanate complexes. They suggested that the two bands result from Fermi resonance, analogous to that which occurs in the free ion,[16] between the actual ν_{CO} band and the first overtone of δ_{NCO}. In the present case, the "center of gravity" of the 1257- and 1077-cm^{-1} bands is reasonably close to $2\delta_{NCO}$ and Fermi resonance would indeed be possible, since (a) the symmetry species of the in-phase ν_{CO} and $2\delta_{NCO}$ vibrational modes are the same (A_1, assuming that the molecule has C_{2v} symmetry), (b) due to anharmonicity, $2\delta_{NCO}$ would be expected to occur at a somewhat lower frequency than exactly twice the fundamental frequency of 606 cm^{-1}, *i.e.*, closer to the center of gravity, mentioned above, at *ca.* 1164 cm^{-1}, and (c) there may be a degree of asymmetry in the splitting itself,[17] so that the exact position of the actual ν_{CO} frequency may be closer to the actual $2\delta_{NCO}$ frequency than the center of gravity and the calculated $2\delta_{NCO}$ frequency would indicate. Although the evidence is not as compelling as that for the N-bonded vanadium(IV) and titanium(III) cyanate complexes, it does serve to substantiate further our claim that the zirconium(IV) and hafnium(IV) cyanate complexes are O bonded. In the case of the titanium(IV) cyanate complex, Fermi resonance may not occur, and the ν_{CO} band is most probably hidden by the cyclopentadienyl band at 1132 cm^{-1}. Indeed, *it alone*, out of all 14 complexes examined, exhibits bands in the 1135–1120- and 1085–1060-cm^{-1} regions which are of comparable intensity (Figure 2). Samuel[1] also concluded that the titanium(IV) cyanate complex is O bonded, albeit on the basis of an incorrect assumption that the δ_{NCO} bands at 626 and 593 cm^{-1} were Ti–O stretching bands.

Barnes and Day[22,23] have shown that, when the energies of the first intense bands in the visible–uv spectra of thiocyanate, cyanate, and selenocyanate complexes of the types $M(NCS)(H_2O)_n{}^{m+}$, $M(SCN)_p{}^{q-}$, and $M(NCX)_4{}^{2-}$ are plotted against the energies of the first intense bands of the corresponding halide complexes, straight lines of almost unit slope (0.7–1.0) are obtained for the N-bonded pseudohalide complexes, but, for the S-bonded thiocyanates, slopes much less than unity (*ca.* 0.3) are obtained. They suggested that, when the thiocyanate ion is bonded to the metal through nitrogen, the first intense band is due to ligand-to-metal charge transfer (as is assumed to be the case for the halide complexes) but, when it is bonded through sulfur, the band is primarily intraligand π–π^* in origin.

Comparable plots of ν_{max}(pseudohalide) *vs.* ν_{max}(chloride) for each of the bands labeled I–III in Table II yield mixed results (Figures 3–5). Of the thiocyanate *vs.* chloride plots, that for band I (slope 1.7) exhibited the least scatter. That for band III, however, exhibited the slope (1.1) closest to unity. All of the cyanate plots exhibited slopes close to unity [I, 1.1; II, 0.7 (not including the titanium(IV) point which strays far from the line); III, 0.9]. It should also be noted that no data points were available for vanadium(IV) and zirconium(IV) in the plots for, respectively, bands I and III. Although, in the cyanate band II plot, it is the titanium(IV) complex which exhibits deviant behavior (not vanadium(IV), as had been anticipated), no firm conclusions can be reached on the basis of these data, since the titanium(IV) and vanadium(IV) points fall on the *same* line as that for hafnium(IV) in the cyanate band III plot.

Coutts and Wailes[8] have cited the existence of a prominent peak at *m/e* 74 ($TiNC^+$) in the mass spectrum of $[(\pi\text{-}C_5H_5)_2TiNCO]$ as evidence for its formulation as an isocyanate. Although, as they noted, the possibility of rapid rearrangement in the mass spectrometer is always present, the data obtained in this study are indeed suggestive. Most of the prominent mass peaks in the spectra of the metallocene chlorides and pseudohalides correspond to fragments resulting from the stepwise loss of chloride or pseudohalide and/or cyclopentadienide from the parent ion. Others result from further fragmentation (*e.g.*, the $C_3H_3{}^+$ peak is quite intense in all of the spectra) or recombination (*e.g.*, $H^{35}Cl^+$ and $H^{37}Cl^+$ appear in all of the chloride spectra, $HNCO^+$ and $HNCS^+$ appear, respectively, in the cyanate and thiocyanate spectra, and $C_5H_6{}^+$ appears in all the spectra). With the exception of the HX^+ peaks, these features closely resemble, in a qualitative manner, those observed in the mass spectra of $(\pi\text{-}C_5H_5)_2MCl_2$ [M = Ti(IV), Zr(IV)] by Dillard and Kiser.[24] However, a number of the remaining major mass peaks appear to reflect the different bonding modes of the ambidentate ligands. For example, very strong peaks corresponding to TiO^+, ZrO^+, and HfO^+ appear in the spectra of the cyanate complexes which are believed to contain O-bonded cyanate groups. However, only a very weak peak at *m/e* 67, corresponding to VO^+, appears in the vandium(IV) cyanate spectrum. Conversely, a medium peak corresponding to VNC^+ appears in the latter spectrum as well as in the V(IV) thiocyanate spectrum, but only weak peaks with *m/e* values corresponding to $TiNC^+$, $ZrNC^+$, and $HfNC^+$ appear in the spectra of the titanium(IV), zirconium(IV), and hafnium(IV) cyanates. Furthermore, whereas the TiO^+, ZrO^+, and HfO^+ peaks are part of characteristic patterns of mass peaks corresponding to the isotopic distributions of these metals, the peaks with *m/e* values corresponding to $TiNC^+$, $ZrNC^+$, and $HfNC^+$ are not, indicating that the latter assignments are questionable. Vanadium has essentially only one naturally occurring isotope (99.75% ^{51}V); hence, this criterion for peak assignment

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[22] J. C. Barnes and P. Day, *J. Chem. Soc.*, 3886 (1964).

[23] P. Day, *Inorg. Chem.*, **5**, 1619 (1966).

[24] J. G. Dillard and R. W. Kiser, *J. Organometal. Chem.* (Amsterdam), **16**, 265 (1969).

does not apply. It should also be noted that, although a very strong peak at *m/e* 100, corresponding to $Ti(NC)_2^+$, is present in the titanium(IV) cyanate spectrum, it also is not part of the typical grouping of five peaks due to the titanium isotope distribution, and the $Ti(NC)_2^+$ assignment is most probably incorrect. Three other strong peaks are significant: that at *m/e* 207 in the vanadium(IV) thiocyanate spectrum, corresponding to $V(C_5H_5)_2NC^+$, and the *m/e* 213 and 303 peaks, both part of characteristic isotope patterns, in the zirconium(IV) and hafnium(IV) cyanate spectra, corresponding to $M(C_5H_5)(OCN)O^+$.

It would appear that the difference in the bonding modes indicated by the infrared and mass spectral data for the metallocene cyanate complexes may be attributed to the presence of the 3d electron in the titanium(III) and vanadium(IV) complexes, since it can participate in $d_\pi \rightarrow \pi^*$ bonding with the larger lobes of the vacant π^* cyanate orbitals located on the nitrogen atom. π bonding involving π(oxygen) $\rightarrow d_\pi$ overlap would be expected to predominate in the d^0 titanium(IV), zirconium(IV), and hafnium(IV) complexes. It will therefore be of considerable interest to learn if the same bonding distinction will be made in the corresponding complexes of niobium and tantalum in their IV and V oxidation states.

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π-Phosphacarbollyl Derivatives of Manganese, Iron, and Cobalt[1]

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The phosphacarboranes 7,8- and 7,9-$B_9H_{10}CHP^-$ and the corresponding $B_9H_{10}CHPCH_3$ derivatives are deprotonated with basic reagents to form "phosphacarbollide" ions. Sandwich-bonded transition metal compounds are formed with all four of the phosphacarbollide ligands. The syntheses, characterization, structures, and a limited number of reactions of some manganese, iron, and cobalt complexes are discussed.

In the past few years a large number of metal and nonmetal elements have been incorporated into various boron hydride cage structures.[3,4] The first example of phosphorus atom insertion into a borane structure involved reaction of $Na_3B_{10}H_{10}CH$ with phosphorus trichloride to form 1,2-$B_{10}H_{10}CHP$.[5] This phosphacarborane has chemical and physical properties quite similar to those of the better known isoelectronic species, 1,2-$B_{10}H_{10}C_2H_2$. Thermal rearrangement of 1,2-$B_{10}H_{10}CHP$ yields both 1,7- and 1,12-$B_{10}H_{10}CHP$.[6] Piperidine at reflux abstracts a boron atom from 1,2- and 1,7-$B_{10}H_{10}CHP$ to give the 7,8- and 7,9-$B_9H_{10}CHP^-$ ions, respectively. The phosphacarborane ions react with methyl iodide at the phosphorus atom to give the neutral derivatives 7,8- and 7,9-$B_9H_{10}CHPCH_3$.[6] The four 11-atom phosphacarboranes are isoelectronic with the previously reported 1,2- and 1,7-$B_9C_2H_{12}^-$ ions.[7]

In this paper we present our results to date on the manganese, iron, and cobalt complexes derived from the $B_9H_9CHP^{2-}$ and $B_9H_9CHPCH_3^-$ ions.

Experimental Section

Apparatus and Materials.—The infrared spectra for which a solvent is not indicated have been recorded as KBr disks. All infrared spectra were measured on a Perkin-Elmer 521 or 621 instrument. Intensities of absorptions are reported as strong (s), medium (m), or weak (w). Low-resolution mass spectra were obtained with an Atlas CH-4 instrument. High-resolution mass spectra were obtained with an AEI MS-9 instrument. Boron (^{11}B) nmr spectra at 32.1 MHz were obtained with a Varian HA-100 spectrometer. Spectral integrals were measured with a planimeter. Boron chemical shift data were measured relative to external trimethyl borate. All data presented in this paper are referenced to the $BF_3 \cdot (C_2H_5)_2O$ standard by addition of −18.15 ppm to the trimethyl borate chemical shift value. Proton nmr spectra were obtained with a Varian A-60, A-60A, or HA-100 spectrometer. Electronic spectra were obtained with a Cary 14 spectrometer. Melting points were obtained in evacuated sealed capillaries and are uncorrected. Elemental analyses (C, H, N, metal) were obtained from the University of Illinois Microanalytical Laboratory. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Magnetic susceptibilities were measured by the Faraday method using a Cahn Model G electrobalance and a Varian Associates D-4004

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(3) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968.

(4) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(5) J. L. Little, J. T. Moran, and L. J. Todd, *J. Am. Chem. Soc.*, **89**, 5495 (1967).

(6) L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969).

(7) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).