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Contribution from the Department of Chemistry,  
Drexel University, Philadelphia, Pennsylvania 19104

## Pyrothiophosphatometal and (Alkyl pyrothiophosphato)metal Complexes<sup>1</sup>

C. M. MIKULSKI,\* L. L. PYTLEWSKI, and N. M. KARAYANNIS

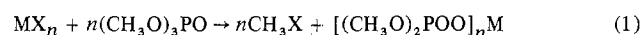
Received March 27, 1974

AIC40198A

Alkali metal iodides ( $M = \text{Li, Na, K, Rb, Cs}$ ) react with triethyl (TETP) and tri-*n*-butyl thiophosphate (TBTP) at elevated temperatures (180–270°), to yield the corresponding (alkyl pyrothiophosphato)metal(I) complexes  $\text{M}_2(\text{PETP})(\text{OH}_2)_2$  and  $\text{M}_2(\text{PBTP})(\text{OH}_2)_n$ , respectively;  $n = 2$  or  $0$ ). Under the same conditions,  $\text{MCl}_2$  ( $M = \text{Mn, Co, Zn}$ ) compounds react with TETP to produce  $\text{M}(\text{PETP})(\text{OH}_2)$  complexes, while the corresponding reactions with TBTP ( $M = \text{Mn, Co, Ni, Zn}$ ) lead to the formation of inorganic metal(II) pyrothiophosphates  $\text{M}_2(\text{PTP})(\text{OH}_2)_6$ .  $\text{AlCl}_3$  reacts with TBTP to yield a complex of the type  $\text{Al}_2(\text{PBTP})_3 \cdot 3\text{H}_2\text{O}$ . The above reactions proceed via formation of a metal halide–TETP or –TBTP adduct, which subsequently decomposes to the corresponding metal dialkyl thiophosphate, with simultaneous formation of alkyl halide, alkene, and hydrogen halide. The last product reacts with the metal dialkyl thiophosphate complex, to yield either an (alkyl hydrogen thiophosphato)- or a (dihydrogen thiophosphato)metal complex, which undergoes a condensation reaction at the reaction temperature, forming  $\text{H}_2\text{S}$  and the corresponding (alkyl pyrothiophosphato)metal or pyrothiophosphatometal complex, respectively. Ir evidence suggests that the PETP, PBTP, and PTP ligands are characterized by the presence of P–S–P rather than P–O–P linkages in the new metal complexes. These compounds were characterized by means of spectral and magnetic studies. Possible structures of the new complexes are discussed. Thus, the  $\text{M}_2(\text{L})(\text{OH}_2)_x$  ( $M = \text{Li, Na, K, Rb, Cs}$ ;  $L = \text{PETP, PBTP}$ ;  $x = 2$  or  $0$ ) and  $\text{M}_2(\text{PTP})(\text{OH}_2)_6$  ( $M = \text{Mn, Co, Ni, Zn}$ ) complexes appear to be monomeric, bimetallic compounds, while  $\text{M}(\text{PETP})(\text{OH}_2)$  ( $M = \text{Mn, Co, Zn}$ ) and  $\text{Al}_2(\text{PBTP})_3 \cdot 3\text{H}_2\text{O}$  are apparently polynuclear.

### Introduction

Neutral phosphate and phosphonate methyl esters react with metal halides at elevated temperatures to form metal complexes of the corresponding dimethyl phosphato and methyl alkyl phosphonato ligands, respectively,<sup>2–4</sup> viz.



Under similar conditions, the corresponding neutral higher alkyl esters (ethyl, propyl, etc.) may lose more than one alkoxy alkyl group per neutral ester molecule, and produce metal complexes of the corresponding phosphate and phosphonate monoalkyl esters or their condensation products (pyrophosphates and pyrophosphonates).<sup>2,5–9</sup> Studies of analogous reactions between metal halides and neutral thiophosphate esters ( $(\text{RO}_3)\text{PS}$ ;  $R = \text{C}_2\text{H}_5$  or  $n\text{-C}_4\text{H}_9$ ) were recently undertaken by this laboratory.<sup>1,10</sup> As already reported, chlorides of  $\text{M}(\text{III})$  ( $M = \text{Ti, V, Cr, Fe, Sc, Y, Ln}$ ),  $\text{M}(\text{IV})$  ( $M = \text{Th, U}$ ),  $\text{Fe}(\text{II})$ , and  $\text{VO}^{2+}$  react with these neutral esters to yield (dialkyl thiophosphato)metal complexes ( $[(\text{RO})_2\text{POS}]_n\text{M}$ ).<sup>1,10</sup> The present communication deals with metal halide–neutral thiophosphate ester reactions, involving elimination of more than one alkyl group per neutral ester molecule.

### Experimental Section

**Reactions.** Reagent grade alkali metal iodides,  $\text{Al}(\text{III})$  and 3d metal chlorides, and triethyl and tri-*n*-butyl thiophosphates (Matheson products) were utilized as received. The reactions, which were carried out in the drybox ( $\text{N}_2$  atmosphere), involved suspension of the anhydrous or hydrated<sup>4–6,9,10</sup> metal halide in an excess of the neutral thiophosphate ester at room temperature and subsequent dissolution

of the salt at ca. 100°. The resulting solutions were then heated to 180–270° for several minutes. Under these conditions, metal ethyl pyrothiophosphates are precipitated when halides of alkali metals,  $\text{Mn}(\text{II})$ ,  $\text{Co}(\text{II})$ , and  $\text{Zn}(\text{II})$  react with  $(\text{C}_2\text{H}_5\text{O})_3\text{PS}$ , and metal *n*-butyl pyrothiophosphates are formed during reactions of  $(n\text{-C}_4\text{H}_9\text{O})_3\text{PS}$  with alkali metal and aluminum(III) halides. These complexes were filtered, washed with acetone and anhydrous diethyl ether, and stored in an evacuated desiccator over calcium chloride. During reaction of  $(n\text{-C}_4\text{H}_9\text{O})_3\text{PS}$  with chlorides of  $\text{Mn}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Zn}(\text{II})$ , the corresponding inorganic metal pyrothiophosphates are formed; their precipitation from the reaction mixture is effected by addition of an excess of ligroin (boiling range 63–75°), after cooling to room temperature. These compounds were filtered, washed with ether, and stored as above. Reactions of  $(\text{C}_2\text{H}_5\text{O})_3\text{PS}$  with chlorides of  $\text{Al}(\text{III})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Cu}(\text{II})$  or  $(n\text{-C}_4\text{H}_9\text{O})_3\text{PS}$  with  $\text{CuCl}_2$  led to solid products of uncertain nature, as shown by analyses. These products were not studied any further.

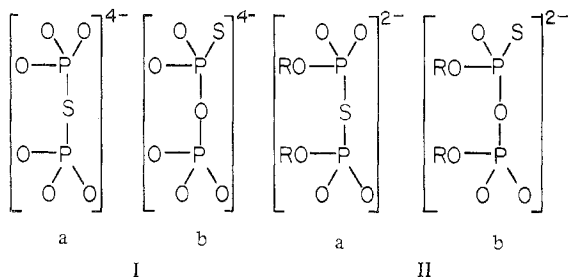
It should be noted that it was established that, for a given metal ion, the same complex is formed, regardless of whether the anhydrous or hydrated metal chloride, bromide, or iodide is used during the synthesis. With the exception of the potassium and cesium *n*-butyl pyrothiophosphates, the new complexes are obtained in the form of hydrates, which are not dehydrated, even after prolonged desiccation over a number of effective drying agents (e.g.,  $\text{CaCl}_2$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{P}_2\text{O}_5$ ). The new compounds reported are insoluble in most common organic solvents (hydrocarbons, halocarbons, acetone, acetonitrile, nitrobenzene, nitromethane, *N,N*-dimethylformamide, etc.), and very sparingly soluble in methanol. The alkali metal complexes are water soluble, while the rest of the complexes show limited solubility in water. During the synthetic reactions, evolution of alkyl halide, alkene ( $\text{C}_2$  or  $\text{C}_4$ ), hydrogen halide,<sup>2,4–6,8–11</sup> and  $\text{H}_2\text{S}$  was observed. These products were collected and identified by methods previously described.<sup>12a</sup> For analytical (Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany), ir and electronic spectral, and magnetic data (obtained by methods described elsewhere<sup>12b,c</sup>)

\* To whom correspondence should be addressed at the Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19174.

see the supplementary material. The abbreviations EPTP, BPTP, and PTP will be used hereafter for the ethyl pyrothiophosphato, *n*-butyl pyrothiophosphato, and pyrothiophosphato ligands respectively. The new complexes are of the following types:  $M_2(\text{EPTP})(\text{OH}_2)_2$  ( $M = \text{Li, Na, K, Rb, Cs}$ );  $M_2(\text{BPTP})(\text{OH}_2)_2$  ( $M = \text{Li, Na, Rb}$ );  $M_2(\text{BPTP})(\text{OH}_2)_2$  ( $M = \text{K, Cs}$ );  $\text{Al}_2(\text{BPTP})_3(\text{OH}_2)_3$ ;  $M(\text{EPTP})(\text{OH}_2)$  ( $M = \text{Mn, Co, Zn}$ );  $M_2(\text{PTP})(\text{OH}_2)_6$  ( $M = \text{Mn, Co, Ni, Zn}$ ).

### Discussion

**Spectral and Magnetic Evidence.** Pyrothiophosphates and alkyl pyrothiophosphates (I and II, respectively) may exist in

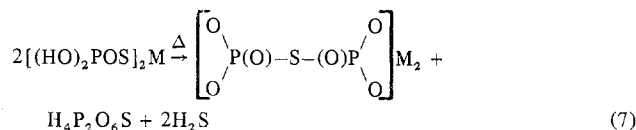
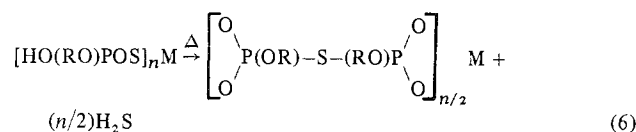
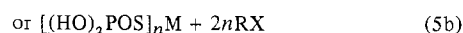
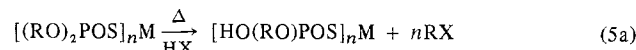
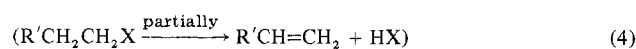
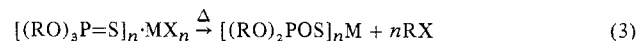
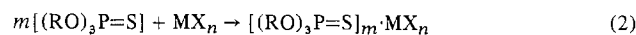


either of the tautomeric forms a and b. Forms Ib and IIb, i.e., those characterized by a P-O-P rather than a P-S-P linkage are more stable, at least in pyrothiophosphate esters.<sup>13-17</sup> Ir evidence may be utilized as a reliable criterion for distinguishing between the presence of P-O-P or P-S-P groupings in compounds of the above types. In fact, the former grouping has a symmetric vibration at 800-600  $\text{cm}^{-1}$  and an asymmetric vibration at 1000-900  $\text{cm}^{-1}$ ,<sup>18,19</sup> whereas the P-S-P grouping reportedly exhibits an absorption at 550-480  $\text{cm}^{-1}$ .<sup>13,14,17</sup> The ir evidence for the complexes reported here is generally in favor of the presence of P-S-P rather than P-O-P groupings. In fact, comparisons of the ir spectra of the alkyl pyrothiophosphato complexes to those of  $[(\text{RO})_2\text{POS}]_n\text{M}$  complexes ( $M = \text{Ti}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Sc}^{3+}, \text{Y}^{3+}, \text{Ln}^{3+}, \text{U}^{4+}, \text{Th}^{4+}$ )<sup>8,10</sup> demonstrates that no bands attributable to  $\nu_{\text{P-O-P}}$  (asym or sym) modes are present, whereas  $\nu_{\text{P-S-P}}$  modes were identified in all cases, including the inorganic pyrothiophosphates. The EPTP and BPTP complexes are also characterized by  $\nu_{\text{POO}}$  (asym and sym) bands, occurring at 1250-1200 and 1100-1050  $\text{cm}^{-1}$ .<sup>2,4,5,20</sup> The PTP complexes, on the other hand, are characterized by the absence of bands associated with P-O-(*n*-C<sub>4</sub>H<sub>9</sub>) modes, which occur as a broad, strong absorption in the 1100-1050- $\text{cm}^{-1}$  region, in thiophosphate butyl ester-metal complexes.<sup>8,10</sup> Instead, a strong, sharp band, associated with the  $\nu_{\text{PO}_3}$  (sym) mode appears at 1062-1026  $\text{cm}^{-1}$ .<sup>18</sup> In general, the ir spectra of the inorganic pyrothiophosphates are distinctly different from those of the (butyl pyrothiophosphato)metal complexes. With two exceptions (K- and Cs-BPTP complexes), the new complexes exhibit ir bands associated with the presence of coordinated aquo ligands ( $\nu_{\text{OH}}$  and  $\delta_{\text{H-O-H}^{21}}$ ). The lower frequency ir region in the spectra of the new complexes (below 600  $\text{cm}^{-1}$ ) is characterized by poorly resolved absorptions, the only exception being the  $\nu_{\text{P-S-P}}$  mode, which generally appears as a distinct peak. No attempts at making  $\nu_{\text{M-O}}$  (EPTP, BPTP, PTP, and aquo) band assignments were made, and the far-ir bands are simply cited in the supplement. It should be noted that in methyl pyrophosphonato analogs,  $\nu_{\text{M-O}}$  modes were tentatively assigned to bands at 370-340 and 280-260  $\text{cm}^{-1}$ , for  $M = \text{Li}^+, \text{Na}^+, \text{K}^+$  and 465-438 and 348-320  $\text{cm}^{-1}$  for  $M = \text{Ca}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$ .<sup>6</sup>

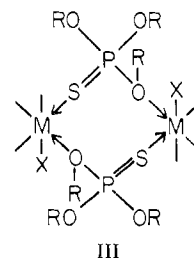
The electronic spectrum of  $\text{Co}(\text{EPTP})(\text{OH}_2)$  may be interpreted in terms of a pentacoordinated configuration.<sup>6,22,23</sup> The Mn(II) and Zn(II) analogs are of about the same structure, as suggested by X-ray powder diffraction patterns. Likewise, pentacoordinated configurations are suggested by the electronic spectra of the Co(II)- and Ni(II)-PTP complexes.<sup>6,22,23</sup> Again the Mn(II) and Zn(II) analogs exhibit

X-ray patterns similar to those of the cobalt(II) and nickel(II) pyrothiophosphates. The magnetic moments of the Mn(II), Co(II), and Ni(II) complexes (5.82-5.92, 5.14-5.28, and 3.46 BM, respectively) are generally within the range of values reported for high-spin pentacoordinated complexes of these metal ions.<sup>24</sup>

**Possible Reactions and Structures.** The reactions between trialkyl thiophosphates and the metal halides under study may be summarized as follows ( $R = \text{C}_2\text{H}_5$ ,  $n\text{-C}_4\text{H}_9 \equiv \text{R}'\text{CH}_2\text{CH}_2$ ;  $R' = \text{H, CH}_3\text{CH}_2$ ;  $X = \text{Cl, I}$ ;  $n = 1, 2, \text{ or } 3$ )



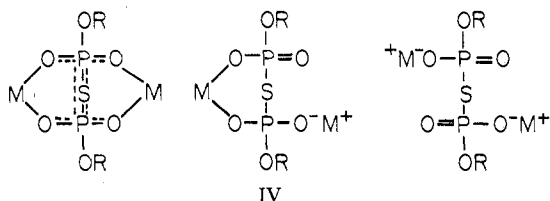
Initially, adducts of the metal halides with the trialkyl thiophosphato ligands are formed<sup>2,25</sup> (reaction 2). These adducts are subsequently converted to the corresponding (dialkyl thiophosphato)metal complexes (reaction 3), at the temperatures used during the syntheses, via an intermediate (III) involving coordination of both the sulfur atom and one



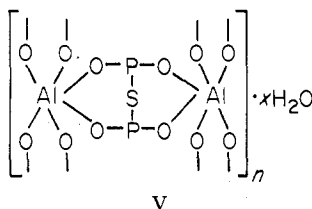
alkoxy oxygen.<sup>2-10</sup> This intermediate catalyzes the partial decomposition of the alkyl halide formed to alkene and hydrogen halide<sup>11,26</sup> (reaction 4). The nature of the final product depends on the thermal stability of the (dialkyl thiophosphato)metal complex formed. The (dialkyl thiophosphato)metal complexes are generally less thermally stable than the corresponding dialkyl phosphato analogs, which decompose at temperatures of 300° or higher.<sup>8,27</sup> Thus, even the relatively stable iron(II) and lanthanide(III) dialkyl thiophosphates<sup>10</sup> yield complexes of the products of further dealkylation and desulfurization of these ligands, if allowed to remain in the reaction mixture and subjected to higher temperatures (ca. 180-200°). The formation of the (alkyl pyrothiophosphato)metal and pyrothiophosphatometal complexes herein reported probably proceeds via dealkylation of the dialkyl thiophosphato ligands to the corresponding alkyl hydrogen thiophosphato or dihydrogen thiophosphato ligand, respectively (reactions 5a and 5b), in the presence of the hydrogen halide liberated during reaction 4.<sup>28,29</sup> Since the latter reaction is not quantitative, the reaction 5 products are obtained in lower than the theoretical amounts. The EPTP or BPTP and the PTP metal complexes are then formed by a condensation

reaction of the products of reactions 5a and 5b, occurring at the elevated temperatures of the synthetic procedure.<sup>2,5,6,30</sup> The condensation involves elimination of H<sub>2</sub>S and formation of (alkyl pyrothiophosphato)metal and pyrothiophosphatometal complexes (reactions 6 and 7, respectively).

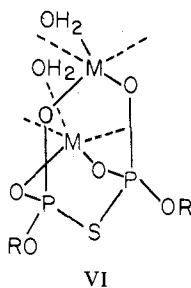
Possible structures for the alkali metal complexes are shown in IV. These are similar to those proposed for the corre-



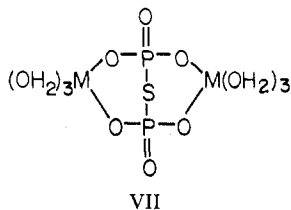
sponding (methyl pyrophosphonato)metal(I) complexes, for which  $\nu_{M-O}$  band assignments were made.<sup>5</sup> The poor resolution of the far-ir spectra of the complexes under study does not allow distinction between the various possibilities depicted in IV. The water in the EPTP and BPTP complexes of alkali metals may be present in the lattice rather than as coordinated aquo groups. A possible structure for the Al(III)-PBTP complex, which is of the type Al<sub>2</sub>(BPTP)<sub>3</sub>·xH<sub>2</sub>O, is structure V (x is most



probably 3, as suggested by the analytical data). The structure of the M(PETP)(OH<sub>2</sub>) complexes (M = Mn, Co, Zn) is probably similar to that proposed by Matrosov et al.<sup>20</sup> for tetrahedral pyrophosphato complexes with divalent metal ions, with an additional aquo ligand coordinated to each metal ion imparting a pentacoordinated structure (VI). Finally,



structure VII may be considered as likely for the inorganic



pyrothiophosphatometal(II) complexes (M = Mn, Co, Ni, Zn), which are apparently of the type M<sub>2</sub>(PTP)(OH<sub>2</sub>)<sub>6</sub>. It should be noted that the  $\nu_{P=O}$  modes, corresponding to uncoordinated P=O groups in this structure,<sup>31</sup> most probably overlap with the  $\nu_{PO_3}$  (asymmetric) bands.

Structural formulas III and VII involve binuclear structures, whereas V and VI suggest that these complexes are polynuclear. These structural assignments are also supported by the fact that the alkali metal complexes are readily soluble in water, while among the rest of the new complexes, which

are sparingly soluble in this medium, the M<sub>2</sub>(PTP)(OH<sub>2</sub>)<sub>6</sub> complexes are somewhat more water soluble.

**Registry No.** LiI, 10377-51-2; NaI, 7681-82-5; KI, 7681-11-0; RbI, 7790-29-6; CsI, 7789-17-5; MnCl<sub>2</sub>, 7773-01-5; CoCl<sub>2</sub>, 7646-79-9; NiCl<sub>2</sub>, 7718-54-9; ZnCl<sub>2</sub>, 7646-85-7; AlCl<sub>3</sub>, 7446-70-0; TETP, 126-68-1; TBTP, 78-47-7; Li<sub>2</sub>(EPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-18-3; Na<sub>2</sub>(EPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-19-4; K<sub>2</sub>(EPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-20-7; Rb<sub>2</sub>(EPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-21-8; Cs<sub>2</sub>(EPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-22-9; Li<sub>2</sub>(BPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-23-0; Na<sub>2</sub>(BPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-24-1; Rb<sub>2</sub>(BPTP)(OH<sub>2</sub>)<sub>2</sub>, 54484-25-2; K<sub>2</sub>(BPTP), 54484-26-3; Cs<sub>2</sub>(BPTP), 54484-27-4; Al<sub>2</sub>(BPTP)<sub>3</sub>(OH<sub>2</sub>)<sub>3</sub>, 54575-91-6; Mn(EPTP)(OH<sub>2</sub>), 54484-36-5; Co(EPTP)(OH<sub>2</sub>), 54484-34-3; Zn(EPTP)(OH<sub>2</sub>), 54484-32-1; Mn<sub>2</sub>(PTP)(OH<sub>2</sub>)<sub>6</sub>, 54484-37-6; Co<sub>2</sub>(PTP)(OH<sub>2</sub>)<sub>6</sub>, 54484-38-7; Ni<sub>2</sub>(PTP)(OH<sub>2</sub>)<sub>6</sub>, 54484-39-8; Zn<sub>2</sub>(PTP)(OH<sub>2</sub>)<sub>6</sub>, 54484-40-1.

**Supplementary Material Available.** A listing of analytical, spectral, and magnetic data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40198A.

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Contribution from the Department of Chemistry,  
The University, Leicester LE1 7RH, England

## Vibrational Analysis of Benzenetricarbonylchromium and Its Deuterated Analog

DAVID M. ADAMS,\* ROGER E. CHRISTOPHER, and DAVID C. STEVENS

Received October 7, 1974

AIC40694Z

An approximate vibrational analysis of the complete benzenetricarbonylchromium molecule and its deuterated analog is presented. Kinematic coupling effects are, in most cases, insufficient to explain the frequency shifts which are observed on coordination of the benzene moiety. The effects of ligation on the force constants of the benzene ring are evaluated and discussed. A description of the normal modes is given and inactive molecular frequencies are calculated.

### Introduction

The structure and properties of the " $\pi$  complexes" of benzene and the cyclopentadienide ion have been intensively researched during the last two decades.<sup>1</sup> In particular, the vibrational spectra of these organometallic species have been closely studied,<sup>2</sup> with much of the interest centering on the spectral changes which accompany coordination of the benzenoid moiety. As it is not always possible to deduce whether changes in the force constants occur, merely by inspection of the frequency shifts (because of kinematic and other effects<sup>3</sup>), there have been several attempts to determine the changes in the molecular force field by calculation.<sup>4-7</sup> The early studies drew different conclusions in several important respects. For example, a report<sup>4</sup> that the coordination shifts of the out-of-plane hydrogen bending modes in dibenzenechromium were due to an increase in the *primary* bending force constant was later disputed, when changes in *interaction* bending force constants were considered to be responsible.<sup>5</sup> In view of these and other disagreements and the fact that the early calculations were very approximate (the benzene ring was "uncoupled" from the rest of the molecule), we have undertaken a vibrational analysis of a complete molecule. Benzenetricarbonylchromium was chosen as its infrared and Raman spectra have been assigned with a moderate degree of certainty,<sup>8</sup> and a complete vibrational assignment exists for benzene itself.<sup>9</sup> While this work was in progress, Cyvin and coworkers<sup>7</sup> published their vibrational analysis of benzenetricarbonylchromium but their conclusions differ from ours in several important respects.

### Calculations and Results

The calculational procedure was as follows. A force field for free benzene was set up and solved in internal valence force constants using the frequencies of the isotopic molecules  $C_6H_6$ ,  $C_6D_6$ , and *sym*- $C_6H_3D_3$ . This refined force field was then applied to benzenetricarbonylchromium; refinement calculations for the organometallic molecule and its deuterated analog were performed subject to the various constraints described below. As a final stage, eigenvector information, potential energy distributions, and cartesian displacement coordinates were obtained.

**A. Force Field for Benzene.** Internal coordinates were selected as in Table I ( $s_1$ – $s_{36}$ ), using the atom-numbering scheme of Figure 1; these involve the redundancies  $A_{1g} + E_{1u} + A_{1u} + E_{1g}$  in  $D_{6h}$  ( $A_1' + E' + A_1'' + E''$  in  $D_{3h}$ ) which were matched by zero eigenvalues in the **G** matrix and subsequently

eliminated as described previously.<sup>10</sup> Bond lengths were taken as  $R_{CC} = 1.397 \text{ \AA}$  and  $R_{CH} = 1.084 \text{ \AA}$ .<sup>11</sup> Symmetry coordinates were generated by the usual methods.<sup>12</sup>

The values of the free benzene force constants are listed in Table II. They were obtained by refinement on the frequencies of  $C_6H_6$ ,  $C_6D_6$ , and *sym*- $C_6H_3D_3$ ,<sup>13</sup> using an in-plane force field similar to that of Duinker and Mills<sup>14</sup> and an out-of-plane force field similar to that of Whiffen<sup>15</sup> except for differences in the definition of the torsional coordinates. Full details concerning the choice and refinement of the benzene force field are given as supplementary material (see note at end of paper), together with details of the frequency fit. We note here only that the mean percentage error over all the frequencies of the three molecules was ca. 0.5%.

**B. Force Field for Benzenetricarbonylchromium.** The molecular symmetry of the organometallic molecule was taken as  $C_{3v}$ , with the tricarbonyl group staggered with respect to the benzene ring (Figure 1); the benzene ring was assumed planar, with sixfold local symmetry. The Cr–C–O groups were assumed linear. Interatomic distances, from the X-ray study,<sup>17</sup> were taken as Cr–C(ring) = 2.22 Å, Cr–C(carbonyl) = 1.84 Å, C–O = 1.14 Å, C–H = 1.08 Å, and C–C = 1.40 Å; the C–Cr–C angles in the tricarbonyl group were taken as 88.5°. Internal coordinates from the benzene moiety were chosen as for benzene itself; these gave rise to the redundancies  $A_1 + A_2 + 2 E$ . Additional internal coordinates for skeletal and tricarbonyl vibrations are listed in Table I; these produce the further redundancies  $A_1 + A_2 + 2 E$ . All redundancies were matched by zero eigenvalues in the **G** matrix and subsequently eliminated.<sup>10</sup> Symmetry coordinates were generated in the usual way;<sup>12</sup> they are listed in the supplementary material. The assignment of fundamental frequencies to their symmetry species was taken as that of Adams and Squire<sup>8a</sup> for Cr-( $\pi$ - $C_6H_6$ )(CO)<sub>3</sub>, except that carbonyl stretching frequencies were from the hexane solution data of Fritz and Manchot.<sup>8b</sup> In addition the frequency order of the  $\nu$ (CH) modes was arbitrarily assumed to follow that in benzene itself,  $A_1 > E > A_2 > E$ . For Cr-( $\pi$ - $C_6D_6$ )(CO)<sub>3</sub> the frequency assignment was that of Fritz and Manchot,<sup>8b</sup> with some modifications. Thus,  $\nu_{14}$  was taken as 1286  $cm^{-1}$ , following Hyams and Lippincott,<sup>8c</sup> because the shift on coordination of  $C_6D_6$  then becomes much closer to that observed on coordination of benzene itself. For the same reason,  $\nu_{15}$  was taken as 815  $cm^{-1}$  and  $\nu_9$  as 850  $cm^{-1}$ . As recently discussed,<sup>8d</sup>  $\nu_{11}$  is reassigned at 582  $cm^{-1}$  and  $\nu_6$  at 575  $cm^{-1}$ . Finally,  $\nu_8$  was taken as 1465  $cm^{-1}$ .<sup>8a</sup>