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Vibrational Analysis of Benzenetricarbonylchromium and Its Deuterated Analog

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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 "π complexes" of benzene and the cyclopentadienide ion have been intensively researched during the last two decades.[1] In particular, the vibrational spectra of these organometallic species have been closely studied,[2] 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[3]), there have been several attempts to determine the changes in the molecular force field by calculation.[4-7] The early studies drew different conclusions in several important respects. For example, a report[4] 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.[5] 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,[8] and a complete vibrational assignment exists for benzene itself.[9] While this work was in progress, Cyvin and coworkers[7] 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.[10] Bond lengths were taken as R_{CC} = 1.397 Å and R_{CH} = 1.084 Å.[11] Symmetry coordinates were generated by the usual methods.[12]

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*-$C_6H_3D_3$,[13] using an in-plane force field similar to that of Duinker and Mills[14] and an out-of-plane force field similar to that of Whiffen[15] 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,[17] 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.[10] Symmetry coordinates were generated in the usual way;[12] they are listed in the supplementary material. The assignment of fundamental frequencies to their symmetry species was taken as that of Adams and Squire[8a] for $Cr(\pi\text{-}C_6H_6)(CO)_3$, except that carbonyl stretching frequencies were from the hexane solution data of Fritz and Manchot.[8b] In addition the frequency order of the ν(CH) modes was arbitrarily assumed to follow that in benzene itself, $A_1 > E > A_2 > E$. For $Cr(\pi\text{-}C_6D_6)(CO)_3$ the frequency assignment was that of Fritz and Manchot,[8b] with some modifications. Thus, ν_{14} was taken as 1286 cm^{-1}, following Hyams and Lippincott,[8c] 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, ν_{15} was taken as 815 cm^{-1} and ν_9 as 850 cm^{-1}. As recently discussed,[8d] ν_{11} is reassigned at 582 cm^{-1} and ν_6 at 575 cm^{-1}. Finally, ν_8 was taken as 1465 cm^{-1}.[8a]

Table I. Internal Coordinate Definitions

Coordinate no.	Type[a]	Atoms defining coordinate	Weight[b]	$\Gamma(C_{3v})$
s_1–s_6	ν(CH)	1-7, 3-9, 5-11, 2-8, 4-10, 6-12		$A_1 + A_2 + 2\,E$
s_7–s_9	ν(CC)[c]	1-2, 3-4, 5-6		$A_1 + E$
s_{10}–s_{12}	ν(CC)[c]	2-3, 4-5, 6-1		$A_1 + E$
s_{13}–s_{18}	α(CCC)	6-1-2, 2-3-4, 4-5-6, 1-2-3, 3-4-5, 5-6-1	R(CC)	$A_1 + A_2 + 2\,E$
s_{19}–s_{24}	β(CH)	(2-1-7)-(6-1-7), (4-3-9)-(2-3-9), (6-5-11)-(4-5-11), (3-2-8)-(1-2-8), (5-4-10)-(3-4-10), (1-6-12)-(5-6-12)	r(CH)	$A_1 + A_2 + 2\,E$
s_{25}–s_{30}	γ(CH)	7 *oop*,[d] 9 *oop*, 11 *oop*, 8 *oop*, 10 *oop*, 12 *oop*	r(CH)	$A_1 + A_2 + 2\,E$
s_{31}–s_{33}	τ(CCCC)	6-1-2-3, 2-3-4-5, 4-5-6-1	R(CC)	$A_2 + E$
s_{34}–s_{36}	τ(CCCC)	1-2-3-4, 3-4-5-6, 5-6-1-2	R(CC)	$A_2 + E$
s_{37}–s_{39}	ν(CO)	14-17, 15-18, 16-19		$A_1 + E$
s_{40}–s_{42}	ν(CrC)	13-14, 13-15, 13-16		$A_1 + E$
s_{43}–s_{45}	$\delta(\mathrm{CrCO})_z$[e]	13-14-17, 13-15-18, 13-16-19	$[R(\mathrm{CrC})R(\mathrm{CO})]^{1/2}$	$A_1 + E$
s_{46}–s_{48}	$\delta(\mathrm{CrCO})_{xy}$[f]	13-14-17, 13-15-18, 13-16-19	$[R(\mathrm{CrC})R(\mathrm{CO})]^{1/2}$	$A_2 + E$
s_{49}–s_{51}	α(CCrC)	14-13-15, 15-13-16, 14-13-16	R(CrC)	$A_1 + E$
s_{52}–s_{57}	$\nu(\mathrm{CrC^r})$[g]	1-13, 2-13, 3-13, 4-13, 5-13, 6-13		$A_1 + A_2 + 2\,E$
s_{58}–s_{63}	$\alpha(\mathrm{C^rCrC})$	1-13-16, 6-13-16, 2-13-14, 3-13-14, 4-13-15, 5-13-15	$[R(\mathrm{CrC})R(\mathrm{CrC^r})]^{1/2}$	$A_1 + A_2 + 2\,E$

[a] Nomenclature as in ref 12, Chapter 10. [b] Weight of internal coordinate in potential energy expression. [c] In D_{6h}, s_7–s_{12} are all members of the same symmetry-related set (as are s_{31}–s_{36}). [d] Out-of-plane CH bend, as defined by Wilson, Decius, and Cross. [e] Linear Cr–C–O bend, in z direction. [f] Linear Cr–C–O bend, perpendicular to corresponding $\delta(\mathrm{CrCO})_z$. [g] Ring carbon atoms are denoted $\mathrm{C^r}$ where confusion with carbonyl carbon atoms might otherwise exist.

Table II. Valence Force Constant Definitions and Refined Values (mdyn/Å)

No.	Definition[a]	Type[b]	Value in benzene	Value in $\mathrm{Cr(CO)_3C_6H_6}$[c]
f_1	s_1^2	P ν(CH)	5.11 (0.02)	5.07 (0.14)
f_2	s_7^2, s_{10}^2	P ν(CC)	7.05 (0.06)	6.13 (0.34)
f_3	s_{13}^2	P α(CCC)	0.59 (0.03)	0.48 (0.05)
f_4	s_{19}^2	P β(CH)	0.223 (0.002)	0.21 (0.007)
f_5	s_{25}^2	P γ(CH)	0.390 (0.003)	0.45 (0.02)
f_6	s_{31}^2, s_{34}^2	P τ(CCCC)	0.131 (0.005)	0.14 (0.01)
f_7	s_7s_{10}, $-s_7s_8$, s_7s_{11}	I ν(CC), ν(CC)[d]	0.54 (0.01)	0.36 (0.08)
f_8	$s_{13}s_{16}$	I α(CCC), α(CCC)	−0.034 (0.015)	[−0.034][e]
f_9	$s_{19}s_{22}$	I β(CH), β(CH)	0.0061 (0.0008)	[0.0061][e]
f_{10}	$s_{19}s_{20}$	I β(CH), β(CH)	−0.0044 (0.001)	[−0.0044][e]
f_{11}	$s_{19}s_{23}$	I β(CH), β(CH)	−0.0084 (0.0016)	[−0.0084][e]
f_{12}	s_7s_{13}	I ν(CC), α(CCC)	0.345 (0.035)	0.31 (0.18)
f_{13}	s_7s_{19}	I ν(CC), β(CH)	0.174 (0.006)	0.13 (0.03)
f_{14}	$s_{13}s_{24}$	I α(CCC), β(CH)	0.029 (0.006)	[0.029][e]
f_{15}	$s_{25}s_{28}$	I γ(CH), γ(CH)	−0.062 (0.002)	[−0.062][e]
f_{16}	$s_{25}s_{29}$	I γ(CH), γ(CH)	−0.014 (0.002)	[−0.014][e]
f_{17}	$s_{31}s_{34}$	I τ(CCCC), τ(CCCC)	−0.035 (0.003)	[−0.035][e]
f_{18}	$s_{25}s_{31}$	I γ(CH), τ(CCCC)	0.103 (0.004)	0.12 (0.01)
f_{19}	$s_{25}s_{34}$	I γ(CH), τ(CCCC)	−0.023 (0.003)	[−0.023][e]
f_{20}	s_{37}^2	P ν(CO)		14.8 (0.5)
f_{21}	s_{40}^2	P ν(CrC)		1.6 (0.1)
f_{22}	s_{43}^2	P $\delta(\mathrm{CrCO})_z$		0.46 (0.02)
f_{23}	s_{46}^2	P $\delta(\mathrm{CrCO})_{xy}$		0.33 (0.02)
f_{24}	s_{52}^2	P $\nu(\mathrm{CrC^r})$		1.3 (0.1)
f_{25}	s_{49}^2	P α(CCrC)		[0.1][f]
f_{26}	s_{58}^2	P $\alpha(\mathrm{CCrC^r})$		[0.1][f]

[a] Thus f_1 is the coefficient of s_1^2 in the potential energy expression. [b] P = primary; I = interaction. [c] Refinement II (variance in parentheses). [d] Kekulé constant.[14] [e] Constrained at value in free benzene. [f] Constrained (see text).

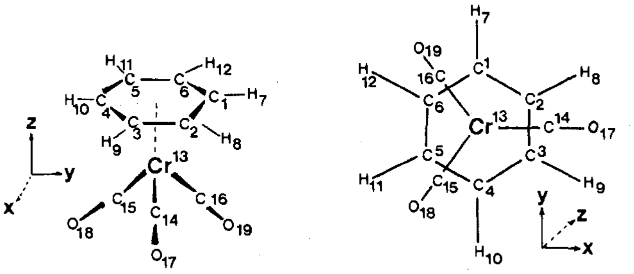

Figure 1. Atom-numbering scheme for $\mathrm{Cr(CO)_3(\pi\text{-}C_6H_6)}$.

Two main types of refinement calculation were performed, one to estimate the magnitude of kinematic effects and the other to obtain the most general refined force field possible with the available frequency data.

Refinement I. For the first refinement, the force constants for the benzene part of the molecule were constrained at those values found for free benzene itself (Table II), while a simple valence force field was assumed for the skeletal force constants (f_{20}–f_{26} in Table II). Initial estimates for some of the skeletal force constants were taken from chromium hexacarbonyl.[18] Refinement was allowed to proceed by varying only the skeletal force constants, using the frequency assignment for the two isotopic molecules (Table III). As the low-energy skeletal deformation modes $\nu_{25}(\mathrm{A_1})$ and $\nu_{33}(\mathrm{E})$, $\nu_{34}(\mathrm{E})$ have not yet been assigned with certainty, the corresponding force constants f_{24} and f_{26} were constrained at 0.1 mdyn/Å, giving calculated deformation frequencies of 140–90 cm^{-1}. The use of different values for f_{24} and f_{26} was found to have only a moderate effect on the values of the refined skeletal force constants, and very little effect on the calculated benzene ring frequencies.

Table III. Frequency Fit and Mode Descriptions for Benzenetricarbonylcrhomium

	$Cr(CO)_3C_6H_6$				$Cr(CO)_3C_6D_6$			
	Obsd	Calcd 1[a]	Calcd 2[b]	Type[c]	Obsd	Calcd 1[a]	Calcd 2[b]	Type[c]
A_1	3110	3077	3056	$\nu_2\nu(\mathrm{CH})$	2285	2292	2272	$\nu_2\nu(\mathrm{CD})$
	1987	1951	1951	$\nu_{21}\nu(\mathrm{CO})$	1987	1951	1951	$\nu_{21}\nu(\mathrm{CO})$
	1316	1316	1302	$\nu_{14}\nu(\mathrm{CC})$	1286	1283	1299	$\nu_{14}\nu(\mathrm{CC})$
	1150	1145	1148	$\nu_{15}\beta(\mathrm{CH})$	815	831	814	$\nu_{15}\beta(\mathrm{CD})$
	979	1029	971	$\nu_1\nu(\mathrm{CC})$	930	978	926	$\nu_1\nu(\mathrm{CC})$
	790	690	762	$\nu_{11}\gamma(\mathrm{CH})$	582	544	587	$\nu_{11}\gamma(\mathrm{CD})$
	666	665	671	$\nu_{22}\delta(\mathrm{CrCO})_z$	674	669	673	$\nu_{22}\delta(\mathrm{CrCO})_z$
	484	497	505	$\left.\begin{matrix}\nu_{24}\\ \nu_{23}\end{matrix}\right\}$ $\nu(\mathrm{CrC^r}) + \nu(\mathrm{CrC})$[d]	484	463	479	$\left.\begin{matrix}\nu_{24}\\ \nu_{23}\end{matrix}\right\}$ $\nu(\mathrm{CrC^r}) + \nu(\mathrm{CrC})$[d]
	298	317	308		288	308	302	
		123	123	(ν_{25})(def)		122	122	(ν_{25})(def)
E	3090	3071	3053	$\nu_{20}\nu(\mathrm{CH})$	2249	2281	2267	$\nu_{20}\nu(\mathrm{CD})$
	3023	3067	3053	$\nu_7\nu(\mathrm{CH})$	2215	2278	2265	$\nu_7\nu(\mathrm{CD})$
	1918	1951	1951	$\nu_{28}\nu(\mathrm{CO})$	1918	1951	1951	$\nu_{28}(\mathrm{CO})$
	1519	1610	1519	$\nu_8\nu(\mathrm{CC})$	1465	1583	1485	$\nu_8\nu(\mathrm{CC})$
	1448	1496	1454	$\nu_{19}\nu(\mathrm{CC})$	1292	1318	1262	$\nu_{19}\nu(\mathrm{CC})$
	1161	1196	1142	$\nu_9\beta(\mathrm{CH})$	806	865	826	$\nu_9\beta(\mathrm{CD})$
	1017	996	1042	$\nu_{17}\gamma(\mathrm{CH})$	850	833	856	$\nu_{17}\gamma(\mathrm{CD})$
	965	1042	973	$\nu_{18}\beta(\mathrm{CH})$	791	831	792	$\nu_{18}\beta(\mathrm{CD})$
	904	865	933	$\nu_{10}\gamma(\mathrm{CH})$	762	694	743	$\nu_{10}\gamma(\mathrm{CD})$
	637	626	634	$\nu_{29}\delta(\mathrm{CrCO})_z$	635	630	631	$\nu_{29}\delta(\mathrm{CrCO})_z$
	614	658	621	$\nu_6\alpha(\mathrm{CCC})$	575	613	580	$\nu_6\alpha(\mathrm{CCC})$
	543	546	546	$\nu_{30}\delta(\mathrm{CrCO})_{xy}$	541	544	544	$\nu_{30}\delta(\mathrm{CrCO})_{xy}$
	490	465	458	$\nu_{16}\tau(\mathrm{CCCC})$	380	398	403	$\nu_{16}\tau(\mathrm{CCCC})$
	424	437	434	$\left.\begin{matrix}\nu_{32}\\ \nu_{31}\end{matrix}\right\}$ $\nu(\mathrm{CrC^r}) + \nu(\mathrm{CrC})$[d]	490	430	421	$\left.\begin{matrix}\nu_{32}\\ \nu_{31}\end{matrix}\right\}$ $\nu(\mathrm{CrC^r}) + \nu(\mathrm{CrC})$[d]
	330	321	322		311	299	305	
		136	136	(ν_{33})(def)		132	132	(ν_{33})(def)
		86	86	(ν_{34})(def)		86	86	(ν_{34})(def)
A_2		3069	3057	$\nu_{13}\nu(\mathrm{CH})$		2281	2273	$\nu_{13}\nu(\mathrm{CD})$
		1361	1320	$\nu_3\beta(\mathrm{CH})$		1058	1027	$\nu_3\beta(\mathrm{CD})$
		1002	1030	$\nu_5\gamma(\mathrm{CH})$		863	806	$\nu_5\gamma(\mathrm{CD})$
		1052	966	$\nu_{12}\alpha(\mathrm{CCC})$		998	929	$\nu_{12}\alpha(\mathrm{CCC})$
		749	710	$\nu_4\tau(\mathrm{CCCC})$		617	636	$\nu_4\tau(\mathrm{CCCC})$
		503	504	$\nu_{26}\delta(\mathrm{CrCO})_{xy}$		503	504	$\nu_{26}\delta(\mathrm{CrCO})_{xy}$
		47	47	(ν_{27})(def)		44	44	(ν_{27})(def)

[a] From refinement I (kinematic effect). [b] From refinement II. [c] Mode descriptions from PED matrix and cartesian displacement, refinement II. Mode numbers correspond to benzene modes with similar mode descriptions. [d] Heavily mixed modes (see text).

Table IV. Predicted and Observed Coordination Shifts and Kinematic Effects[a]

	Mode no.[b]	Type[b]	Δ		
			Kinematic[c]	Predicted[d]	Obsd[e]
A_1	ν_{14}	$\nu(\mathrm{CC})$	1 (1)	−13 (17)	7 (4)
	ν_{15}	$\beta(\mathrm{CH})$	3 (3)	6 (−14)	4 (−9)
	ν_1	$\nu(\mathrm{CC})$	39 (37)	−19 (−15)	−14 (−15)
	ν_{11}	$\gamma(\mathrm{CH})$	15 (48)	87 (91)	117 (86)
E	ν_8	$\nu(\mathrm{CC})$	4 (3)	−87 (−95)	−80 (−93)
	ν_{19}	$\nu(\mathrm{CC})$	7 (7)	−35 (−48)	−34 (−41)
	ν_9	$\beta(\mathrm{CH})$	4 (7)	−50 (−52)	−17 (−63)
	ν_{17}	$\gamma(\mathrm{CH})$	19 (38)	65 (61)	50 (57)
	ν_{18}	$\beta(\mathrm{CH})$	15 (14)	−54 (−26)	−72 (−23)
	ν_{10}	$\gamma(\mathrm{CH})$	16 (34)	84 (83)	58 (102)
	ν_6	$\alpha(\mathrm{CCC})$	50 (34)	13 (1)	8 (−4)
	ν_{16}	$\tau(\mathrm{CCCC})$	62 (48)	55 (53)	86 (29)

[a] ν(CH) modes omitted. [b] From Table III. [c] Refinement I frequency minus calculated frequency for corresponding benzene mode (value for deuterated compounds in parentheses). [d] Refinement II frequency minus calculated frequency for corresponding benzene mode. [e] From the assignment in Table III.

Refinement proceeded smoothly to a mean absolute error over all the assigned frequencies of 30 cm^{-1} (mean error for the skeletal modes 14 cm^{-1}). The calculated frequencies are listed in Table III; those for the skeletal modes are very close (within 4 cm^{-1} on average) to the calculated values in refinement II. Since in this calculation the force constants for the benzene ring were constrained at the values in free benzene, any differences in the calculated frequencies of the benzene ring modes (compared with the values of free benzene) must represent the effect of kinematic coupling via nonzero off-diagonal elements in the **G** matrix of benzenetricarbonylchromium. The calculated kinematic effects are listed in Table IV, together with the observed coordination shifts. These shifts are discussed in more detail below; we only note here that kinematic effects are insufficient to explain all the observed coordination shifts.

Refinement II. The most general force field to converge successfully was that referred to here as refinement II. Table II lists the refined force constants, and Table III the frequency fit obtained for the two isotopic molecules. In refinement II, all the primary force constants were allowed to float (excluding f_{25} and f_{26} which were fixed at 0.1 mdyn/Å as in refinement I), including the benzene primary force constants. In addition, the large benzene interaction force constants f_7, f_{12}, f_{13}, and f_{18} were also allowed to adjust. All other benzene interaction force constants (f_8–f_{11}, f_{14}–f_{17}, and f_{19}) were constrained at the values obtained for free benzene; these force constants were all smaller than 0.07 mdyn/Å in benzene. Furthermore, all other interaction force constants (skeletal–skeletal and skeletal–ring, etc.) were constrained to zero.

The force field used in refinement II was selected after investigation of a large number of force fields and a study of the effects of various constraints on the force constant solution. Details of this work form part of the supplementary material.

Discussion

Kinematic Coupling Effects. As discussed above (refinement I), the calculated kinematic coupling effects were derived using a force field for the benzene ring which is constrained at that of uncoordinated benzene, together with a simple valence skeletal force field which reproduces the frequencies of the skeletal modes with an average error of 14 cm^{-1}. Note especially that the magnitudes of both the calculated kinematic coupling effects and the observed coordination shifts are dependent on the correct matching of the appropriate pairs of frequencies in the free benzene molecule and in the organometallic species. For a compound with a "crowded" vibrational spectrum, which shows large coordination shifts, we depend on a vibrational analysis to provide mode descriptions so that corresponding pairs of frequencies may be correctly indentified. Table IV gives the kinematic and coordination shifts thus obtained from refinement I. Although mode mixing occurs in some of the frequencies, this is sufficiently small in nearly all of the benzene ring modes not to invalidate the concepts of coordination and kinematic shifts.

It is evident that kinematic effects, although present, do not account for most of the observed coordination shifts. In particular, the *direction* of the observed coordination shifts is opposite to that predicted from kinematic effects for most of the ν(CC) and β(CH) modes. Furthermore, the magnitude of the observed γ(CH) shifts is considerably larger and that of the α(CCC) modes much smaller than predicted. Only in the case of the ring torsional mode, ν_{16}, is the coordination shift approximately as predicted from kinematic coupling. We conclude, therefore, that changes in the force constants associated with the benzene ring are largely responsible for the observed coordination shifts.

Our conclusions on kinematic coupling differ quantitatively from those of Cyvin and coworkers. They concluded that kinematic effects can explain, at least in part, some of the coordination shifts in benzenetricarbonylchromium,[7] dibenzenechromium, and ferrocene.[6] Thus far, we are in agreement, but the main theme of their conclusions is to emphasize the predominance of the kinematic component, whereas we have shown that this is generally the minor part. Although our choice of frequency assignment differs in some details from that of ref 7, it is probably not sufficiently so to account for the different emphases in our conclusions. It is not impossible that these differences in conclusions arise from differences in the calculational techniques employed (for example, in the choice of symmetry coordinates), but this must be a matter for subsequent study. Nevertheless, we believe that the conclusions which we draw from our calculations are fully compatible with what might reasonably be expected on the basis of chemical bonding arguments.

Refined Force Field for Benzenetricarbonylchromium. Table II gives details of the most general refined force field that we could obtain for benzenetricarbonylchromium from the available frequency data.

A. Frequency Fit. The final force field, which comprised 15 adjustable force constants and 11 fixed force constants (of which 9 of the latter were fixed at the free benzene values and 2 were arbitrarily chosen), gave a fit to the 48 input frequencies with a mean percentage error of 1.9% and a mean absolute error of 17 cm^{-1}. The largest error of 69 cm^{-1} was in ν_{32}, a heavily mixed skeletal mode, for the deuterated molecule; apart from this the largest errors were about 30 cm^{-1}. We believe that this frequency fit is reasonable, in view of the complexity of the molecule and the relatively modest molecular symmetry. As the calculations on free benzene and on the organometallic species both give an inexact frequency fit, it is important to establish whether the changes in the force constants are meaningful in the sense that the calculated frequency shifts agree with the observed coordination shifts. Table IV lists both sets of results. Since the calculated coordination shifts are in reasonable agreement with the observed shifts (in sign and in approximate magnitude), we conclude that changes in the force constant parameters are meaningful.

B. Force Constants of the Benzene Ring. Three of the benzene ring force constants show large changes on ligation; these relate to carbon–carbon stretching (f_2), in-plane ring bending (f_3), and CH out-of-plane bending (f_5) vibrations. In addition, the Kekulé ring interaction constant f_7 decreases markedly on coordination of the benzene ring. None of the other benzene force constants are significantly altered from the free-ligand values. The decrease in f_2 (ca. 13%) may be attributed to the decrease in the ring π-bond order on coordination of the benzene ring;[19] the decreases in the ring bending force constant (of ca. 19%) and in the Kekulé interaction constant (ca. 33%) are probably of similar origin. The CH out-of-plane bending force constant, f_5, shows a 15% increase on coordination. We therefore agree with Snyder[4] that the shifts to higher frequency of the CH out-of-plane bending modes, which occur on coordination of the benzene ring, are essentially due to an increase in the primary force constant, rather than to changes in the interaction force constants as suggested by Saito et al.[5] We cannot, however, exclude the possibility that some changes in the interaction force constant *also* occur. As previously suggested,[4] the increase in f_2 on coordination may be explained in terms of the theory of orbital following during molecular vibrations.[20] Thus, the decrease in the population of the ring π orbitals on coordination renders orbital rehybridization more difficult during the CH out-of-plane bending vibrations (electrophilic substitution of the ring has similar effects[20]); the corresponding force constant, f_5, therefore increases.

C. Skeletal Force Constants. The absolute values of the skeletal force constants are unlikely to be very significant because of the approximations in the present force field. We merely note here that both of the force constants describing chromium–carbon stretching, f_{21} and f_{24}, have similar magnitudes (1.6 and 1.3 mdyn/Å, respectively), but with f_{21} being somewhat larger. Of the two force constants relating to chromium–carbonyl linear bending (f_{22} and f_{23}), that for axial bending parallel to the threefold molecular axis (f_{22}) is considerably larger.

D. Normal Mode Descriptions. Mode descriptions from the potential energy distribution matrix and cartesian displacement coordinates, for refinement II, are given in Table III. The frequency numbering for the ring vibrations in Table III corresponds to that of benzene itself;[9] the skeletal modes are numbered to correspond to the descriptions of Adams and Squire.[8a]

The calculated mode descriptions for benzenetricarbonylchromium in general agree very well with the (intuitive) descriptions of Adams and Squire.[8a,d] However, the calculation interchanges the descriptions of the 1017- and 965-cm^{-1} modes to ν_{17} [γ(CH)] and ν_{18} [β(CH)], respectively; this seems reasonable since all the γ(CH) modes then have positive coordination shifts. Furthermore, mode descriptions in the 490–320-cm^{-1} region of the E block differ from those of ref 8a, although extensive mode mixing occurs in this area; the calculation, however, is subject to some uncertainty in this region because of the large frequency error in the fit of ν_{32} for the deuterated compound.

The calculated mode descriptions for perdeuteriobenzenetricarbonylchromium are in general agreement with the descriptions from the modified Fritz and Manchot assignment (see the Discussion and Results sections, above). However, descriptions for frequencies in the 850–762-cm^{-1} region of the E block (ν_9, ν_{10}, ν_{17}, ν_{18}) are somewhat altered; the main effect here is that the calculation describes the 850-cm^{-1} band as mainly γ(CD) and the 791-cm^{-1} band as mainly β(CD).

Mixing of in-plane ring modes with out-of-plane ring modes, although symmetry allowed, is only slight in the organometallic species, with the exception of ν_{18} [β(CD)] for the deuterated complex. This shows fairly extensive mixing with the neighboring mode ν_{10} [γ(CD)]. Furthermore, the mixing of ring modes with skeletal modes is, in general, slight. Some of the ring modes show extensive mixing of symmetry coordinates of different types; thus in the E block of $Cr(\pi\text{-}C_6H_6)(CO)_3$ the frequency at 1448 cm^{-1} is best labeled ν_{19} [ν(CC)] although mixing with ν_{18} [β(CH)] at 965 cm^{-1} is pronounced. For the deuterated compound, ν_{19} (1292 cm^{-1}) is less heavily mixed with ν_{18} (791 cm^{-1}), but ν_{18} and ν_{10} (762 cm^{-1}) are now heavily mixed. Many of the skeletal modes show contributions from more than one symmetry coordinate. In particular, the chromium–carbon stretching modes are very extensively mixed; this is to be expected as they are mechanically coupled and have similar frequencies. In both the A_1 and E blocks and with both isotopic molecules, the mixing of the chromium–carbon stretching modes is so extensive as to render meaningless descriptions in terms of either ν(Cr–C) or $\nu(Cr\text{–}C^r)$.

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Supplementary Material Available. Further information on the details of the vibrational analysis 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 Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40694Z.

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Reactions of Ethylene Coordinated to Molybdenum, Tungsten, and Iron

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Nitrogen, phosphorus, and oxygen nucleophiles, as well as cyanide ion, add to ethylene in $CpMo(CO)_3C_2H_4^+$,[1] $CpW(CO)_3C_2H_4^+$, and $CpFe(CO)_2C_2H_4^+$ to form β-substituted ethylmetal derivatives. Deprotonation of cationic products containing an N–H bond, e.g., $CpW(CO)_3CH_2CH_2NH_3^+$, leads to an insertion–cyclization reaction.

Introduction

The reactivity of coordinated olefinic ligands has been of continual interest for over a decade (see ref 2 and references therein). However, there have been relatively few studies on simple coordinated monoolefins. Recently, coordinated ethylene in $CpFe(CO)_2C_2H_4^+$ was shown to be subject to the facile addition of anionic carbon nucleophiles (L) to form $CpFe(CO)_2CH_2CH_2L$[2] and to the addition of triphenylphosphine, methylamine, and methoxide ion to form $CpFe(CO)_2CH_2CH_2PPh_3^+$,[2b] $CpFe(CO)_2CH_2CH_2N(H)CH_3$,[3] and $CpFe(CO)_2CH_2CH_2OCH_3$,[3] respectively. In addition, ammonia and amines have been found to react with simple monoolefins in certain palladium and platinum complexes.[4]

This paper is concerned mainly with the addition of ammonia and other nucleophiles to coordinated ethylene in $CpM(CO)_3C_2H_4^+$ (M = Mo, W) and with further transformations of the reaction products. Further examples of nucleophilic additions to $CpFe(CO)_2C_2H_4^+$ are described and compared with the molybdenum and tungsten systems and some related chemistry arising from the reaction of ethylene oxide with $CpM(CO)_3^-$ (M = Wo, W) is presented.

Results and Discussion

Ammonia readily adds to ethylene in $CpFe(CO)_2C_2H_4^+$ (I), $CpMo(CO)_3C_2H_4^+$ (II), and $CpW(CO)_3C_2H_4^+$ (III). The isolated products tend to be dialkylated; e.g., $[CpFe(CO)_2CH_2CH_2]_2NH_2^+$ (IV), $[CpMo(CO)_3CH_2CH_2]_2NH_2^+$ (V), and $[CpW(CO)_3CH_2CH_2]_2NH_2^+$ (VI) have been obtained, although $CpW(CO)_3CH_2CH_2NH_3^+$ (VII) has also been isolated. Most of this work involved preparation, isolation, and characterization of these cations as the hexafluorophosphate salts. Reactions of I–III with ammonia are facile and exothermic and proceed in good yield when ammonia vapor is passed over the solid salt or through an acetonitrile solution. Deprotonation of V–VII by sodium hydroxide is accompanied by a cyclization–insertion reaction as in eq 2 and 3. If the reaction of ammonia with II is run in benzene, monoalkylation