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The Stability of the Borazole-to-Metal Bond in $R_3B_3N_3R'_3Cr(CO)_3$. Kinetic and Thermochemical Studies*

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Kinetic studies for the reaction of $R_3B_3N_3R'_3Cr(CO)_3$ (R and R' = Me, Et, n-Pr, i-Pr) with tertiary phosphites are reported. The results indicate that steric factors are most important for the rate of ring ligand displacement. There is no correlation between $\Delta G^{\ddagger}$ (293 K) and the strength of the borazole–chromium bond. The bond enthalpy contribution $B_3N_3R_6$–Cr has been determined by thermal decomposition and by iodination and shown to be 25 ± 3 kcal/mol for R = Me and Et. The value of $D[B_3N_3R_6–Cr]$ is much less than $D[C_6R_6–Cr]$ which is discussed with regard to the different type of bonding modes.

Introduction

Following the synthesis of the first borazole–metal complex, $B_3N_3Me_6Cr(CO)_3$ [2, 3], recently we have prepared a number of ring-substituted derivatives $R_3B_3N_3R'_3Cr(CO)_3$ (R and R' = Me, Et, n-Pr or i-Pr) either by reaction of *fac*-$Cr(CO)_3(MeCN)_3$ and borazole or by ring ligand exchange, *e.g.* from $Et_3B_3N_3Me_3Cr(CO)_3$ and $R_3B_3N_3R'_3$ [4, 5]. We were particularly interested to learn whether the size of the substituents R and R' influences the bonding between the borazole and the metal, and to what extent steric factors determine the kinetic stability of the $Cr(CO)_3$ complexes.

An initial answer to these questions came from the spectroscopic studies and the experiments following the synthesis of the complexes. Varying the alkyl substituents both at the boron and the nitrogen atoms of the ring had almost *no effect* both on the carbonyl stretching frequencies in the i.r. and on the absorption maxima in the u.v. spectra [4]. The reactivity, however, towards Lewis bases proved to be remarkably dependent on R and R'. Whereas the hexamethyl compound reacts with dioxane or toluene at room temperature to give $Cr_2(CO)_6(dioxane)_3$ [6] and $C_6H_5CH_3Cr(CO)_3$, respectively, the hexaethyl complex is quite stable under these conditions.

In order to get more precise and quantitative information on the stability of the bond between the borazole and the $Cr(CO)_3$ fragment we have tried to determine the corresponding bond enthalpy contribution and to evaluate exact kinetic data for the ring ligand displacement reactions of $R_3B_3N_3R'_3Cr(CO)_3$ with Lewis bases, *e.g.* tertiary phosphites. The results of these studies are reported in the present paper.

Kinetic Data

The methods used to determine the rates of the reactions according to eq. (1) were the same as described previously for the system $B_3N_3Me_6Cr(CO)_3$/$P(OR)_3$ [7]. Whereas all the borazole complexes exhibit an absorption maximum at ~390 nm, the absorption of the products (IX) and (X) in this region is extremely small and can be ignored for the calculation of the rate constants.

$$R_3B_3N_3R'_3Cr(CO)_3 + 3\ P(OR)_3 \longrightarrow Cr(CO)_3[P(OR)_3]_3 + R_3B_3N_3R'_3 \qquad (1)$$

(I) : R = Me, R' = Me
(II) : R = Et, R' = Me
(III) : R = Me, R' = Et
(IV) : R = Et, R' = Et
(V) : R = n-Pr, R' = Me
(VI) : R = Me, R' = n-Pr
(VII) : R = i-Pr, R' = Me
(VIII) : R = Me, R' = i-Pr
(IX) : R = Et
(X) : R = Ph

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*Part XVII of the series "Kinetic studies on reactions of metal complexes". For Part XVI see ref. 1a. Also Part VIII of the series "Borazole metal complexes". For Part VII see ref. 1b.

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TABLE I. Second-order Rate Constants k_2 for the Reactions of $R_3B_3N_3R'_3Cr(CO)_3$ with Triphenylphosphite in Cyclohexane.

Complex	Temp. (°C)	10^2 k_2 (l/mol•sec)
(II)	20	4.39
	30	6.23
	40	8.75
(III)	10	0.148
	20	0.284
	30	0.562
(IV)	25	0.034
	35	0.077
	45	0.164
(V)	7	0.765
	10	1.123
	17	1.919
	24	2.566
(VI)	7	0.093
	13	0.143
	20	0.257

It was originally intended to use the cage phosphite $P(OCH_2)_3CMe$ as reacting ligand also. The corresponding complex $Cr(CO)_3L_3$ [ν(CO): 1980 and 1890 cm^{-1}, in KBr], however, turned out to be very much less soluble in cyclohexane which was generally employed as the solvent for the kinetic studies. In 1,2-$C_2H_4Cl_2$ (which had partly been used for the reactions of (I) and $P(OR)_3$ [7]) the rates of decomposition of (II), (III), (V) and (VI) are nearly comparable to the rates of the ligand substitution according to eq. (1). Therefore, this solvent has not been used.

The rate measurements with triphenylphosphite were always made under pseudo-first-order conditions in solutions containing a 80–560-fold excess of (X). In all cases, except for the reactions of (VII) and (VIII) with $P(OPh)_3$, linear plots of k_{ps} against phosphite concentration were obtained. The i.r. spectra showed that by reacting dilute solutions (4×10^{-4} mol/l) of (VII) or (VIII) with $P(OPh)_3$, the tricarbonyl (X) is not formed.

TABLE II. Second-order Rate Constants k_2 for the Reactions of $R_3B_3N_3R'_3Cr(CO)_3$ with Triethylphosphite in Cyclohexane.

Complex	Temp. (°C)	10^2 k_2 (l/mol•sec)
(II)	10	98
	20	135
	30	184
(III)	10	6.7
	20	11.4
	30	16.9
(IV)	20	1.85
	30	3.20
	40	5.68
(V)	7	49.3
	13	59.5
	20	72.0
(VI)	7	3.2
	13	5.4
	20	7.9
(VII)	7	1.46
	13	2.28
	20	3.63

With triethylphosphite, ratios of complex to phosphite between 1:6 and 1:20 [for (II), (V) and (VI)] and 1:50 and 1:900 [for (III), (IV) and (VII)] were used. For non-pseudo-first-order conditions the k_2 values were calculated by standard equations using a WANG-600 computer. The rate constants and activation parameters are summarised in Tables I–III.

For both phosphites, the rate data are accurately represented by the expression:

$$-\frac{d[R_3B_3N_3R'_3Cr(CO)_3]}{dt} = k_2[R_3B_3N_3R'_3Cr(CO)_3]\,[P(OR)_3] \qquad (2)$$

In general, at a particular temperature the rate constants k_2 are larger for $P(OEt)_3$ than for $P(OPh)_3$

TABLE III. Activation Parameters for the Reactions of $R_3B_3N_3R'_3Cr(CO)_3$ with Tertiary Phosphites in Cyclohexane.

Complex		$P(OPh)_3$			$P(OEt)_3$		
	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	10^2 k_2 (20°) (l/mol•sec)	(kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	10^2 k_2 (20°) (l/mol•sec)	$\frac{k_2(20°)[P(OEt)_3]}{k_2(20°)[P(OPh)_3]}$
(I)	6.90	–43.3	4.04	5.95	–40.9	73	18
(II)	6.30	–45.3	4.39	5.40	–41.5	135	31
(III)	11.40	–33.3	0.284	7.90	–37.9	11.4	40
(IV)	14.97	–26.3	0.022	10.20	–33.7	1.85	84
(V)	11.70	–28.1	2.07	4.80	–44.9	72	35
(VI)	12.80	–28.5	0.257	11.50	–27.0	7.9	31
(VII)	–	–	–	11.40	–27.9	3.63	–

which is in accord with the results of other ligand displacement processes following a second-order rate law [8]. The ratios of the rate constants at 20 °C for the reactions of the borazole complexes with $P(OEt)_3$ and $P(OPh)_3$ are included in Table III.

Reaction Mechanism

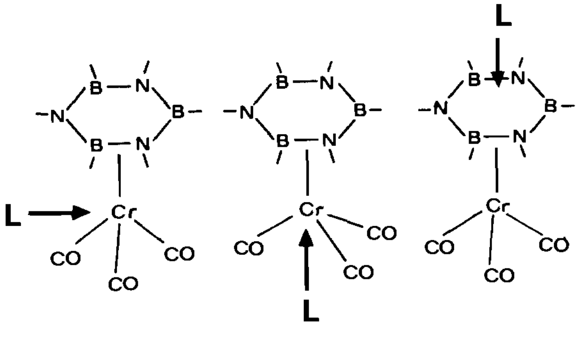
The following order of reactivities can be established from the kinetic data: $Et_3B_3N_3Me_3Cr(CO)_3 \gtrsim B_3N_3Me_6Cr(CO)_3 \gtrsim (n\text{-}Pr)_3B_3N_3Me_3Cr(CO)_3 > Me_3B_3N_3Et_3Cr(CO)_3 \gtrsim Me_3B_3N_3(n\text{-}Pr)_3Cr(CO)_3 > (i\text{-}Pr)_3B_3N_3Me_3Cr(CO)_3 > B_3N_3Et_6Cr(CO)_3$. Therefore, three general statements can be made:

(a) For the tris-N-methylborazole complexes, substitution of Me by Et or n-Pr at the *boron* atoms has very small effect on the reactivity, but on going from $(n\text{-}Pr)_3B_3N_3Me_3Cr(CO)_3$ to $(i\text{-}Pr)_3B_3N_3Me_3Cr(CO)_3$, the rate of ligand displacement markedly decreases.

(b) For the tris-B-methylborazole complexes, subsitution of Me by Et, n-Pr and i-Pr at the *nitrogen* atoms influences the reactivity quite markedly. The rate falls as the bulkiness of the alkyl group increases, *i.e.* N-Me > N-Et > N-n-Pr > N-i-Pr.

(c) From the isomeric complexes (IV)–(VIII), the hexaethylborazole derivative (IV) seems to be the most inert or at least as unreactive as the tris-N-isopropyl derivative (VII).

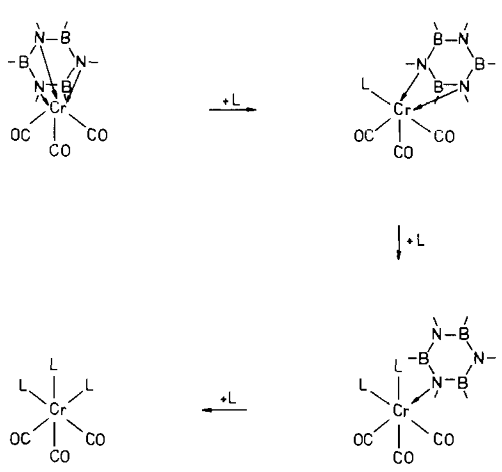
It follows from these observations that steric factors play a dominant role in determining the reactivities of the borazole complexes towards Lewis bases. This leads us to conclude that the phosphite is probably attacking the metal according to (A), that is to say in a plane which is approximately parallel to the borazole ring plane. We feel that this type of interaction reflects the importance of steric requirements at *both the boron and the nitrogen atoms* of the borazole ligands.



(A) (B) (C)

Attack according to (B), that is *below* the metal along the threefold axis of the molecule, seems to be unreasonable considering the influences of the different alkyl groups. The third possibility (C) which might be classified as most unusual at first sight could be supported by the argument that Lewis bases like PR_3 or $P(OR)_3$ react with complexes of the type $[dienylFe(CO)_3]^+$ or $[C_7H_7M(CO)_3]^+$ (M = Cr, Mo, W) by preferential attack *at the ring ligand* [9]. However, even by assuming that the boron atoms in the borazoles are rather electrophilic and the attack according to (C) could be primarily directed to these atoms, it is hard to understand why $Et_3B_3N_3Me_3Cr(CO)_3$ reacts at least as fast as $B_3N_3Me_6Cr(CO)_3$ and why there is only a slight decrease in reactivity by going from the hexamethyl to the tris-B-n-propyl-tris-N-methyl complex (V). It should be mentioned that also for the ring ligand displacement reactions of $(arene)Mo(CO)_3$ and $C_7H_8M(CO)_3$ (M = Cr, Mo, W) with ligands L, the attack of L is supposed to occur in the same manner as described in (A) for the borazole complexes. The large negative entropies of activation are in accord with this proposal.

Scheme 1



The complete course of the displacement process can be represented as in scheme I. It is generally accepted both from X-ray data [10] and from the results of detailed spectroscopic studies [4, 11] that it is mainly the nitrogen atoms which determine the donor properties of the borazole ligands. The assumption is therefore made that coordination of the borazole ring in the (hypothetical) intermediates $R_3B_3N_3R'_3Cr(CO)_3L$ and $R_3B_3N_3R'_3Cr(CO)_3L_2$, also takes place *via* the nitrogen atoms. That the second intermediate containing two ligands L certainly possesses a *cis* configuration is strongly supported by the isomeric purity of the products.

There is one further comment to be made. The order of reactivities of the borazole complexes (I)–(VIII) mentioned above clearly reflects the value of $\Delta G^\ddagger$, *i.e.* the ease with which the transition state of the rate-determining step (probably represented by (A)) can be reached. The question remains whether there exists a relation between $\Delta G^\ddagger$ and some ground-state properties, in particular, between $\Delta G^{\ddagger}$ and the strength of the borazole–chromium bond.

In order to answer this question, we have measured the corresponding bond enthalpy contributions $R_3B_3N_3R'_3$–Cr for the hexamethyl and the hexaethylborazole complexes (I) and (IV) both by thermal decomposition and by iodination. Since (I) and (IV) differ quite markedly in their reactivities towards tertiary phosphites (see Table III) we hoped that some definite conclusions could be drawn from these results.

Thermochemical Studies

$B_3N_3Me_6Cr(CO)_3$

Thermal decomposition

The solid complex decomposes readily on heating at temperatures as low as 403K. This is in marked contrast to $C_6Me_6Cr(CO)_3$ which requires temperatures of greater than 570K before thermal decomposition takes place. The heat of decomposition was measured at 404K by the vacuum sublimation method [12]. On pumping, a whitish film formed on the cool part of the exit tube which gradually disappeared on continued pumping. Some yellow crystals condensed below these white crystals. We believe that the white crystals are $Cr(CO)_6$ and hexamethylborazole, and that the yellow solid is probably unchanged $B_3N_3Me_6Cr(CO)_3$. The capillary in the reaction vessel contained a black powder at the end of the reaction. A metal mirror was not observed. The value of ΔH_{obs} at this temperatures is 21.3 kcal/mol.

Earlier we reported $\Delta H^{298}_{sub}[C_6Me_6Cr(CO)_3]$ = 29.5 kcal/mol [13]. We have been unable to measure $\Delta H_{sub}[B_3N_3Me_6Cr(CO)_3]$ directly, but we find $\Delta H^{298}_{sub}[B_3N_3Me_6]$ = 16.4 kcal/mol so that, following the pattern of our previous results [13], we suggest $\Delta H^{298}_{sub}[B_3N_3Me_6Cr(CO)_3]$ *ca.* 28 kcal/mol. This would place ΔH_{obs} for the process

$$[B_3N_3Me_6Cr(CO)_3](c, 298) \rightarrow [B_3N_3Me_6Cr(CO)_3](g, 404)$$

at *ca.* 35 kcal/mol, which is considerably larger than the measured ΔH_{obs} of 21.3 kcal/mol. Let the effect arising from sublimation of undecomposed complex be accounted for by writing $\Delta H_{obs}(corr) = (21.3 - x)$ and consequently $\Delta H^{298}_{obs}(corr) = (11.4 - x)$. The amount of sublimate was always small, and x is probably less than 2 kcal/mol.

If now we suppose that thermal decomposition takes place exclusively by way of the reaction,

$$[B_3N_3Me_6Cr(CO)_3](c) \rightarrow B_3N_3Me_6(g) + 1/2\ Cr(c) + 1/2\ Cr(CO)_6(g)$$

then, for decomposition at 298K in the gas phase to give entirely gaseous products

$$\Delta H^{298}_{disrupt} = (11.4 - x) + 47.4 - 28 = (30.8 - x)$$

accepting that $H^{\circ}_f[Cr, g]$ = 94.8 kcal/mol. In this case $\Delta H^{298}_{disrupt}$ is equivalent to the bond enthalpy contribution $D[B_3N_3Me_6–Cr]$.

Iodination.

The results are summarised as follows:

Temp. (K)	$B_3N_3Me_6Cr(CO)_3$ (mg)	I_2 (mg)	n	ΔH_{obs}	ΔH^*_{obs} (kcal/mol)	ΔH^*_{298}
470	3.860	9.95	1.93	– 4.5	45.7	28.4
471	3.890	10.04	1.85	– 4.2	43.9	26.6
520	2.590	9.88	2.90	–15.0	54.1	30.6

n represents the extent of iodination in CrI_n, and ΔH^*_{obs} corrects ΔH_{obs} for the exothermic contribution of the reaction $Cr + n/2\ I_2\ (g) \rightarrow CrI_n\ (c)$. The interaction of $B_3N_3Me_6$ with iodine at elevated temperature has not been allowed for in ΔH^*_{298}; our measurements of this quantity gave rather erratic results but at 495K the exothermal contribution was approximately 10 kcal/mol. The mean value ΔH^*_{298} = 28.6 corresponds to $D[B_3N_3Me_6–Cr]$ = 18.3 kcal/mol. If the exothermal effect of the $I_2/B_3N_3Me_6$ reaction is allowed for, then the bond enthalpy contribution could rise to about 28 kcal/mol.

The results of the thermal decomposition and iodination measurements permit us to conclude that the bond enthalpy contribution $D[B_3N_3Me_6–Cr]$ must be less than 30.8 kcal/mol (thermal decomposition) and greater than 18.3 kcal/mol (iodination). We believe that the true value is probably in the range (25 ± 3) kcal/mol.

$B_3N_3Et_6Cr(CO)_3$

Thermal decomposition

The heat of decomposition was measured by the vacuum sublimation method in the temperature range 390–405 K. At the lower end of this range decomposition was slow and incomplete.

Temp. (K)	$B_3N_3Et_6Cr(CO)_3$ (mg)	ΔH_{obs} (kcal/mol)	ΔH_{298}
395	4.14	34.8	21.8
395	4.12	38.3	25.3
399	3.66	33.2	19.7
399	5.42	34.5	21.0
		Mean value	22.0

We find ΔH^{298}_{sub} for $B_3N_3Et_6$ = 23.4 kcal/mol so that we estimate $\Delta H^{298}_{sub}[B_3N_3Et_6Cr(CO)_3]$ ~35 kcal/mol. As before, we take account of the sublimation contribution to ΔH_{298} by writing $\Delta H_{298}(corr) = (22.0 - x)$. If it is assumed that thermal decomposition takes place exclusively by the reaction

$$[B_3N_3Et_6Cr(CO)_3](c) \rightarrow B_3N_3Et_6(g) + 1/2\ Cr(c) + 1/2\ Cr(CO)_6(g)$$

then in the gas phase

$$\Delta H^{298}_{disrupt} = (22.0 - x) + 47.4 - 35 = (34.4 - x)$$

which gives an upper limit to the bond enthalpy contribution $D[B_3N_3Et_6–Cr]$ of 34.4 kcal/mol.

Iodination

We have studied this reaction at several temperatures in the range 395–435K and find that two features are apparent. At the lower end of the range there is no significant thermal interaction between $B_3N_3Et_6$ and iodine, and some $Cr(CO)_6$ may escape from the reaction even with iodine present as indicated by the low iodination figure *n*.

Temp. (K)	$B_3N_3Et_6Cr(CO)_3$ (mg)	I_2 (mg)	*n*	ΔH_{obs}	ΔH^*_{obs} (kcal/mol)	$\Delta H^{‡}_{298}$
400	4.89	8.83	0.98	7.35	33.3	19.6
400	4.91	8.52	0.12	25.6	28.7	15.0
400	3.92	9.44	0.59	12.8	28.4	14.7
399	3.65	10.66	1.32	–6.4	27.9	14.4
399	3.04	13.36	1.14	1.65	31.3	17.8
				Mean value		16.3

At the upper end of the range there is some evidence of interaction between $B_3N_3Et_6$ and iodine (*ca.* 5 kcal/mol), but no $Cr(CO)_6$ escapes from the reaction as indicated by the higher iodination figure *n*.

Temp. (K)	$B_3N_3Et_6Cr(CO)_3$ (mg)	I_2 (mg)	*n*	ΔH_{obs}	ΔH^*_{obs} (kcal/mol)	$\Delta H^{‡}_{298}$
421	4.03	11.56	2.20	–5.2	50.6	33.8
431	4.46	11.19	1.85	1.0	49.1	30.7
432	4.27	12.00	2.48	–5.1	54.4	35.8
				Mean value		33.4

We can interpret $\Delta H^{‡}_{298}$ = 16.3 kcal/mol as due to the formation of 1/2 Cr + 1/2 $Cr(CO)_6$ products only, because no $B_3N_3Et_6Cr(CO)_3$ was observed to sublime unchanged in the presence of iodine. This gives an upper limit to $D[B_3N_3Et_6–Cr]$ of 29 kcal/mol. In a similar way, we can interpret $\Delta H^{‡}_{298}$ = 33.4 kcal/mol as due to the formation of Cr + 3 CO as the only products, which gives a lower limit to $D[B_3N_3Et_6–Cr]$ of 16 kcal/mol. After correction for the thermal interaction between $B_3N_3Et_6$ and iodine this enthalpy contribution may be put at a lower limit of 21 kcal/mol.

Discussion

The parent borazole $B_3N_3H_6$ has sometimes been called "inorganic benzene" [14] with regard to the isosteric and isoelectronic character of the compound with benzene. The fact that hexaalkyl derivatives of both ring systems form $Cr(CO)_3$ complexes with a range of similar properties may formally support the comparison.

There are two important differences, however, between the two classes of compounds $C_6R_6Cr(CO)_3$ and $B_3N_3R_6Cr(CO)_3$, and that is (i) the kinetic stability and (ii) the bond enthalpy D[ring-Cr]. Although it was not possible to determine the bond enthalpy contribution of the hexaalkylborazole–chromium bond very accurately by measuring the heat of decomposition or the heat of iodination of the corresponding $Cr(CO)_3$ complexes, we have succeeded in defining limits within which this contribution should lie, namely,

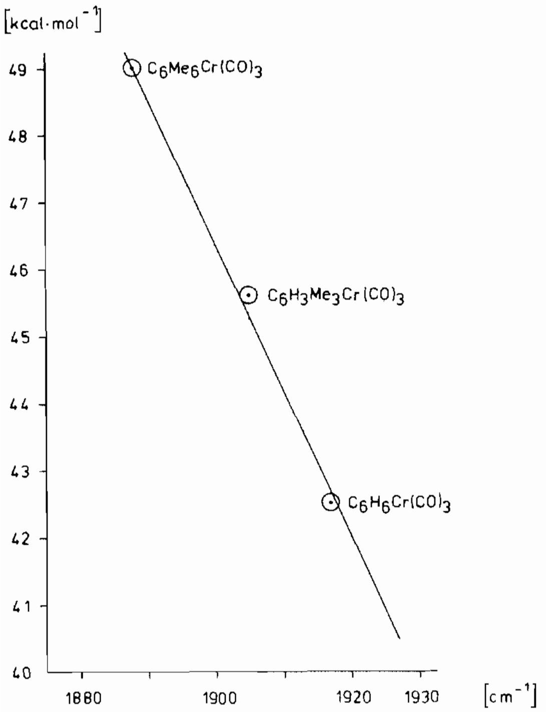


Figure 1. Plot of bond enthalpy D[C_6R_6–Cr] and ν(CO)[E] of $C_6R_6Cr(CO)_3$.

D[$B_3N_3Me_6$–Cr] < 30.8 and > 18.3 kcal/mol

and

D[$B_3N_3Et_6$–Cr] < 34.4 and > 16 kcal/mol

assuming that $\bar{D}$[CO–Cr] = 25.6 kcal/mol. Furthermore, we believe that the true value of the hexaalkylborazole–chromium bond enthalpy is in the range of 25 ± 3 kcal/mol for both of these compounds.

The value of D[$B_3N_3R_6$–Cr] is much less than D[C_6R_6–Cr]. A reasonable explanation is that whereas the donor properties of hexaalkylborazoles and hexaalkylbenzenes are probably comparable [3, 4] the acceptor properties are supposed to be markedly different. There are good reasons to suggest [11, 15] that the borazoles behave in some respects more like cyclic triamines than like pseudo-arenes in the $Cr(CO)_3$ complexes. This would fit with some preliminary results obtained in our laboratories which indicate that an approximate value for the pyridine–chromium bond enthalpy is ~10 kcal/mol so that the $B_3N_3R_6$–Cr enthalpy is consistent with bonding between the metal and the three ring nitrogen atoms.

The bond enthalpy D[C_6R_6–Cr] is 42.5 (C_6H_6), 45.6 ($C_6H_3Me_3$) and 49 (C_6Me_6) kcal/mol in the $Cr(CO)_3$ complexes [13]. These values demonstrate that on increasing the donor character of the arene the bond enthalpy C_6R_6–Cr is also increasing.

Since the donor properties of the arene in $C_6R_6Cr(CO)_3$ could be related to the CO stretching frequency of the E band in the i.r. [16] it may be supposed that there is also a direct relation between D[C_6R_6–Cr] and ν(CO) [E]. This is supported by the experimental data (Fig. 1). If there exists a similar but different relation between D[$B_3N_3R_6$–Cr] and ν(CO) [E] for $B_3N_3R_6Cr(CO)_3$ (R = Me and R = Et: 1867 cm^{-1}, in C_6H_{12} [4]) it follows from these numbers that a difference in bond enthalpy for the hexamethyl and the hexaethylborazole complexes is not to be expected. The values D[$B_3N_3Me_6$–Cr] and D[$B_3N_3Et_6$–Cr] are in accord with this proposition.

The final conclusion is that since D[$B_3N_3Me_6$–Cr] ≈ D[$B_3N_3Et_6$–Cr] the difference in kinetic stability between $B_3N_3Me_6Cr(CO)_3$ and $B_3N_3Et_6Cr(CO)_3$ towards tertiary phosphites is *not* determined by a difference in the enthalpy of the borazole–chromium bond. We feel that there is no other possibility than to explain the different rates of ring ligand displacement by the dominating influence of *steric factors* for the energy of the transition state. The difference in kinetic stability between $C_6Me_6Cr(CO)_3$ and $B_3N_3Me_6Cr(CO)_3$, on the one hand, and between $C_6H_3Me_3Cr(CO)_3$ and $Me_3B_3N_3H_3Cr(CO)_3$ [5] on the other hand, cannot be explained by steric arguments alone and probably reflects a distinct difference in D[ring–Cr] for the borazole and benzene chromiumtricarbonyl complexes.

Experimental

The borazole complexes were prepared according to [3, 4]. The techniques used for the rate measurements were the same as described in one previous paper [7]. At zero time the prethermostatted solutions of the borazole complex and the phosphite were mixed in the spectrometer ["Eppendorf"] cell which was placed in a thermostatted block. The decrease in absorption was measured with a filter at 405 nm and was recorded with a Methrom Labograph E 478. During the measurements, exclusion of air was guaranteed by passing a slow stream of purified nitrogen around the cell compartment.

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