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Thermochemistry of bis-Arene- and Arenetricarbonyl-Chromium Compounds containing Hexamethylbenzene, 1,3,5-Trimethylbenzene and Naphthalene.[†]

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Summary

Microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and iodination have led to values of the standard enthalpies of formation of the following crystalline compounds (values given in kJ mol^{-1}) at 298K: $[Cr(\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3)_2]$ = (63±12); $[Cr(\eta^6\text{-}C_6(CH_3)_6)_2]$ = -(88±12); $[Cr(1,2,3,4,4a,8a\text{-}\eta\text{-}C_{10}H_8)_2]$ = (407±11); $[Cr(CO)_3(1,2,3,4,4a,8a\text{-}\eta\text{-}C_{10}H_8)]$ = -(258±8). Separate measurements by the vacuum sublimation microcalorimetric technique gave the following values for the enthalpy of sublimation at 298K (kJ mol^{-1}) : $[Cr(\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3)_2]$ = (104±1); $[Cr(\eta^6\text{-}C_6(CH_3)_6)_2]$ = (119±4); $[Cr(CO)_3(1,2,3,4,4a,8a\text{-}\eta\text{-}C_{10}H_8)]$ = (107±3). From these and other data, the bond enthalpy contributions of the metal-ligand bonds in the gaseous metal complexes were evaluated as follows: $[(\eta^6\text{-}C_6(CH_3)_6)\text{-}Cr]$ (155±7); $[(\eta^6\text{-}C_6H_3(CH_3)_3)\text{-}Cr]$ (151±6); $[(1,2,3,4,4a,8a\text{-}\eta\text{-}C_{10}H_8)\text{-}Cr]$ (145±6) kJ mol^{-1}

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The question of the transferability of the enthalpy contributions of chromium-ligand bonds between organochromium complexes is discussed with the aid of information from structural and spectroscopic investigations. The limitations of the procedure are defined..

The thermodynamic data are used to discuss various substitution, redistribution and exchange reactions of $\mathrm{Cr}(\eta\text{-arene})_2$ and $[\mathrm{Cr(CO)_3}(\eta\text{-arene})]$ compounds.

Introduction

The enthalpies of combustion of a number of *bis*(η-arene) chromium complexes, $\mathrm{Cr(arene)_2}$ have been reported [1,2,3], in which the arene is benzene, ethylbenzene, 1,2-diethylbenzene, 1,2-di(1-methylethyl)benzene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene. The available data were examined by Tel'noi and Rabinovich [4], and used to derive the mean bond enthalpy contributions, $\bar{D}$(Cr-arene), associated with the arene-chromium bonds in these molecules. These values of $\bar{D}$(Cr-arene) do not deviate by more than ±10 kJ mol^{-1} from that in $[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2]$ itself.

Thermochemical studies on selected η-arene tricarbonyl chromium complexes, $[\mathrm{Cr(CO)_3(arene)}]$ were interpreted [5,6] to indicate that the arene-chromium bond enthalpy contributions, $\bar{D}$(Cr-arene), increase on replacing benzene by methyl-substituted benzenes. This interpretation, however, depends on the questionable assumption that the contributions $\bar{D}$(Cr-CO) are the same in the complexes $[\mathrm{Cr(CO)_3(arene)}]$ as in $\mathrm{Cr(CO)_6}$ itself. Test of the validity of this assumption required measurements on a broader range of $[\mathrm{Cr(CO)_3(arene)}]$ compounds involving arene ligands known to be readily displaced by other arenes, and, more important, by measurements on a comparable variety of $\mathrm{Cr(arene)_2}$ compounds.

The present studies extend the range of compounds to include *bis*-(1,2,3,4,4a,8a-η-napthalene)chromium, *bis*-(η-1,3,5-trimethylbenzene)chromium, *bis*-(η-hexamethylbenzene)chromium and tricarbonyl (1,2,3,4,4a,8a-η-naphthalene)chromium. The resulting enthalpies of formation have been used to provide values for the enthalpies of redistribution and exchange reactions.

Experimental

Calorimeter

The thermal measurements were made using a Calvet twin-cell microcalorimeter (Setaram, Lyon) adapted to the drop calorimetric technique [5]. Heats of sublimation were measured by using the microcalorimetric vacuum sublimation method [6].

Compounds

Samples of (1,2,3,4,4a,8a-η-naphthalene)$Cr(CO)_3$ were prepared by a standard method from chromium hexacarbonyl [7]. The purity of the compound was established by microanalysis and spectroscopic measurements (IR, NMR, mass) which were in agreement with published values. Samples of the bis-η-arene chromium compounds (arene is naphthalene [8], 1,3,5-trimethylbenzene and hexamethylbenzene [9]) prepared by metal vapour synthesis were supplied by Professor C. Elschenbroich, University of Marburg, West Germany. These samples, with the exception of $[Cr(C_{10}H_8)_2]$, were resublimed before use, but not further characterised.

Auxiliary data

All heat quantities are given in joules (J) or in kilojoules (kJ). The following auxiliary heats of formation (in kJ mol^{-1}) were used in evaluating the experimental results: $\Delta H_f^o(CO,g) = -(110.524\pm0.17)$ [10]; $\Delta H_f^o(I_2,g) = (62.44\pm0.04)$ [11]; ΔH_f^o(1,3,5-trimethylbenzene,g) = $-(15.94\pm1.4)$ [12]; ΔH_f^o(hexamethylbenzene,g) = $-(86.82\pm2.6)$ [12]; ΔH_f^o(naphthalene,g) = (150.4 ± 1.4) [12]; $\Delta H_f^o(CrI_2,c) = -(156.9\pm4)$ [10]; $\Delta H_f^o(CrI_3,c) = -(205.0\pm4)$ [10]; $\Delta H_f^o(Cr,g) = (396.6\pm4)$ [10]; $\Delta H_f^o(Cr(CO)_6,g) = -(908.3\pm1.7)$ [14].

In order to reduce heats of reaction, ΔH^* (measured at elevated temperatures, T) to the corresponding values ΔH^{298} at 298K, (H_T-H_{298}) values for CO, $I_2(g)$ and the various hydrocarbon ligands in the gas state were taken from the compilation of Stull, Westrum and Sinke [15] and for chromium metal from Hultgren, Orr, Anderson and Kelley [16]. Enthalpies of fusion (kJ mol^{-1}) were assumed to be ±12 for [$Cr(CO)_3(C_6H_6)$] and [$Cr(CO)_3(C_6H_3Me_3)$], +14 for [$Cr(CO)_3(C_6Me_6)$] and [$Cr(CO)_3(C_{10}H_8)$], +16 for [$Cr(C_6H_6)_2$] and [$Cr(C_6H_3Me_3)_2$] and +18 for [$Cr(C_6Me_6)_2$] and [$Cr(C_{10}H_8)_2$].

Results

1. Bis(η-hexamethylbenzene)chromium

Studies on the thermal decomposition of $Cr(C_{12}H_{18})_2$ were made over the temperature range 523-588K, by dropping the samples into the argon-filled hot zone of the microcalorimeter. At the lower temperatures, only partial thermal decomposition occurred, some of the sample subliming unchanged from the reaction vessel (hot zone); at 588K, thermal decomposition appeared to be complete and to occur totally within the capillary tubes containing the samples. There was no mirror formation on the walls of the reaction vessel, but the capillary tubes became coated with a bright chromium film. Hexamethylbenzene vapour escaping the hot-zone condensed in cooler parts of the exit tube as a white film deposit. Typical results are given in Table 1, in which ΔH^*_{dec} refers to the calorimeter reaction

$$[Cr(C_{12}H_{18})_2](c,298) \rightarrow Cr\ (c,588) + 2C_{12}H_{18}(g,588) \quad ....(1)$$

ΔH^{298}_{dec} refers to the same process, carried out isothermally at 298K. The mean value, ΔH^{298}_{dec} = (35.8±8) kJ mol^{-1} corresponds to $\Delta H^o_f[Cr(C_{12}H_{18})_2,c]$ = -(209.4±9) kJ mol^{-1}.

TABLE 1. Thermal decomposition of [$Cr(C_{12}H_{18})_2$]

$\frac{T}{K}$	$\frac{[Cr(C_{12}H_{18})_2]}{mg}$	$\frac{\Delta H^*_{dec}}{kJ\ mol^{-1}}$	$\frac{\Delta H^{298}_{dec}}{kJ\ mol^{-1}}$
588	2.500	238.6	38.7
586	2.390	239.6	39.8
588	2.745	240.0	40.1
587	2.440	223.6	24.5

The iodination of [$Cr(C_{12}H_{18})_2$] was studied over the temperature range 524-549K. Samples of the chromium complex mixed with iodine were dropped into the hot zone containing iodine/argon vapour. The solid product of reaction remaining as a black powder in the capillary tube containers analysed as $CrI_{\underline{n}}$, with $\underline{n}$ values in the range 2.1-2.75. Excess iodine and hexamethylbenzene escaped from the hot zone as vapours to condense in the exit tube. Results are summarised in Table 2, where ΔH^*_{iod} refers to the cell reaction

$$[Cr(C_{12}H_{18})_2](c,298) + \frac{n}{2}I_2(g,T) \rightarrow CrI_{\underline{n}}(c,T) + 2C_{12}H_{18}(g,T) \quad .....(2)$$

The values of ΔH^*_{dec} were obtained from ΔH^*_{iod} by allowing for the exothermal heat of formation of CrI_n

$$Cr(c,T) + \frac{n}{2}I_2(g,T) \rightarrow CrI_{\underline{n}}(c,T) \quad .....(3)$$

as described previously [5]. The mean ΔH^{298}_{dec} leads to $\Delta H^o_f[Cr(C_{12}H_{18})_2,c]$ = $-(205.7\pm7)$ kJ mol^{-1}, in fair agreement with that [$-(209.4\pm9)$ kJ mol^{-1}] obtained from direct thermal decomposition studies, and an intermediate value, $\Delta H^o_f[Cr(C_{12}H_{18})_2,c] = -(207\pm11)$ kJ mol^{-1} is adopted.

TABLE 2 Iodination of $[Cr(C_{12}H_{18})_2]$

$\underline{T}$ K	$[Cr(C_{12}H_{18})_2]$ mg	I_2 mg	$\underline{n}$	ΔH^*_{iod} kJ mol^{-1}	ΔH^*_{dec} kJ mol^{-1}	ΔH^{298}_{dec} kJ mol^{-1}
546	2.465	9.255	2.47	-46.7	206.6	40.3
546	2.590	9.585	2.75	-76.7	198.8	32.4
546	4.795	7.105	2.18	-43.9	188.5	22.2
546	2.735	7.865	2.26	-39.2	197.5	31.2
549	2.260	9.160	2.27	-35.4	202.2	33.4
549	2.845	9.825	2.26	-62.0	201.5	32.8

Sublimation studies of $[Cr(C_{12}H_{18})_2]$ over the temperature range 472-478K were made using the microcalorimetric vacuum-sublimation technique [6]. There was slight thermal decomposition within the capillary tube containers during the sublimation measurements, for which corrections were made based on the mass of residue. The mean of four measurements gave ΔH^*_{sub} = (232 ± 4) kJ mol^{-1} for the process

$[Cr(C_{12}H_{18})_2](c,298)] \rightarrow [Cr(C_{12}H_{18})_2](g,478)$ ......(4)

corresponding to $\Delta H^{298}_{sub} = (118.5\pm4)$ kJ mol^{-1}

2. Bis-(η-1,3,5-trimethylbenzene)chromium

Thermal decomposition studies of $[Cr(C_9H_{12})_2]$ in argon were made over the temperature range 519-586K. Decomposition appeared to be complete within hot zone at temperatures above 580K, but at lower temperatures there was only partial decomposition, and appreciable amounts of the sample sublimed unchanged from the reaction vessel. Vacuum sublimation measurements were made between 403-422K, at which temperatures the samples sublimed without visible decomposition. Results are summarised in Table 3.
The mean ΔH^{298}_{dec} leads to $\Delta H^{o}_{f}[Cr(C_9H_{12})_2,c] = -(41.9\pm7)$ kJ mol^{-1}

TABLE 3 Thermal decomposition and sublimation of $[Cr(C_9H_{12})_2]$

T / K	$[Cr(C_9H_{12})_2]$ / mg	Method	ΔH_{obs} / kJ mol^{-1}	ΔH^{298} / kJ mol^{-1}
422	4.105	V.S	152.1	104.5
404	3.850	V.S	143.5	104.0
403	4.435	V.S	144.2	105.2
402	3.715	V.S	141.9	103.4
		Mean value	ΔH^{298}_{sub} =	(104.3±0.8)
583	2.050	T.D	141.4	14.0
586	2.190	T.D	132.0	3.3
593	2.205	T.D	145.2	12.6
		Mean value	ΔH^{298}_{dec} =	(10.0±6.7)

Iodination studies in the temperature range 545-548K gave the results summarised in Table 4. The mean value $\Delta H^{298}_{dec} = (7.2\pm10)$ kJ mol^{-1} from iodination leads to $\Delta H^{o}_{f}[Cr(C_9H_{12})_2,c] = -(39.1\pm10)$ kJ mol^{-1} which is in reasonable agreement with the result of thermal decomposition studies. The intermediate value, $\Delta H^{o}_{f}[Cr(C_9H_{12})_2,c] = -(40.5\pm12)$ kJ mol^{-1} is accepted.

TABLE 4 Iodination of $[Cr(C_9H_{12})_2]$

T K	$[Cr(C_9H_{12})_2]$ mg	I_2 mg	n	ΔH^*_{iod} kJ mol^{-1}	ΔH^*_{dec} kJ mol^{-1}	ΔH^{298}_{dec} kJ mol^{-1}
545	2.195	8.640	2.25	-120.0	116.1	9.0
545	2.495	9.160	2.04	-118.1	101.4	-5.7
548	2.525	9.730	2.08	-100.0	122.7	14.2
548	2.900	8.165	2.03	-88.1	130.6	22.0
548	3.350	10.625	1.95	-106.1	104.8	-3.4

3. Bis-(1,2,3,4,4a,8a-η-naphthalene)chromium

Thermal decomposition of $[Cr(C_{10}H_8)_2]$ at temperatures in the range 524-586K led to complete decomposition; the capillary tube sample containers became coated with metallic chromium and bright metallic spots appeared on the walls of the reaction vessel close to the containers. The results are summarised in Table 5. The mean value $\Delta H^{298}_{dec} = -(0.10 \pm 1.6)$ kJ mol^{-1} corresponds to $\Delta H^0_f[Cr(C_{10}H_8)_2,c] = (300.9 \pm 3)$ kJ mol^{-1}.

TABLE 5 Thermal decomposition of $[Cr(C_{10}H_8)_2]$

T K	$[Cr(C_{10}H_8)_2]$ mg	ΔH^*_{obs} kJ mol^{-1}	ΔH^{208}_{dec} kJ mol^{-1}
524	4.865	88.2	-0.59
525	5.165	90.9	1.67
525	5.190	90.6	1.30
548	4.925	102.8	2.09
548	4.925	97.7	-3.01
586	1.730	118.3	-2.05

Attempts to measure the heat of sublimation of $[Cr(C_{10}H_8)_2]$ by the vacuum sublimation microcalorimetric technique were unsuccessful. At temperaturesin the range 388-420K, naphthalene vapour escaped the hot zone on evacuation, the samples slowly decomposing to leave a black involatile residue in the capillary tube containers.

Microcalorimetric measurements of the reaction of $[Cr(C_{10}H_8)_2]$ with iodine were made at 433K and at 490K by dropping capillary containers (in which the iodine and $[Cr(C_{10}H_8)_2]$ were separately packed) into the argon-filled hot zone. Even at the lower temperature thermal decomposition was the dominant reaction, and the degree of iodination of the chromium metal deposit was small ($CrI_{\underline{n}}$, $\underline{n}$ ~0.8). The results are summarised in Table 6.

TABLE 6 Iodination of $[Cr(C_{10}H_8)_2]$

$\frac{T}{K}$	$\frac{[Cr(C_{10}H_8)_2]}{mg}$	$\frac{I_2}{mg}$	$\underline{n}$	$\frac{\Delta H^{*}_{iod}}{kJ\ mol^{-1}}$	$\frac{\Delta H^{*}_{dec}}{kJ\ mol^{-1}}$	$\frac{\Delta H^{298}_{dec}}{kJ\ mol^{-1}}$
490	4.025	6.670	0.59	0.51	15.80	-1.56
433	3.475	5.610	0.80	-10.61	9.16	-2.41
433	3.655	7.030	0.77	-9.35	10.68	-0.89

The mean $\Delta H^{298}_{dec} = -(1.62\pm0.8)$ kJ mol^{-1} is in good agreement with the result from direct thermal decomposition, and leads to $\Delta H^{o}_{f}[Cr(C_{10}H_8)_2,c] = (302.4\pm2.9)$ kJ mol^{-1}. The intermediate value, $\Delta H^{o}_{f} = (301.7\pm4)$ kJ mol^{-1} is accepted.

4. Tricarbonyl(1,2,3,4,4a,8a-η-naphthalene)chromium

Thermal decomposition studies of $[Cr(CO)_3(C_{10}H_8)]$ were made over the temperature range 472-517K. The compound appeared to decompose readily at these temperatures, forming a chromium mirror and metal powder within the capillary tube sample containers. A white film of naphthalene condensed on cooler parts of the exit line.

Vacuum sublimation measurements were made at temperatures in the range 394-408K. In the range 394-401K, samples sublimed from the hot zone on evacuation without any decomposition being apparent; but at 408K, some thermal decomposition accompanied sublimation, leaving a small residue of metal powder in the capillary and slight mirror formation on the walls and exit of the reaction vessel. The thermal measurements are summarised in Table 7.

TABLE 7 Thermal Decomposition and Sublimation of $[Cr(CO)_3(C_{10}H_8)]$

$\frac{T}{K}$	$\frac{[Cr(CO)_3(C_{10}H_8)]}{mg}$	Method	$\frac{\Delta H^*_{obs}}{kJ\ mol^{-1}}$	$\frac{\Delta H^{298}}{kJ\ mol^{-1}}$
394	2.260	V.S	132.0	106.0
398	2.090	V.S	131.2	109.7
401	2.130	V.S	137.7	104.1
		Mean value ΔH^{298}_{sub}	= (106.6±3.3)	
472	3.085	T.D	160	110
517	2.425	T.D	188	123
517	2.020	T.D	196	131
		Mean value ΔH^{298}_{dec}	= (121±13)	

The mean ΔH^{298}_{dec} from direct thermal decomposition measurements is lowered from the true value, due to exothermal side-effects from absorption of carbon monoxide on the active surface of the deposits of chromium metal. Decomposition in the presence of iodine vapour avoids this difficulty, and the results of measurements on the iodination process, ΔH^*_{iod}

$$[Cr(CO)_3(C_{10}H_8)](c,298) + \frac{n}{2}I_2(g,T) \rightarrow CrI_{\underline{n}}(c,T) + C_{10}H_8(g,T) + 3CO(g,T) \quad \ldots(5)$$

are summarised in Table 8. The mean value ΔH^{298}_{dec} = (184±7) kJ mol^{-1} leads to $\Delta H^o_f[Cr(CO)_3(C_{10}H_8),c] = -(365\pm7)$ kJ mol^{-1}

TABLE 8 Iodination of $[Cr(CO)_3(C_{10}H_8)]$

$\frac{T}{K}$	$\frac{[Cr(CO)_3(C_{10}H_8)]}{mg}$	$\frac{I_2}{mg}$	$\underline{n}$	$\frac{\Delta H^*_{iod}}{kJ\ mol^{-1}}$	$\frac{\Delta H^*_{dec}}{kJ\ mol^{-1}}$	$\frac{\Delta H^{298}_{dec}}{kJ\ mol^{-1}}$
508	2.225	9.190	2.25	2.2	239	177
508	2.120	10.185	2.42	-14.3	236	174
517	2.150	9.580	2.47	-1.5	252	187
517	2.210	10.445	2.41	6.4	255	190
517	2.255	10.300	2.06	35.8	257	192

Discussion

The available information, including the present results, on the enthalpies of formation of bis(η-arene)chromium and of (η^6-arene)tricarbonylchromium compounds is listed in Table 9. The data listed include $\Delta H_f^o(c)$, ΔH^o_{sub}, $\Delta H_f^o(g)$ and the derived $\Delta H_{disrupt}$ values, the latter referring to the total enthalpy of disruption of the gaseous compounds into Cr(g) and the ligands (arene, CO) in the gas state at 298K.

TABLE 9 Thermochemical data (kJ mol^{-1}) for η^6-arene chromium compounds

A. Bis-(η-arene)chromium compounds

Arene	State	$\Delta H_f^o(\ell$ or c)	ΔH^o_{sub}	$\Delta H_f^o(g)$	$\Delta H_{disrupt}$	Ref
Benzene	c	(142±8)	(91±4)	(233±9)	(330±9)	5
		(144±4)	(82±5)	(226±7)	(337±7)	1,4
Ethylbenzene	ℓ	(67±3)	(75±8)	(142±9)	(314±9)	2,4
1,2-Diethylbenzene	ℓ	-(47±7)				2,4
1,2-Di(1-methylethyl)benzene	ℓ	-(195±8)				2,4
1,3,5-Trimethylbenzene	c	-(41±12)	(104±1)	(63±12)	(302±12)	a
		-(46±13)				3,4
1,2,4-Trimethylbenzene	c	-(38±8)				3,4
Hexamethylbenzene	c	-(207±11)	(119±4)	-(88±12)	(311±13)	a
Naphthalene	c	(302±4)	[105±10]^b	(407±11)	(290±12)	a

B. (η-Arene)tricarbonylchromium compounds

Arene	State	$\Delta H_f^o(\ell$ or c)	ΔH^o_{sub}	$\Delta H_f^o(g)$	$\Delta H_{disrupt}$	Ref
Benzene	c	-(443±8)	(91±4)	-(352±9)	(500±9)	5
Methylbenzene	c	-(476±6)	(94±4)	-(382±7)	(497±7)	6
1,3,5-Trimethylbenzene	c	-(571±8)	(108±4)	-(463±9)	(512±9)	6
Hexamethylbenzene	c	-(671±8)	(123±4)	-(548±13)	(526±13)	17
Chlorobenzene	c	-(467±21)	(102±4)	-(365±21)	(481±21)	6
Naphthalene	c	-(365±7)	(107±3)	-(258±8)	(474±8)	a
Hexacarbonylchromium	c	-(980±2)	(72±1)	-(908±2)	(642±2)	14

a. This work; b. estimated value

In the two cases ($[Cr(\eta\text{-}C_6H_6)_2]$ and $[Cr(\eta\text{-}C_6H_3Me_3)_2]$ where comparison is possible, there is satisfactory agreement between independent investigators as regards the value of $\Delta H_f^o(c)$.

The $\Delta H_{disrupt}$ values for the $[Cr(\eta\text{-arene})_2]$ compounds lead directly to the mean bond dissociation enthalpy values, $\bar{D}$(Cr-arene) listed in Table 10.

TABLE 10 Mean Bond Dissociation Enthalpy, $\bar{D}$(Cr-arene) in $[Cr(\eta\text{-arene})_2]$

Arene	$\Delta H_{disrupt}$ / kJ mol^{-1}	$\bar{D}$(Cr-arene) / kJ mol^{-1}
Benzene	(330±9)	(165±5)
Ethylbenzene	(314±9)	(157±5)
1,3,5-Trimethylbenzene	(302±12)	(151±6)
Hexamethylbenzene	(311±13)	(155±7)
Naphthalene	(290±12)	(145±6)

The values of $\bar{D}$(Cr-arene) indicate weaker bonding to chromium by the substituted benzenes than by benzene itself, the weakest bonding being in *bis*-(η^6-naphthalene)chromium. As this conclusion conflicts with the commonly held views that increasing methyl substitution leads to stabilisation of the Cr-arene bond, and that there is a major difference in the strength of the Cr-hexamethylbenzene and Cr-naphthalene bonds in $[Cr(CO)_3(\eta\text{-arene})]$ compounds, we have made a detailed reassessment of the physical properties of both $[Cr(CO)_3(\eta\text{-arene})]$ and $[Cr(\eta\text{-arene})_2]$ compounds. The major features and the conclusions are as follows.

Mass- and photoelectron spectroscopy

Estimation of $\bar{D}$(Cr-(η-arene)) from the mass spectrometrically determined appearance potential of Cr^+ ion in $[Cr(\eta\text{-arene})_2]$ provides only upper limit values of $\bar{D}$(Cr-arene) because of the (unknown) contribution of electronic excitation and of kinetic energy of the fragment ions. The values obtained in this way (Table 11) suggest that $\bar{D}$(Cr-arene) increases with increasing methyl substitution but, in reality may merely reflect the increasing importance of the kinetic energy/electronic excitation contributions where large fragments (e.g. C_6Me_6) are involved.

TABLE 11. $\overline{D}$(Cr-arene)/kJ mol^{-1} from appearance potential (eV) of Cr^+ ion in [Cr(η-arene)$_2$].

Arene	$\overline{D}$(Cr-arene)		Δ^a
Benzene	193[18]	149[19]	6
1,3,5-Trimethylenezene	255[18]	279[19]	116
Hexamethylbenzene	347[18]		192

a. Δ =[D(Cr-arene) (ref. 18)]-[D(Cr-arene) (Table 10)]

A further indication of unreliability in the use of the mass spectroscopic A.P(Cr^+) for deriving $\overline{D}$(Cr-arene) may be obtained from consideration of the measured first ionisation energies I_1 shown in Table 12. The highest occupied molecular orbital (h.o.m.o) in $Cr(CO)_6$, [$Cr(CO)_3$(η-arene)] and [Cr(η-arene)$_2$] is principally Cr3d in character in each case (Table 12). The effect of the ligands can be either to increase (CO)

TABLE 12 First Ionisation Energy I_1 (eV) and Cr 3d atomic orbital Contribution to the h.o.m.o of [$Cr(CO)_{6-3x}$(arene)$_x$] (x = 0,1,2)

	I_1 (eV)				
	UPS		MS	HOMO(Cr 3d%)	
$Cr(CO)_6$	8.40[20]			$2t_{2g}$(75)	[21]
$Cr(CO)_3$(η-C_6H_6)	7.42[22]	7.30[23]	6.74[24]	17a(51) 17e(79)	[22]
$Cr(CO)_3$(η-$C_6H_3Me_3$)	7.20^a	7.05[23]	6.60[24]		
$Cr(CO)_3$(η-C_6Me_6)	7.00^a	6.88[23]	6.35[24]		
Cr, atom	6.76				
Cr(η-C_6H_6)$_2$	5.45[22]	5.91[18]		$8a_{1g}$(92)	[22]
Cr(η-$C_6H_3Me_3$)$_2$	5.01[25]	5.47[18]			
Cr(η-C_6Me_6)$_2$	4.68^a	5.19[18]			

a - This work

or to decrease (arene) the first ionisation energy from its value in the free chromium atom. The effect of methyl substituents in decreasing I_1, is apparent from both UPS and MS measurements, but there are discrepancies between the measurements by photoelectron spectroscopy [22, 25] and mass spectrometry [18, 23, 24].

Nuclear magnetic resonance spectroscopy. The ^{1}H and ^{13}C n.m.r. spectra of η-arene chromium complexes show a progressive shift to higher field of both the ring proton and the ring carbon resonances in passing from the free arene, to $[Cr(CO)_3(\eta\text{-arene})]$ and then to $[Cr(\eta\text{-arene})_2]$ complexes. These observations are summarised in representative examples in Table 13.

The progressive shift to high field is consistent with a decrease in the aromatic character of the carbocyclic ring on complexation. This has been attributed to arene π → chromium 3d charge transfer [31]. We note that there is evidence for intramolecular metal-to-arene ligand charge transfer

TABLE 13 N.m.r. spectra of $Cr(CO)_{6-3x}(\eta\text{-arene})_x$ (x = 1,2)

A. ^{1}H n.m.r. ring proton chemical shifts, δ/p.p.m (vs. TMS)

Arene	Free ligand	$[Cr(CO)_3(\eta\text{-arene})]$	Δ^a	$[Cr(\eta\text{-arene})_2]$	Δ^b
$C_{10}H_8$	7.68, 7.34	6.09 5.48[26]	1.59 1.86	5.28 4.35[27]	2.40 2.99
C_6H_6	7.35	5.30 [28]	2.05	4.12 [29]	3.23
$C_6H_3Me_3$	6.80	4.88 [28]	1.92	3.95 [29]	2.85

B. ^{13}C n.m.r. ring carbon chemical shifts, δ/p.p.m. (vs. TMS)

Arene	Free ligand		$[Cr(CO)_3(\eta\text{-arene})]$		Δ^a		$[Cr(\eta\text{-arene})_2]$		Δ^b	
	CH	CMe	CH	CMe	CH	CMe	CH	CMe	CH	CMe
C_6H_6	128.0		93.5	[30]	34.5		74.1	[31]	53.9	
$C_6H_3Me_3$	127.0	138.6	92.4	111.5[32]	35.2	27.1	79.6	87.5[31]	48.0	51.1
C_6Me_6		132.5		107.5[32]		25.0		83.5[c]		49.0

a. Δ= δ(free ligand) -δ($[Cr(CO)_3(arene)]$; b.Δ = δ(free ligand) -δ($[Cr(arene)_2]$)

c. This work. C_6D_6 solution.

in the low energy (ca. 317 nm) absorption spectra of [$Cr(CO)_3$(η-arene)] complexes [33]. It is apparent from Table 13 that the decrease in aromatic character is not noticeably influenced by the number of methyl groups attached to the ring.

N.m.r. studies of [$Cr(CO)_3$(η-arene)] complexes in which the arene is a substituted naphthalene have shown [34] that the metal is not localised in one ring and, in the case of 1,2,3,4-tetramethylnaphthalene, the $Cr(CO)_3$-group is attached to both the substituted (54%) and unsubstituted (46%) rings with similar probability. There is no exchange between the rings at room temperature [35].

Structural chemistry. The principal features of the structural chemistry of [$Cr(CO)_3$(η-arene)] complexes were reviewed by Mills in 1969 [36]. Of particular importance is the fact that in these complexes the η^6-arene ligand is slightly folded, with the $Cr(CO)_3$-group on the same side of the ring plane as the ring carbon atoms C1 and C4. The dihedral angle is about 4.5^0. In Table 14, we present structural data for [$Cr(CO)_{6-3x}(\eta\text{-}C_6H_6)_x$] (x = 0,1,2) which have been determined with high precision by X-ray, neutron and electron diffraction in recent years, and for an "average" [$Cr(CO)_3$(η-arene)] structure of which 19 examples are known at the present time [57].

The following conclusions can be drawn;

1. There is a decrease in the non-bonded distance (Cr...O) from $Cr(CO)_6$ to [$Cr(CO)_3(\eta\text{-}C_6H_6)$] (and other [$Cr(CO)_3$(η-arene)] compounds). The net decrease is composed of a decrease in r(Cr–C) and an increase in r(C–O), the former being the larger of the two. This is consistent with the arene ligand being a weaker π-acceptor than CO.

2. The vertical distance from the chromium atom to a plane through the arene ring carbon atoms, $r(Cr\text{-}ArH)_{\perp}$ decreases from [$Cr(CO)_3(\eta\text{-}C_6H_6)$] to [$Cr(\eta\text{-}C_6H_6)_2$].

3. The benzene ring in both [$Cr(CO)_3(\eta\text{-}C_6H_6)$] and [$Cr(\eta\text{-}C_6H_6)_2$] has C_{3v} (unequal C-C bond lengths) in contrast to the D_{6h} (equal C-C bond lengths) symmetry in benzene itself. Moreover, the average C-C bond length in these

TABLE 14 Structural features of $[Cr(CO)_{6-3x}(\eta\text{-}C_6H_6)_x]$ (x = 0,1,2) and for other $[Cr(CO)_3(\eta\text{-arene})]$ complexes. Distances in pm.

	$Cr(CO)_6$	$[Cr(CO)_3(\eta\text{-}C_6H_6)]$	$[Cr(\eta\text{-}C_6H_6)_2]$	$[Cr(CO)_3(\eta\text{-arene})]$ [57]
Cr-CO	191.37 X [37]	184.5 X [38]		
	191.51 N [37]	184.5 N [38]		182.5
	192 E [39]	186.3 E [40]		
C-O	113.99 X	115.8 X		
	114.02 N	115.9 N		115.9
	116 E	115.2 E		
Cr...O	305.36 X	300.3 X		
	305.53 N	300.4 N		298.5
	308 E	301.5 E		
(Cr-ArH)⊥		172.6 X,N	161.6 X [41]	
		173.2 E	157.5 N [42]	173.2
			161.3 E [43]	
Cr-C(ArH)		223.2(ave) X	213.4(ave) X	
		223.3(ave) N	211.6(ave) N	221.7
		220.8(ave) E	215.0(ave) E	
C-C		140.6,142.3 X,	138.6,140.7 X	
		140.6,142.3 N	140.6,142.4 N	
		141.7 E	142.3 E	
C-H		110.9(ave) N	104.8(ave) N	

X = X-Ray; N = Neutron; E = Electron Diffraction.

complexes is progressively longer than in the free ligand (139.7 pm). This suggests that the aromaticity of the benzene ligand is (partially) destroyed, in agreement with the conclusions drawn from n.m.r. spectroscopy. Comparison with the structure of cyclohexa-1,3-diene [44] suggests that if the length of the [=C-C=] single bond is considered as an index of "aromatic character", the loss of aromatic resonance energy in the complexed benzene of $[Cr(\eta\text{-}C_6H_6)_2]$ might be ca. 60 kJ mol^{-1}.

The structure of $[Cr(CO)_3(\eta^6\text{-naphthalene})]$ shows [45] that two Cr-C(arene) distances (av. 232.1 pm) are greater than the other four (av. 202.2 pm), so that the coordination of the naphthalene ring can be compared with that of the η^4-ring in $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$ in which [46] however, the two non-bonded carbon atoms are much further from the metal (av. 303 pm) than the other four (av. 215 pm) which comprise a butadiene-like fragment. The difference between the energies of the two ring conformations is calculated to be 151 kJ mol^{-1} [46]. This is greater than the enthalpy of activation (65.3±5.4) kJ mol^{-1} of the fluxional process which interconverts the canonical forms of $[Ru(\eta\text{-}C_6Me_6)_2]$ which has been measured in solution [47]. We note that η^4-bonding of the arene is favourable as an intermediate in the hydrogenation of arenes [48], for which both $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ [49] and $[Ru(\eta\text{-}C_6Me_6)_2]$ are known [50] to be active catalysts. In $[Cr(CO)_3(\eta\text{-naphthalene})]$ the dihedral angle in the coordinated arene ring is 8.6^0 [36], but in $[Ru(\eta\text{-}C_6Me_6)]$ the dihedral angle in the η^4-arene ring is 42.8^0 [46]. We believe that the ensemble of these results shows that coordination of an arene to chromium produces a reduction in the aromatic character of the ligand, and a significant reduction of the 'aromatic' resonance energy relative to that of the free arene. The mean values, $\bar{D}$(Cr-arene), include the reorganization energy of the arene on its release from the metal, and the latter probably varies in magnitude from one arene to another. This 'reorganization' effect may be larger for naphthalene (dihedral angle in coordinated ring, 8.6^0) than for benzene (dihedral angle 4^0) and other monocyclic benzene derivatives, and could account in part for the lower value of $\bar{D}$ when the arene is naphthalene.

Substitution, redistribution and exchange reactions

The occurrence of arene displacement,

$$[Cr(\eta\text{-arene}_A)_2] + 2\ \text{arene}_B \rightarrow [Cr(\eta\text{-arene}_B)_2] + 2\ \text{arene}_A \qquad (6)$$

$$[Cr(CO)_3(\eta\text{-arene}_A)] + \text{arene}_B \rightarrow [Cr(CO)_3(\eta\text{-arene}_B)] + \text{arene}_A \qquad (7)$$

redistribution,

$$[Cr(\eta\text{-arene})_2] + 3CO \rightarrow [Cr(CO)_3(\eta\text{-arene})] + \text{arene} \qquad (8)$$

$$[Cr(CO)_3(\eta\text{-arene})] + 3CO \rightarrow Cr(CO)_6 + \text{arene} \qquad (9)$$

$$Cr(CO)_6 + Cr(\eta\text{-arene})_2 \rightarrow 2[Cr(CO)_3(\eta\text{-arene})] \qquad (10)$$

and arene exchange reactions,

$$[Cr(CO)_3(\eta\text{-arene})] + \text{arene*} \rightarrow [Cr(CO)_3(\eta\text{-arene*})] + \text{arene} \qquad (11)$$

is well established. Apart from substitution reactions either at the organic ligand or at the chromium atom, the reactions (6)-(11) are the most important forthese classes of compound. The results of our studies enable consideration of the reactions (6)-(11) and the related substitution processes

$$[Cr(CO)_3(\eta^6\text{-cyclo } C_7H_8)] + \text{arene} \rightarrow [Cr(CO)_3(\eta\text{-arene})] + \text{cyclo-}C_7H_8 \qquad (12)$$

$$[Cr(CO)_4(\eta^2,\eta^2\text{-}C_7H_8)] + \text{arene} \rightarrow [Cr(CO)_3(\eta\text{-arene})] + CO + C_7H_8 \qquad (13)$$

in general thermodynamic terms, since the enthalpy changes are arguably dominant in determining ΔG for these displacement and arene exchange reactions.

Arene displacement reactions. An arene displacement reaction (cf(6)) will normally be attempted by refluxing a solution of $[Cr(\eta\text{-arene}_A)_2]$ in excess of arene_B at an elevated temperature. In separate experiments, for example, we find that on refluxing $[Cr(\eta\text{-}C_6H_3Me_3)_2]$ in benzene, exchange to form $[Cr(\eta\text{-}C_6H_6)_2]$ is complete within one hour. The arene displacement is expected to reach completion more readily the more exothermic the process. The thermal data in Table 9 can readily provide ΔH_r values for substitution, redistribution and exchange reactions of $[Cr(\eta\text{-arene})_2]$ and of $[Cr(CO)_3(\eta\text{-arene})]$ in the ideal gas state at 298K. More realistically, we should consider ΔH_r for the same reactions in solution at elevated temperatures. To change to these conditions requires further data (heat capacities, heats of solution and of mixing) which are not available; however, approximate corrections can be made.

As an example, consider the displacement of naphthalene in $[Cr(\eta\text{-}C_{10}H_8)_2]$ by benzene. The gas phase reaction at 298K,

$$[Cr(\eta\text{-}C_{10}H_8)_2,g] + 2C_6H_6(g) \rightarrow [Cr(\eta\text{-}C_6H_6)_2,g] + 2C_{10}H_8(g) \qquad (14)$$

has $\Delta H_r = [\Delta H_{disrupt}(Cr(\eta\text{-}C_{10}H_8)_2) - \Delta H_{disrupt}(Cr(\eta\text{-}C_6H_6)_2)]$, and the values in Table 9 lead to $\Delta H_r = -(40\pm15)$ kJ mol^{-1}. For the same reaction, in benzene at 298K,

$$[\mathrm{Cr}(\eta\text{-}\mathrm{C_{10}H_8})_2,\mathrm{c}] + (2+\underline{n})\mathrm{C_6H_6}(\ell) \rightarrow \{[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2] + 2\mathrm{C_{10}H_8}\} \text{ solution in } \underline{n}\ \mathrm{C_6H_6} \qquad (15)$$

($\underline{n}$ indicates the excess benzene solvent), the corresponding ΔH_r (soln) is related to ΔH_r(gas) by

$$\begin{aligned}\Delta H_r(\mathrm{soln}) = {} & \Delta H_r(\mathrm{gas}) + \Delta H^{298}_{\mathrm{sub}}(\mathrm{Cr}(\eta\text{-}\mathrm{C_{10}H_8})_2) + 2\Delta H^{298}_{\mathrm{vap}}(\mathrm{C_6H_6}) \\ & -\Delta H^{298}_{\mathrm{sub}}(\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2) - 2\Delta H^{298}_{\mathrm{sub}}(\mathrm{C_{10}H_8}) + \\ & 2\Delta H_{\mathrm{soln}}(\mathrm{C_{10}H_8(c)} \text{ in } (n/2)\mathrm{C_6H_6}(\ell)) + \\ & \Delta H_{\mathrm{soln}}(\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2(\mathrm{c}) \text{ in } \{2\mathrm{C_{10}H_8},\underline{n}\mathrm{C_6H_6}\}\text{solvent}) \qquad (16)\end{aligned}$$

Literature values [51] are available for $\Delta H^{298}_{\mathrm{vap}}(\mathrm{C_6H_6}) = 33.8$ kJ mol^{-1}, $\Delta H^{298}_{\mathrm{sub}}(\mathrm{C_{10}H_8}) = 72.9$ kJ mol^{-1} and for ΔH_{soln} of $\mathrm{C_{10}H_8(c)}$ in benzene (0.9 wt %) = 18.2 kJ mol^{-1}. From solution calorimetric measurements in this laboratory we obtain $\Delta H_{\mathrm{soln}}[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2$ (c) in benzene; 0.5 wt %] ~ 11.8 kJ mol^{-1}. We note that the enthalpy of melting, $\Delta H^{\mathrm{o}}_{m}(\mathrm{C_6H_6}) = 9.84$ kJ mol^{-1} at 278.68K [15]. Substitution of these values into eqn. (16) gives $\Delta H^{298}_r(\mathrm{soln}) = [\Delta H^{298}_r(\mathrm{gas}) - 16]$ kJ mol^{-1}.

Another example,

$$[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_3Me_3})_2] + 2\mathrm{C_6H_6} \rightarrow [\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2] + 2\mathrm{C_6H_3Me_3} \qquad (17)$$

has $H^{298}_r(\mathrm{gas}) = -(28\pm15)$ kJ mol^{-1}, and the solution phase reaction,

$$[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_3Me_3})_2,\mathrm{c}] + (2+\underline{n})\mathrm{C_6H_6}(\ell) \rightarrow \{[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2] + 2\mathrm{C_6H_3Me_3}\}(\text{soln in } \underline{n}\mathrm{C_6H_6}) \qquad (18)$$

is calculated (using additional thermal data from [51] and [52]) to have $\Delta H^{298}_f(\mathrm{soln}) \simeq [\Delta H^{298}_r(\mathrm{gas}) - 2]$ kJ mol^{-1}. In both these cases the solvent effect is not sufficiently large to alter conclusions based on the use of ΔH_r(gas) values. In our view, the gas phase ΔH_r values provide a satisfactory basis for discussion of solution reactions, provided that the ΔH_r values are sufficiently large (exo-or endothermic), and that the reaction conditions do not involve exceptionally high temperatures or pressures. In this respect, we note that the displacement of benzene in $[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2]$ by 1,3,5-trimethylbenzene can be brought about in the presence of $\mathrm{AlCl_3}$ as catalyst when $\{3[\mathrm{Cr}(\eta\text{-}\mathrm{C_6H_6})_2]\mathrm{AlCl_4}.4\mathrm{AlCl_3}\}$ is formed as an intermediate. There is no exchange in the absence of $\mathrm{AlCl_3}$ [53].

The reverse reaction is predicted and is observed on refluxing a solution of $[Cr(\eta\text{-}C_6H_3Me_3)_2]$ in benzene, in the absence of catalysts, at atmospheric pressure.

Table 15 presents ΔH_r values for various arene displacement reactions, in the gas phase, including the two examples discussed above.

TABLE 15. Enthalpy change (kJ mol^{-1}) calculated for arene displacement
$[Cr(\eta\text{-arene}_A)_2,g] + 2\ \text{arene}_B(g) \rightarrow [Cr(\eta\text{-arene}_B)_2,g] + 2\ \text{arene}_A(g)$.

		Arene$_B$		
$Cr(\eta\text{-arene}_A)_2$	$C_{10}H_8$	C_6H_6	$C_6H_3Me_3$	C_6Me_6
Arene$_A$ = $C_{10}H_8$	-	-(40±15)	-(12±17)	-(21±18)
C_6H_6	+(40±15)	-	+(28±15)	+(19±16)
$C_6H_3Me_3$	+(12±17)	-(28±15)	-	-(9 ±17)
C_6Me_6	+(21±18)	-(19±16)	+(9±17)	-

The calculations suggest that naphthalene is readily displaced from $[Cr(\eta\text{-}C_{10}H_8)_2]$ by monocyclic arenes, and that benzene displaces any other arene from $Cr(\eta\text{-arene})_2$.

Similar enthalpy changes can be calculated for a wider range of examples of reaction (7), and these are shown in Table 16, together with calculations for reactions (12) and (13).

We have also estimated the enthalpy changes for the corresponding liquid phase reactions (liquid arene$_B$) with broadly similar results. Where arene$_B$ is methylbenzene results are similar to those for benzene. These results have relevance to studies of arene displacement reactions at high temperature in a donor solvent by ^1H n.m.r. spectroscopy [54], which showed that the position of the equilibirum (7) is not very temperature dependent and that the order of displacement, that is the extent to which arene$_B$ displaces arene$_A$ from $[Cr(CO)_3(\eta\text{-arene}_A)]$, is arene$_B$ = hexamethylbenzene>1,2,4,5-tetramethylbenzene > 1,3,5-trimethylbenzene > N,N-dimethylbenzenamine > 1,4-dimethylbenzene > methylbenzene > benzene > phenylethanone > methoxybenzene > methylbenzoate > chlorobenzene ~fluorobenzene > naphthalene. The agreement

TABLE 16. Enthalpy change (kJ mol^{-1}) for the displacement reactions (at 298K):

$[Cr(CO)_3(\eta\text{-arene}_A,g] + \text{arene}_B(g) \rightarrow [Cr(CO)_3(\eta\text{-arene}_B),g] + \text{arene}_A(g)$

$[Cr(CO)_3(\eta^6\text{-}C_7H_8),g] + \text{arene}_B(g) \rightarrow [Cr(CO)_3(\eta\text{-arene}_B),g] + C_7H_8\ (g)$

$[Cr(CO)_4(\eta^2,\eta^2\text{-}C_7H_8),g] + \text{arene}_B(g) \rightarrow [Cr(CO)_3(\eta\text{-arene}_B),g] + CO(g) + C_7H_8(g)$

$[Cr(CO)_{\underline{n}}L]$	Arene$_B$				
$\underline{n}$ = 3; L =	$C_{10}H_8$	C_6H_5Cl	C_6H_6	$C_6H_3Me_3$	C_6Me_6
$\eta\text{-}C_{10}H_8$	-	-(7±22)	-(26±12)	-(38±12)	-(52±15)
$\eta\text{-}C_6H_5Cl$	+(7±22)	-	-(19±23)	-(31±23)	-(45±24)
$\eta\text{-}C_6H_6$	+(26±12)	+(19±23)	-	-(12±13)	-(26±16)
$\eta\text{-}C_6H_3Me_3$	+(39±12)	+(31±23)	+(12±13)	-	-(14±16)
$\eta\text{-}C_6Me_6$	+(53±15)	+(45±24)	+(26±16)	+(14±16)	-
$\eta^6\text{-}C_7H_8$	-(3±14)	-(10±24)	-(29±15)	-(41±15)	-(55±17)
$\underline{n}$ = 4; L = $\eta^2,\eta^2\text{-}C_7H_8$	+(34±14)	+(27±24)	+(8±15)	-(4±15)	-(18±17)

between this order and the calculations in Table 16 is very close. The displacement reaction (13), involving release of coordinated carbon monoxide as well as the diene ligand, bicyclohepta-[2,2,1]diene, is rather more limited than the reaction (12) which simply involves the displacement of cycloheptatriene (at 298K).

Redistribution reactions. The enthalpy changes calculated for reactions (8), (9) and (10) which involve displacement of a π-bonded arene by CO and the eventual formation of $Cr(CO)_6$ from $[Cr(\eta\text{-arene})_2]$ are shown in Table 17.

The sum $[\Delta H(8) + \Delta H(9)]$ indicates the ease with which $Cr(CO)_6$ is formed by displacement of the arene ligand, a reaction which is particularly favourable in the case of $[Cr(\eta\text{-}C_{10}H_8)_2]$ [27]. The magnitude of $[\Delta H(10)]/2$ is a measure of the transferability of the bond enthalpy contributions $\bar{D}$(Cr-arene) and $\bar{D}$(Cr-CO) from $[Cr(\eta\text{-arene})_2]$ and from $Cr(CO)_6$ to $[Cr(CO)_3(\eta\text{-arene})]$. If

TABLE 17. Enthalpy change (kJ mol^{-1}) for the redistribution reactions (at 298K)

$[Cr(\eta\text{-arene})_2,g] + 3CO(g) \rightarrow [Cr(CO)_3(\eta\text{-arene}),g] + \text{arene}(g)$ (8)

$[Cr(CO)_3(\eta\text{-arene}),g] + 3CO(g) \rightarrow Cr(CO)_6(g) + \text{arene}(g)$ (9)

$[Cr(\eta\text{-arene})_2,g] + Cr(CO)_6(g) \rightarrow 2[Cr(CO)_3(\eta\text{-arene}),g]$ (10)

Arene	ΔH(8)	ΔH(9)	ΔH(10)
$C_{10}H_8$	-(184±14)	-(168±8)	-(16±20)
C_6H_6	-(170±13)	-(142±9)	-(28±20)
$C_6H_3Me_3$	-(210±15)	-(130±9)	-(80±22)
C_6Me_6	-(215±18)	-(116±13)	-(99±29)

transferability is perfect, ΔH(10) = 0; deviations from this can be represented as

$$-[\Delta H(10)]/2 = \Delta(\text{Cr-arene}) + 3\Delta(\text{Cr-CO}) \quad (14)$$

where Δ(Cr-arene) and Δ(Cr-CO) represent a change in the bond enthalpy concerned, in $[Cr(CO)_3(\eta\text{-arene})]$. From the evidence already discussed, to which may be added measurements of ν(CO), the carbonyl ligand stretching frequency in the infrared spectra of $[Cr(CO)_3(\eta\text{-arene})]$ compounds [55], it is established that the Cr-CO bond in these complexes has a greater multiple (π) bond character than in $Cr(CO)_6$. When the major differences in decomposition temperature between, for example, $[Cr(CO)_3(\eta\text{-}C_{10}H_8)]$ (~470K) and $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ (~630K) are also considered, it would appear that Δ(Cr-CO) is positive and primarily responsible for the exothermal heats of redistribution, ΔH(10). If it is assumed that the whole of this heat is taken up by Δ(Cr-CO), then in the case of $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ the value of $\overline{D}$(Cr-CO) increases by 17kJ mol^{-1}. If Δ(Cr-arene) is also positive - as is most likely the case, then Δ(Cr-CO) will be less. This work has indicated the limits within which Cr-ligand bond enthalpy contributions are able to change when the ligands are η-arene or carbon monoxide.

Exchange reactions. Examples of reaction (11) have been known for many years [56]. Studies of the kinetics of some of these reactions which occur in donor (coordinating) solvents (e.g. methyl cyanide) have shown that the rate law can be expressed as

$$k = k_2[Cr(CO)_3(\eta\text{-arene})]^2 + k_2'[Cr(CO)_3(\eta\text{-arene})][arene] \qquad (19)$$

where arene is benzene, methylbenzene or chlorobenzene, or as

$$k = k_1[Cr(CO)_3(\eta\text{-arene})] + k_2'[Cr(CO)_3(\eta\text{-arene})][arene] \qquad (20)$$

where arene is cycloheptatriene or naphthalene. The activation enthalpies for these reactions are given in Table 18

TABLE 18. Activation Enthalpy (kJ mol^{-1}) for Arene ligand Exchange in $[Cr(CO)_3(\eta\text{-arene})]$ [56]

Arene	E_2'	E_2	E_1
Benzene	106	125	
Methylbenzene	133	146	
Chlorobenzene	123	124	
Naphthalene	69		79
Cycloheptatriene	144		127

The mechanism of these exchange reactions has been reconsidered recently [54]. It was concluded that the role of the donor solvent (L) is to assist in the formation of $[Cr(CO)_3(L)(\eta^4\text{-arene})]$ from $[Cr(CO)_3(\eta^6\text{-arene})]$. This process is clearly most favourable for $[Cr(CO)_3(\eta\text{-}C_{10}H_8)]$, in the light of previous discussion. The process (19) which contains a term of second order in $[Cr(CO)_3(\eta\text{-arene})]$ is thought to involve CO as a donor ligand as in

$$2[Cr(CO)_3(\eta^6\text{-arene})] \rightarrow [Cr(CO)_2(\eta^6\text{-arene})] + [Cr(CO)_4(\eta^4\text{-arene})] \qquad (21)$$

The results we have obtained do not enable us to develop these mechanisms further. However, we note that D(Cr-NCMe) (<100 kJ mol^{-1}) is less than $\bar{D}$(Cr-CO), that 2D(Cr-triene) ~3D(Cr-diene), and that D(Cr-cyclo-C_7H_8) ~D(Cr-$C_{10}H_8$) < D(Cr-C_6H_6), which would be required by the proposals made by Pauson [54].

Conclusions

The results obtained in this study, together with those from previous work are listed in Table 9. If ΔH_f^o(arene,g) is plotted against ΔH_f^o([Cr(η-arene)$_2$],g) and against ΔH_f^o([Cr(CO)$_3$(η-arene)],g), it is found that the two can be related by the equations

$$\Delta H_f^o([\mathrm{Cr}(\eta\text{-arene})_2],g) = 2.03\ \Delta H_f^o(\text{arene},g) + 88 \tag{22}$$

and

$$\Delta H_f^o([\mathrm{Cr(CO)_3}(\eta\text{-arene})],g) = 1.30\ \Delta H_f^o(\text{arene},g) -445\ . \tag{23}$$

the correlation coefficient is 0.997 in each case. These empirical relationships may be useful in estimating the enthalpies of formation of other chromium complexes where these are not known, as well as in assessing the outcome of substitution and redistribution reactions. The limitations on the transferability of bond enthalpy contributions have been established. The procedure is seen to be generally valid in the systems we have considered.

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