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THE THERMOCHEMISTRY OF CARBONYL COMPLEXES OF Cr, Mo, W AND Co WITH ARENES, CYCLOHEPTATRIENE, AND NORBORNADIENE *

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Summary

Microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and of iodination of a number of arenemetal carbonyls have led to values for the standard enthalpies of formation of the following crystalline compounds (values given in kJ mol^{-1}) at 25°C: $(C_6H_6)Co_3(CO)_9$ = —(1313 ± 13); $(C_6H_3Me_3)Co_4(CO)_9$ = —(1444 ± 13); $(C_6Me_6)Co_3(CO)_9$ = —(1555 ± 17); $(C_6H_3Me_3)Mo(CO)_3$ = —(533 ± 13); $(C_6H_3Me_3)W(CO)_3$ = —(477 ± 13); $(C_6Me_6)Cr(CO)_3$ = —(671 ± 13); $(C_6Me_6)Mo(CO)_3$ = —(631 ± 8); (cyclo-C_7H_8)Mo(CO)$_3$ = —(297 ± 8); (cyclo-C_7H_8)W(CO)$_3$ = —(236 ± 8); (nor-C_7H_8)Cr-(CO)$_4$ ~ —(400 ± 13); (nor-C_7H_8)Mo(CO)$_4$ = —(428 ± 10).

Separate measurements by the vacuum-sublimation microcalorimetric technique gave the following values for ΔH_{sub}^{298} (kJ mol^{-1}): (cyclo-C_7H_8)Cr(CO)$_3$ = (87.9 ± 4); (cyclo-C_7H_8)Mo(CO)$_3$ = (87.9 ± 4); (cyclo-C_7H_8)W(CO)$_3$ = (92.0 ± 4); (nor-C_7H_8)Cr(CO)$_4$ = (88.7 ± 4) and (nor-C_7H_8)Mo(CO)$_4$ = (91.6 ± 4).

From these (and other) data, the bond-enthalpy contributions of the various ligand—metal bonds (D(L—M)) in the gaseous metal complexes were evaluated as follows (values in kJ mol^{-1}): (C_6H_6)—Co = 270; $(C_6Me_3H_3)$—Co = 285; (C_6Me_6)—Co = 310; $(C_6Me_3H_3)$—Cr = 191; $(C_6Me_3H_3)$—Mo = 279; $(C_6Me_3H_3)$—W = 334; (C_6Me_6)—Cr = 205; (C_6Me_6)—Mo = 292; (cyclo-C_7H_8)—Cr = 150; (cyclo-C_7H_8)—Mo = 264; (cyclo-C_7H_8)—W = 311; (nor-C_7H_8)—Cr ~ (80); (nor-C_7H_8)—Mo, ~ 187.

The bond-enthalpy contribution, D(M—L), for a given ligand increases on ascending the series M = Cr → Mo → W, and for a given metal, D(M—L) increases on changing L along the series L = benzene → mesitylene → hexamethylbenzene.

Thermal stability, however, is not generally determined by the magnitude of the bond-enthalpy contributions, D(M—L) and D(M—CO), and complexes of Mo and W are frequently less stable to heat than the corresponding complexes of Cr. It is suggested that the thermal decomposition of some complexes may

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take place in the condensed state, and involve the initial formation of poly-
nuclear metal carbonyl products, and of the metal hexacarbonyls.

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1. Introduction

The present paper extends earlier thermochemical studies [1,2] on ((arene)Cr-
(CO)$_3$) complexes to similar complexes of Mo, W and Co.

2. Experimental

Calorimeter

The thermal measurements were made using a Calvet high temperature twin-
cell microcalorimeter (Setaram, Lyon), and the drop-calorimetric technique
was applied as previously [1,3]. The calorimeter was calibrated over the tem-
perature range 373—593 K from measurements of the enthalpy of sublimation
of iodine [4], I_2(c, 298) → I_2(g, T), and of benzoic acid [5], C_6H_5COOH (c, 298)
→ C_6H_5COOH(g, T).

Compounds

Samples of [(η-arene)Co$_3$(CO)$_9$] (arene = benzene, 1,3,5-trimethyl benzene,
hexamethylbenzene) complexes [6] were donated to us by Professor P.L.
Pauson, University of Strathclyde. Samples of ((η-cycloheptatriene)M(CO)$_3$)
(M = Cr [7], Mo [7], W [8]), (η-{1,3,5-trimethylbenzene}M(CO)$_3$) (M = Mo [9],
W [9]) and ({(2,3,5,6-η)-bicyclo[2,2,1]hepta-2,5-diene}M(CO)$_3$) (M = Cr [10],
Mo [10]) were prepared by standard methods or slight modifications thereof.
[(η-hexamethylbenzene)Mo(CO)$_3$] was prepared by refluxing Mo(CO)$_5$ and
C$_6$Me$_6$ in di-n-butylether, followed by recrystallization of the precipitate from
petroleum ether [11]. This procedure was unsuccessful when applied to the
synthesis of the tungsten analogue. The purity of all the metal complexes used
was established by microanalysis and by spectroscopic measurements (IR, NMR
and mass) which were in agreement with published values.

Auxiliary data

All heat quantities are given in joules (J) or kilojoules (kJ). The following
auxiliary heat of formation data (kJ mol^{-1}) were used in evaluating the experi-
mental results: ΔH_f^0(CO, g) = —(110.524 ± 0.17) [12]; ΔH_f^0(I$_2$, g) = (62.442
± 0.04) [4]; ΔH_f^0(Co, g) = (424.7 ± 4) [12]; ΔH_f^0(Cr, g) = (396.6 ± 4) [12];
ΔH_f^0(Mo, g) = (658.1 ± 4) [12]; ΔH_f^0(W, g) = (851.0 ± 6) [4]; ΔH_f^0(Cr(CO)$_6$, g)
= —(908.3 ± 1.7) [13]; ΔH_f^0(Mo(CO)$_6$, g) = —(915.9 ± 1.7) [13]; ΔH_f^0(W(CO)$_6$, g)
= —(883.7 ± 3.3) [13]; ΔH_f^0(benzene, g) = (82.88 ± 0.52) [14]; ΔH_f^0(mesitylene,
g) = —(15.94 ± 1.38) [14]; ΔH_f^0(hexamethylbenzene, g) = —(86.82 ± 2.6) [14];
ΔH_f^0(cycloheptatriene, g) = (183.68 ± 1.5) [14]; ΔH_f^0(2,5-norbornadiene, g)
= (242.7 ± 2.5) [15]; ΔH_f^0(CoI$_2$, c) = —(88.7 ± 2.1) [12]; ΔH_f^0(CrI$_2$, c) = —(156.9
± 4) [12]; ΔH_f^0(CrI$_3$, c) = —(205.0 ± 4) [12]; ΔH_f^0(MoI$_3$, c) = —(113.0 ± 10.5)
[16]; ΔH_f^0(WI$_3$, c) = —(46.0 ± 12.5) [16].

To reduce ΔH^T values to ΔH^{298}, ($H_T — H_{298}$) values for the metals Co, Cr,
Mo and W were taken from the compilation of Hultgren, Orr, Anderson and

Kelley [17], and for the hydrocarbon ligands in the gas state from the data compilation of Stull, Westrum and Sinke [18].

Results

1. (Benzene)tetracobalt nonacarbonyl, [(C₆H₆)Co₄(CO)₉]

1. (Benzene)tetracobalt nonacarbonyl, [(C$_6$H$_6$)Co$_4$(CO)$_9$]

Thermal decomposition studies in argon gas were made at 495 K. Spots of cobalt metal were deposited on the wall of the reaction vessel, and black powdered metal remained in the capillary tube containers. The decomposition thermograms showed slight exothermal tailing on returning to the baseline. Measured enthalpies of decomposition, ΔH^*_{dec}, refer to the calorimeter reaction (eq. 1) and are listed in Table 1; the values ΔH^{298}_{dec} refer to the same decomposition reaction carried out isothermally at 298 K. The mean value, ΔH^{298}_{dec} 401.2

$$[(C_6H_6)Co_4(CO)_9](c, 298) \rightarrow C_6H_6(g, 495) + 4Co(c, 495) + 9CO(g, 495) \qquad (1)$$
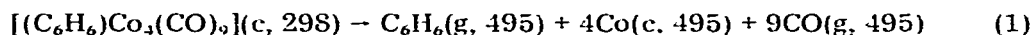
kJ mol^{-1} is considered subject to uncertainty limits of ca. ±3%, and leads to the value $\Delta H^0_f[(C_6H_6)Co_4(CO)_9, c] = -(1313.0 \pm 12)$ kJ mol^{-1}.

2. (Mesitylene)tetracabalt nonacarbonyl, [(C₆H₃Me₃)Co₄(CO)₉]

2. (Mesitylene)tetracabalt nonacarbonyl, [(C$_6$H$_3$Me$_3$)Co$_4$(CO)$_9$]

Thermal-decomposition studies in argon gas were made over the range 477—533 K. Cobalt metal deposited as spots on the wall of the reaction vessel and as black powder in the capillary tube containers. The thermograms showed light exothermic tailing at the higher range of temperatures. Attempts to measure the heat of sublimation by the vacuum-sublimation microcalorimetric technique [2] at temperatures in the range 396—403 K were not successful, as evacuation of the reaction vessel induced thermal decomposition of the samples at these temperatures. Decomposition appeared to take place entirely within the capillary tube containers, and there was no deposition of metal on the wall of the reaction vessel. Results are included in Table 1, the mean value $\Delta H^{298}_{dec} = 433.5$ kJ mol^{-1} leading to $\Delta H^0_f[(C_6H_3Me_3)Co_4(CO)_9, c] = -(1444 \pm 12)$ kJ mol^{-1}.

A single measurement of the heat of iodination of [(mesitylene)Co₄(CO)₉] at 478 K was not entirely satisfactory, as the thermogram traced a lengthy exothermal tail following the decomposition endotherm, due to the slow iodination of cobalt powder deposited in the capillary container. The measured heat of iodination led to $\Delta H^{298}_{dec} = (442 \pm 20)$ kJ mol^{-1}, the uncertainty being accentuated by the the the tailing of the thermogram.

3. (Hexamethylbenzene)tetracobalt nonacarbonyl, [(C₆Me₆)Co₄(CO)₉]

3. (Hexamethylbenzene)tetracobalt nonacarbonyl, [(C$_6$Me$_6$)Co$_4$(CO)$_9$]

Thermal decomposition in argon gas was studied over the range 513—553 K. Metal deposited as a mirror on the cell wall, and in the capillary tube containers. The thermograms showed exothermal tailing, more noticably at the highest temperatures. Vacuum sublimation over the range 400—412 K induced thermal decomposition, the metal depositing totally within the capillary tube containers. The thermograms from vacuum sublimation decomposition showed no tailing. Results are summarized in Table 1; the mean value, $\Delta H^{298}_{dec} = 457.3$ kJ mol^{-1} corresponds to $\Delta H^0_f[(C_6Me_6)Co_4(CO)_9, c] = -(1555 \pm 17)$ kJ mol^{-1}.

A single measurement of the heat of iodination at 543 K was based on a thermogram showing a lengthy exothermic tail, due to slow and incomplete iodina-

tion of the cobalt metal ($CoI_{0.85}$). The derived $\Delta H_{dec}^{298} = 450.0$ kJ mol^{-1} from this measurement is considered uncertain to ± 20 kJ mol^{-1}.

4. Tetracobalt dodecacarbonyl, [Co₄(CO)₁₂]

Attempts to measure the heat of sublimation by the vacuum-sublimation microcalorimetric technique over the range 352—395 K were unsuccessful, evacuation inducing thermal decomposition even at the lowest temperatures used. Decomposition led to the deposition of an extensive and shiny cobalt mirror on the wall of the reaction vessel, extending to the exit tube from the hot zone. In this respect, the vacuum induced thermal decomposition of $Co_4(CO)_{12}$ differed from the decompositions of [(arene)Co₄(CO)₉] complexes, when mirrors were not formed. At 352 K, vacuum sublimation gave a trace of a blue powder deposit in the cooler part of the exit tube, probably because some vapour $[Co_2(CO)_x]$ or $[Co_4(CO)_{12}]$ managed to escape the hot-zone without decomposition.   •

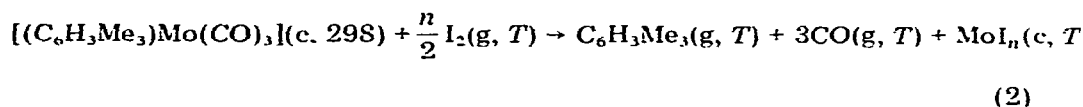## 5. (Mesitylene)molybdenum tricarbonyl, [(C₆H₃Me₃)Mo(CO)₃]

The vacuum-sublimation technique was applied over the range 393—419 K; thermal decomposition was induced on evacuation, molybdenum metal being formed as a black powder within the capillary tube containers. A few colour-less crystals condensed in the cooler part of the exit tube, indicating that a small amount of $Mo(CO)_6$ vapour escaped without decomposition from the reaction vessel. Thermal decomposition appeared to be more nearly complete on dropping samples into the argon-filled reaction vessel at 471 K. Total decomposition within the reaction vessel resulted on dropping samples into argon—iodine vapour at temperatures ranging from 471—508 K. The measured heats of

TABLE 1

THERMAL DECOMPOSITION OF [(arene)Co₄(CO)₉] COMPLEXES

| Compound	Sample (mg)	T (K)	Method [a]	ΔH_{dec}^{T} (kJ mol^{-1})	ΔH_{dec}^{298} (kJ mol^{-1})
[(C₆H₆)Co₄(CO)₉]	4.085	495	TD	497.1	402.5
	3.670	495	TD	489.9	395.4
	4.470	495	TD	495.4	400.8
	3.895	495	TD	500.4	405.8
	Mean $\Delta H_{dec}^{298} = 401.2$ kJ mol^{-1}				
[(C₆H₃Me₃)Co₄(CO)₉]	3.390	533	TD	565.3	430.9
	3.250	480	TD	528.9	426.8
	3.315	477	TD	534.3	434.3
	5.630	403	VS-TD	500.4	443.9
	5.440	403	VS-TD	495.8	439.3
	6.000	401	VS-TD	480.7	425.5
	Mean $\Delta H_{dec}^{298} = 433.5$ kJ mol^{-1}				
[(C₆Me₆)Co₄(CO)₉]	3.675	543	TD	617.6	447.3
	4.420	513	TD	590.8	443.9
	5.555	412	VS-TD	551.9	477.8
	5.340	400	VS-TD	525.1	459.4
	Mean $\Delta H_{dec}^{298} = 457.3$ kJ mol^{-1}				

[a] TD, thermal decomposition technique; VS, vacuum sublimation technique.

iodination, ΔH_{iod}^*, refer to the process shown in eq. 2, where T = temperature

$$[(C_6H_3Me_3)Mo(CO)_3](c, 298) + \frac{n}{2} I_2(g, T) \rightarrow C_6H_3Me_3(g, T) + 3CO(g, T) + MoI_n(c, T \tag{2}$$

of the calorimeter hot-zone. The contributions to ΔH_{iod}^* arising from iodination of the metal (eq. 3) were evaluated from data given by Virmani, Barnes and

$$Mo(c, T) + \frac{n}{2} I_2(g, T) \rightarrow MoI_n(c, T) \tag{3}$$
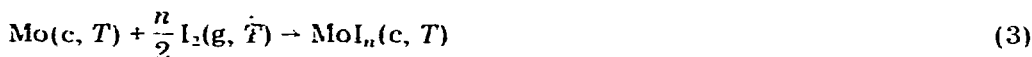
Skinner [16], in order to extract values, ΔH_{dec}^*, for the thermal decomposition process per se (eq. 4). Values of n (eq. 3) were determined from analysis of the

$$[(C_6H_3Me_3)Mo(CO)_3](c, 298) \rightarrow C_6H_3Me_3(g, T) + 3CO(g, T) + Mo(c, T) \tag{4}$$
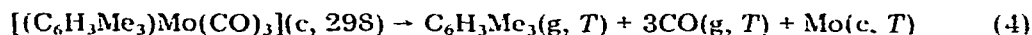
iodine content in the solid product, MoI_n, formed in each experiment.

Results from both thermal decomposition and iodination studies are summarized in Table 2. The values ΔH_{dec}^{298} from vacuum sublimation thermal decomposition are expected to be slightly low, as some $Mo(CO)_6$ vapour escaped decomposition in these experiments. The mean value, ΔH_{dec}^{298} = 185.3 kJ mol^{-1} from iodination is preferred, leading to $\Delta H_f^0[(C_6H_3Me_3)Mo(CO)_3, c]$ = $-(533.0 \pm 12)$ kJ mol^{-1}.

6. (Mesitylene)tungsten tricarbonyl. [(C_6H_3Me_3)W(CO)_3]

The vacuum-sublimation technique was applied over the range 407—415 K;

TABLE 2

THERMAL DECOMPOSITION AND IODINATION OF [(C$_6$H$_3$Me$_3$)Mo(CO)$_3$] AND OF [(C$_6$H$_3$Me$_3$)W-(CO)$_3$]

Sample (mg)	T (K)	Method	I_2 (mg)	n	ΔH_{iod}^* (kJ mol^{-1})	ΔH_{dec}^* (kJ mol^{-1})	ΔH_{dec}^{298} (kJ mol^{-1})
Mesitylene molybdenum tricarbonyl							
4.995	419	VS-TD	—	—	—	195.4	160.2
5.430	419	VS-TD	—	—	—	190.0	154.8
5.170	471	TD	—	—	—	225.1	172.4
5.280	471	Iod.	10.08	1.62	115.5	227.6	174.9
5.185	471	Iod.	10.15	1.85	106.7	236.0	182.0
5.110	471	Iod.	13.09	2.43	88.3	256.1	203.3
4.255	508	Iod.	11.68	2.80	53.1	246.0	181.2
			Mean ΔH_{dec}^{298} = 184.5 kJ mol^{-1}				
Mesitylenetungsten tricarbonyl							
5.605	411	VS-TD	—	—	—	149.8	117.2
5.415	506	TD	—	—	—	177.8	114.2
5.865	524	TD	—	—	—	187.4	118.4
5.315	501	Iod.	11.52	1.56	122.0	192.0	129.3
5.110	502	Iod.	10.23	1.84	114.0	197.1	133.9
5.290	503	Iod.	10.56	1.39	128.0	191.6	128.4
5.575	523	Iod.	10.68	1.67	127.0	202.1	133.0
5.775	523	Iod.	10.40	1.35	133.0	193.3	124.7
			Mean ΔH_{dec}^{298} = 129.7 kJ mol^{-1}				

evacuation induced thermal decomposition, albeit slowly, at these temperatures. Thermal decomposition in argon gas was examined from 502—524 K, and appeared to be complete at the higher temperatures. Iodination measurements were made over the range 501—523 K. The contributions to $\Delta H^*_{iod.}$ due to iodination of the metal were evaluated from data of Virmani et al. [16]. Results are included in Table 2, and the mean value $\Delta H^{298}_{dec} = 129.7$ kJ mol^{-1} from iodination studies, is preferred, corresponding to $\Delta H^0_f[(C_6H_3Me_3)W(CO)_3, c] = -(477.4 \pm 12)$ kJ mol^{-1}.

7. (Hexamethylbenzene)chromium tricarbonyl, [(C₆Me₆)Cr(CO)₃]

Previous studies [1] reported measurements of the heat of reaction of [(C₆Me₆)-Cr(CO)₃] with iodine vapour, leading to $\Delta H^{298}_{dec} = (276 \pm 12)$ kJ mol^{-1}. Improvements in calorimetric and analytical procedures gave reason to repeat these studies, with results as summarized in Table 3. The contributions to $\Delta H^*_{iod.}$ from iodination of Cr metal were made as before [1].

The present value for ΔH^{298}_{dec} is based on a wider range of n (CrI$_n$, $n = 1.7$—2.85) than in earlier measurements, and is preferred. The mean value, $\Delta H^{298}_{dec} = (252.7 \pm 12)$ kJ mol^{-1} corresponds to $\Delta H^0_f[(C_6Me_6)Cr(CO)_3, c] = -(671 \pm 12)$ kJ mol^{-1}.

8. (Hexamethylbenzene)molybdenum tricarbonyl, [(C₆Me₆)Mo(CO)₃]

Attempts to measure the heat of sublimation by the vacuum-sublimation technique were not successful, as evacuation induced thermal decomposition at temperatures as low as 410 K. Thermal decomposition studies by the vacuum-sublimation technique were made over the range 463—484 K; decomposition resulted in deposition of a bright metallic mirror on the walls of the reaction vessel and capillary tube container, and a white film of hexamethylbenzene condensed on cooler parts of the exit tube. Only small amounts of Mo(CO)₆ escaped the reaction vessel at these temperatures. The thermograms showed slight exothermic tailing on returning to the baseline. Results are summarized in Table 4. The mean $\Delta H^{298}_{dec} = (212.5 \pm 6.3)$ kJ mol^{-1} corresponds to $\Delta H^0_f[(C_6Me_6)\cdot Mo(CO)_3, c] = -(630.9 \pm 8.5)$ kJ mol^{-1}.

9. (Cycloheptatriene)molybdenum tricarbonyl, [(C₇H₈)Mo(CO)₃]

The vacuum-sublimation technique was applied from 377—393 K. The samples sublimed readily, but with some decomposition (2—5%). The measured sublimation enthalpies reduced to $\Delta H_{sub} = (88 \pm 4)$ kJ mol^{-1} at 298 K. Decomposition was incomplete at temperatures below 473 K, some Mo(CO)₆ vapour

TABLE 3

IODINATION OF [(C₆Me₆)Cr(CO)₃]

Sample (mg)	T (K)	Method	I₂ (mg)	n	$\Delta H^*_{iod.}$ (kJ mol^{-1})	ΔH^*_{dec} (kJ mol^{-1})	ΔH^{298}_{dec} (kJ mol^{-1})
3.140	595	Iod.	8.546	2.40	139.7	386.2	253.1
3.430	593	Iod.	8.360	2.85	94.1	377.8	246.0
4.300	593	Iod.	11.390	2.10	167.4	390.8	259.0
4.075	593	Iod.	13.890	1.70	202.1	385.3	253.6
				Mean $\Delta H^{298}_{dec} = 252.7$ kJ mol^{-1}			

TABLE 4

THERMAL DECOMPOSITION OF [(C$_6$Me$_6$)Mo(CO)$_3$]

Sample (mg)	T (K)	Method	ΔH^*_{dec} (kJ mol^{-1})	ΔH^{298}_{dec} (kJ mol^{-1})
3.345	465	VS-TD	273.2	203.8
2.885	470	VS-TD	288.7	217.1
2.705	471	VS-TD	285.8	213.8
2.725	473	VS-TD	289.1	216.3
			Mean ΔH^{298}_{dec} = 212.5 kJ mol^{-1}	

escaping the hot zone to condense in the exit tube. Decomposition appeared to be complete at temperatures >515 K, metallic mirror formation being confined to the wall of the reaction vessel. Results from the decomposition studies at the higher temperatures are summarized in Table 5. The mean value, ΔH^{298}_{dec} = (149 ± 4) kJ mol^{-1} corresponds to $\Delta H^0_f[(C_7H_8)Mo(CO)_3, c] = -(297 ± 6)$ kJ mol^{-1}.

10. (Cycloheptatriene)tungsten tricarbonyl, [(C$_7$H$_8$)W(CO)$_3$]

The heat of sublimation was measured by the vacuum-sublimation technique at 396 K, leading to ΔH^{298}_{sub} = (92 ± 4) kJ mol^{-1}. Sublimation took place cleanly, without visible signs of decomposition, at this temperature.

Thermal decomposition in argon gas was investigated over the range 516—597 K. Decomposition was not complete at temperatures below ca. 570 K, some W(CO)$_6$ vapour escaping the hot zone. The thermograms showed slight exothermal tailing on return to the baseline. The thermal results at temperatures >570 K are summarized in Table 5. The mean value of ΔH^{298}_{dec} = (87 ± 4) kJ mol^{-1} corresponds to $\Delta H^0_f[(C_7H_8)W(CO)_3, c] = -(236 ± 6)$ kJ mol^{-1}.

11. (Cycloheptatriene)chromium tricarbonyl, [(C$_7$H$_8$)Cr(CO)$_3$]

Vacuum sublimation measurements at 396 K led to ΔH^{298}_{sub} = (88 ± 4) kJ mol^{-1}. Thermal decomposition in argon appeared to be complete at temperatures

TABLE 5

THERMAL DECOMPOSITION OF [(cyclo-C$_7$H$_8$)Mo(CO)$_3$] AND OF [(cyclo-C$_7$H$_8$)W(CO)$_3$]

| Compound	Sample (mg)	T (K)	Method	ΔH^*_{dec} (kJ mol^{-1})	ΔH^{298}_{dec} (kJ mol^{-1})
[(C$_7$H$_8$)Mo(CO)$_3$]	1.950	516	TD	201.0	142.0
	1.940	516	TD	207.5	148.5
	1.960	516	TD	209.0	150.0
	2.415	523	TD	215.0	155.0
	2.495	523	TD	211.0	151.0
			Mean ΔH^{298}_{dec} = 149.0 kJ mol^{-1}		
[(C$_7$H$_8$)W(CO)$_3$]	1.960	573	TD	164.0	87.0
	3.155	588	TD	167.0	85.4
	3.255	588	TD	169.0	87.4
	2.390	593	TD	173.0	90.0
	2.575	597	TD	171.0	86.6
			Mean ΔH^{298}_{dec} = 87.4 kJ mol^{-1}		

>500 K, the measured values of ΔH_{dec}^* ranging from 100—125 kJ mol^{-1} at temperatures from 500—590 K. These values are too low to relate to the simple thermal decomposition reaction, and include exothermal effects of unknown magnitude arising from surface absorption of carbon monoxide and the organic ligand on the active chromium powder deposit. (On the microcalorimetric scale, chemisorption effects can be substantial on chromium at elevated temperatures [3]).

Surface absorption difficulties are largely eliminated by decomposing in the presence of iodine vapour, which method (applied in earlier studies [1]) gave $\Delta H_{dec}^{298} = (159 \pm 12)$ kJ mol^{-1}, corresponding to $\Delta H_f^0[(\text{cyclo-}C_7H_8)\text{cr}(CO)_3, c]$ $= -(310 \pm 12)$ kJ mol^{-1}. The iodination method is, however, suspect in this case because of extensive side reactions of the ligand with iodine and it is intended to seek confirmation of, or improve upon this value from heat of combustion measurements on this compound.

12. (Norbornadiene)chromium tetracarbonyl, [(nor-C_7H_8)Cr(CO)$_4$]

Vacuum-sublimation measurements at 387 K led to $\Delta H_{sub}^{298} = (89 \pm 4)$ kJ mol^{-1}. Thermal decomposition studies over the range 451—460 K gave thermograms in which the initial endotherm returned to base thence to trace out an exothermal peak. Decomposition was incomplete, white crystals condensing in the reaction vessel on cooling, and some Cr(CO)$_6$ escaping the hot-zone to condense in cooler parts of the exit tube. Mass-spectroscopic analysis indicated the presence both of dimer (mol. wt. 184) of norbornadiene, and of Cr(CO)$_6$ in the crystalline residue. At higher temperatures (513—520 K) the decomposition thermograms were totally endothermic, giving $\Delta H_{dec}^{513} \sim 96$ kJ mol^{-1}; the reaction vessel became coated with a thin brownish film, and a whitish film (probably containing norbornadiene dimer) condensed in the exit line. The measured ΔH_{dec} is low in relation to simple thermal decomposition, and includes exothermal effects of unknown magnitude from surface absorption of CO and norbornadiene on the metal deposit.

Iodination of [(nor-C_7H_8)Cr(CO)$_4$] was studied from 513—520 K, giving a black powder (CrI$_n$, $n = 2.3$—2.6) in the reaction vessel, and a brown liquid film on the cell walls extending into the exit tube. A relatively involtatile, almost colourless liquid distilled from the mixture of reaction products on heating in vacuo. Norbornadiene is itself attacked by iodine at these temperatures, similarly leaving a brown liquid film in the reaction vessel from which a colorless liquid distilled on heating in vacuo. Separate measurements were made to determine the thermal effect of the norbornadiene—iodine reaction, leading to $\Delta H_5 = -(39 \pm 4)$ kJ mol^{-1} for the process shown in eq, 5.

$$(\text{nor-}C_7H_8, \text{liq}, 298) + \text{excess } I_2(g, 518) \rightarrow \{C_7H_8/I_2\}(518) \tag{5}$$
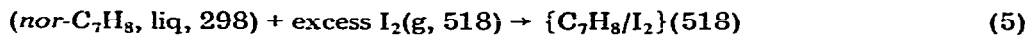
Experimental results from iodination of [(nor-C_7H_8)Cr(CO)$_4$] are summarized in Table 6. ΔH_{obs} is presumed to relate to the process 6 where (C$_7$H$_8$/I$_2$) is the
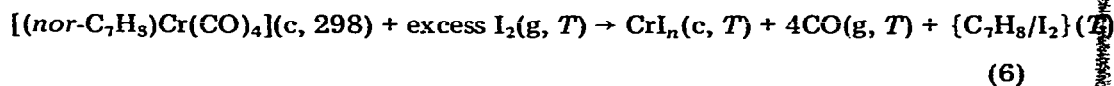
$$[(\text{nor-}C_7H_8)\text{Cr}(CO)_4](c, 298) + \text{excess } I_2(g, T) \rightarrow \text{CrI}_n(c, T) + 4CO(g, T) + \{C_7H_8/I_2\}(T) \tag{6}$$

TABLE 6

IODINATION OF [(nor-C_7H_8)Cr(CO)$_3$]

Sample (mg)	I_2 (mg)	T (K)	ΔH_{obs} (kJ mol^{-1})	n	ΔH_{dec}^{*} ^{a} (kJ mol^{-1})	ΔH_{dec}^{298} (kJ mol^{-1})
2.205	9.825	520	−91.0	2.54	242.0	210.0
2.155	8.755	519	−93.0	2.50	237.0	205.0
2.280	8.870	518	−98.0	2.40	224.0	193.0
2.825	8.725	513	−98.0	2.32	223.0	192.0

Mean ΔH_{dec}^{298} = 200.0 kJ mol^{-1}

same product as formed in eq. 5. In Table 6 ΔH_{dec}^{*} refers to process 7 and

$$[(nor\text{-}C_7H_8)Cr(CO)_3](c, 298) \to (nor\text{-}C_7H_8)(g, 298) + Cr(c, T) + 4CO\ (g, T) \quad (7)$$

derives from ΔH_{obs} by allowing for the exothermic contributions from iodination of norbornadiene (ΔH_5, eq. 5), from formation of CrI$_n$, and for the endothermic contribution from vaporization of norbornadiene, for which measurements by Hall, Smith and Baldt [19] gave ΔH_{vap}^{298} = (34.5 ± 0.4) kJ mol^{-1}. The mean ΔH_{dec}^{298} = (200 ± 9) kJ mol^{-1} corresponds to ΔH_f^0 [(nor-C_7H_8)Cr(CO)$_4$, c] = −(400 ± 12) kJ mol^{-1}. This value is, however, dependent on the assumption that the thermal decomposition of the complex in the presence of iodine vapour gave norbornadiene monomer, which was then exposed to iodine vapour. The thermal corrections made are based on blank experiments using norbornadiene itself, but the thermal decomposition of the complex per se is not straightforward, dimeric norbornadiene being detected among the products. The iodine balance in the iodination experiments with the complex indicated that the iodine consumed per nor-C_7H_8 released was less than in blank experiments, consistent with the possibility that part of the liberated nor-C_7H_8 reacted to form dimeric (and/or higher) oligomers. The mean ΔH_{dec}^{298} of Table 6 is probably less than the true value, and $\Delta H_f^0[(nor\text{-}C_7H_8)Cr(CO)_4, c]$ correspondingly less negative than it should be.

13. (Norbornadiene)molybdenum tetracarbonyl, [(nor-C_7H_8)Mo(CO)$_4$]

From vacuum-sublimation measurements over the range 401—431 K, the value ΔH_{sub}^{298} = (91.6 ± 4) kJ mol^{-1} was obtained; there was only slight decomposition on sublimation at these temperatures. Vacuum-sublimation at 474 K involved appreciable thermal decomposition, with formation of a grey metallic mirror on the wall of the reaction vessel, and a black powder deposit in the capillary tube container. Some Mo(CO)$_6$ vapour escaped the reaction zone to condense in the exit line, and a less volatile white film (probably dimeric norbornadiene) also formed in the exit line. Thermal decomposition in argon appeared to be more nearly complete at 513 K, leaving a bright metallic mirror deposit in the reaction vessel, but there were also a few white crystals which condensed near the exit from the hot zone. ΔH_{dec}^{513} was measured at 218 kJ mol^{-1}.

Iodination of [(nor-C_7H_8)Mo(CO)$_4$] was studied in the temperature range 513—532 K, yielding a black powder (MoI$_n$), and a brown film, similar to that observed with [(nor-C_7H_8)Cr(CO)$_4$] and iodine. Results are summarized in

TABLE 7

IODINATION [(nor-C$_7$H$_8$)Mo(CO)$_4$]^a

Sample (mg)	I$_2$ (mg)	T (K)	ΔH_{obs} (kJ mol^{-1})	n	ΔH^*_{dec} (kJ mol^{-1})	ΔH^{298}_{dec} (kJ mol^{-1})
4.230	10.78	513	41.0	2.20	264.0	233.0
4.315	9.46	513	44.8	2.10	261.0	230.0
4.105	10.19	513	31.0	2.20	254.0	223.0
4.375	10.35	513	34.7	2.26	264.0	233.0
2.475	8.18	532	24.3	2.30	254.0	220.0

Mean ΔH^{298}_{dec} = (228 ± 6) kJ mol^{-1}

^{a} The mean ΔH^{298}_{dec} leads to $\Delta H^0_f[(nor$-C$_7$H$_8$)Mo(CO)$_4$, c] = −(427.6 ± 10) kJ mol^{-1}.

Table 7. The values ΔH^*_{dec} refer to the thermal decomposition process 8 and

$$[(nor\text{-}C_7H_8)Mo(CO)_4][c, 298] \to nor\text{-}C_7H_8(g, 298) + Mo(c, T_2) + 4CO(g, T_2) \quad (8)$$

were obtained from ΔH_{obs} by removing the exothermic contributions from iodination of molybdenum [15] and of norbornadiene, and adding the endothermic contribution, $\Delta H^{298}_{vap}(nor$-C$_7$H$_8$).

The derived heat of formation (as for the similar chromium complex) depends on the correction made for iodination of liberated nor-C$_7$H$_8$, and ignores possible formation of oligomers of nor-C$_7$H$_8$ as a side-reaction. The overall iodine balance, however, indicated rather less oligomer formation than in the case of the chromium complex.

Discussion

The thermochemical results from the present study are collected together in Table 8, and include the derived heats of formation, $\Delta H^0_f(c)$, heats of sublimation,

TABLE 8

HEATS OF FORMATION, $\Delta H^0_f(c)$ AND $\Delta H^0_f(g)$

Compound	$\Delta H^0_f(c)$ (kJ mol^{-1})	ΔH^{298}_{sub} (kJ mol^{-1})	$\Delta H^0_f(g)$ (kJ mol^{-1})
Co$_4$(CO)$_{12}$	−(1845 ± 17) [20]	(96 ± 21)^a	−(1749 ± 25)
^{1}C$_6$H$_6$)Co$_4$(CO)$_9$	−(1313 ± 12)	(117 ± 21)^a	−(1196 ± 25)
(C$_6$H$_3$Me$_3$)Co$_4$(CO)$_9$	−(1444 ± 12)	(134 ± 21)^a	−(1310 ± 25)
(C$_6$Me$_6$)Co$_4$(CO)$_9$	−(1555 ± 17)	(148 ± 25)^a	−(1407 ± 25)
(C$_6$H$_3$Me$_3$)Cr(CO)$_3$	−(571 ± 8) [2]	(108 ± 4) [2]	−(463 ± 10)
(C$_6$H$_3$Me$_3$)Mo(CO)$_3$	−(533 ± 12)	(109 ± 6)^a	−(424 ± 15)
(C$_6$H$_3$Me$_3$)W(CO)$_3$	−(477 ± 12)	(111 ± 6)^a	−(366 ± 15)
(C$_6$Me$_6$)Cr(CO)$_3$	−(671 ± 12)	(123 ± 4) [2]	−(548 ± 12)
(C$_6$Me$_6$)Mo(CO)$_3$	−(631 ± 8)	(123 ± 4)^a	−(508 ± 10)
(cyclo-C$_7$H$_8$)Cr(CO)$_3$	−(310 ± 12)	(88 ± 4)	−(222 ± 12)
(cyclo-C$_7$H$_8$)Mo(CO)$_3$	−(297 ± 8)	(88 ± 4)	−(209 ± 10)
(cyclo-C$_7$H$_8$)W(CO)$_3$	−(235.5 ± 8)	(92 ± 4)	−(143 ± 10)
(nor-C$_7$H$_8$)Cr(CO)$_4$	−(400 ± 12)	(89 ± 4)	−(311 ± 12)
(nor-C$_7$H$_8$)Mo(CO)$_4$	−(428 ± 10)	(92 ± 4)	−(336 ± 12)

^{a} Estimated value.

TABLE 9

BOND ENTHALPY CONTRIBUTIONS, $D(L-M)$

Compound	ΔH_{disr} (kJ mol^{-1})	$D(M-CO)$ (kJ mol^{-1})	$D(L-M)$ (kJ mol^{-1})
Cr(CO)$_6$	642	107	
Mo(CO)$_6$	911	152	
W(CO)$_6$	1072	179	
Co$_4$(CO)$_{12}$	2121 [20]	136 [20]	
Co$_4$(CO)$_9$	(1713)		
(C$_6$H$_6$)Co$_4$(CO)$_9$	1984		270
(C$_6$H$_3$Me$_3$)Co$_4$(CO)$_9$	1998	.	284.5
(C$_6$Me$_6$)Co$_4$(CO)$_9$	2023		310
(C$_6$H$_3$Me$_3$)Cr(CO)$_3$	512		191
(C$_6$H$_3$Me$_3$)Mo(CO)$_3$	735		279.5
(C$_6$H$_3$Me$_3$)W(CO)$_3$	870		334
(C$_6$Me$_6$)Cr(CO)$_3$	526		205
(C$_6$Me$_6$)Mo(CO)$_3$	747		292
(cyclo-C$_7$H$_8$)Cr(CO)$_3$	471		150
(cyclo-C$_7$H$_8$)Mo(CO)$_3$	720		264
(cyclo-C$_7$H$_8$)W(CO)$_3$	847		311
(nor-C$_7$H$_8$)Cr(CO)$_4$	508		(80)
(nor-C$_7$H$_8$)Mo(CO)$_4$	795		187

ΔH_{sub}^{298}, and heats of formation of the complexes in the gaseous state at 25°C, $\Delta H_f^0(g)$.

Table 9 lists the derived heats of disruption (ΔH_{disr}) of the gaseous complexes, i.e. ΔH for: [LM(CO)$_3$][g] → L(g) + M(g) + 3CO(g) (M = Cr, Mo, W), and [LCo$_4$-(CO)$_9$][g] → L(g) + 4Co(g) + 9CO(g). Values are also listed for the bond-enthalpy contributions, $D(L-M)$, of the various ligand—metal bonds. These were evaluated from ΔH_{disr} assuming that the bond-enthalpy contributions, $D(M-CO)$, remain unchanged from those in the parent metal carbonyls, M(CO)$_6$ (M = Cr, Mo, W), and [Co$_4$(CO)$_{12}$].

Table 9 shows increasing values of $D(L-M)$ as M changes from Cr → Mo → W for all ligands studied. It was previously noted [2,3] that $D(L-Cr)$ for arene ligands increases as the arene changes from L = benzene → mesitylene → hexamethylbenzene, and this same trend is seen from Table 9 for $D(L-Mo)$ and $D(L-Co)$. Although high bond enthalpies are frequently associated with enhanced thermal stability, this is not the case for the arene Group VI metal carbonyls, those of chromium being in general the most stable to heat. The present studies have shown that the mesitylene and hexamethylbenzene complexes of Mo and W carbonyls, (in contrast to those of Cr) decompose at slightly elevated temperatures, (possibly even before metling) and that Mo(CO)$_6$ and W(CO)$_6$ are formed among the initial products of decomposition.

Thermal decomposition in the condensed state may involve a gradual elimination of CO, assisted by a cooperative mechanism through the simultaneous formation of M—M and M—CO—M bridge bonds, i.e.:
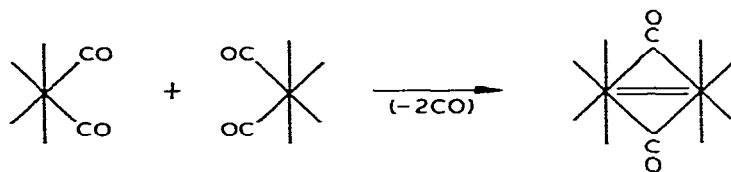
An example is provided from studies of the controlled decomposition of the cyclopentadienyl complexes:

$$C_5H_5M(CO)_3\text{---}M(CO)_3C_5H_5 \xrightarrow[(-2CO)]{} C_5H_5(CO)_2M{\equiv}M(CO)_2C_5H_5$$
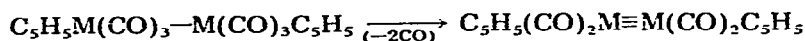
for M = Cr [21] and M = Mo [22], where the evidence supports such a pairwise bridging mechanism. Consistent with this are the flash photolysis studies of Gurvich and co-workers [23,24] on the decomposition of $Cr(CO)_6$, $Mo(CO)_6$ and of mixtures of the two. Photolysis led to the immediate appearance (and subsequent decay) of spectral bands from diatomic Cr_2 (from $Cr(CO)_6$), Mo_2 (from $Mo(CO)_6$) and CrMo (from a mixture of $Cr(CO)_6$ and $Mo(CO)_6$), followed by the appearance of atomic spectral lines. Mention should also be made of the identification recently of the Mo_2 species in a low temperature matrix by Klotzbücher and Ozin [25], and the formulation of sextuple bonding between the metal atoms in this molecule [26]. The suggestion that CO elimination may occur via the formation of bridging carbonyl groups is implicit in earlier papers of Eady, Johnson and Lewis [27], and of Cotton and Troup [28].

Gradual release of CO from $LM(CO)_3$ in the condensed state could account for the presence of $M(CO)_6$ (by replacement of ligand L) among the initial products of thermal decomposition. Table 10 presents thermal data to support this view. Calculated values for the enthalpies of partial decomposition (at 25°C), according to the overall reaction 9 are listed for complexes L = arene, M = Cr,

$$LM(CO)_3, (c) \rightarrow L(c \text{ or liq.}) + 1/2M(CO)_6, (c) + 1/2M(c) \tag{9}$$
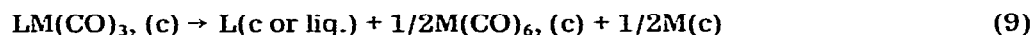
Mo, W.

Of the compounds listed, two are stable enough at elevated temperatures (>150°C) to sublime without decomposition, and for both of these ΔH_9 is positive. The remainder have ΔH_9 negative, and decompose in the condensed state at temperatures well below 200°C. Data are not available from which to evaluate the entropy changes, ΔS_9, associated with values of ΔH_9, but on general considerations it is improbable that these should be large enough to offset the dominating effect of large negative ΔH_9 (as in the case of the arenetungsten carbonyls) on the sign of ΔG_9. The implication from Table 10 is that the molybdenum and tungsten complexes are thermodynamically unstable with respect to the products of eq. 9, whereas the reverse may apply to the hexamethylbenzene and mesitylenechromium tricarbonyls.

TABLE 10

PARTIAL DECOMPOSITION OF LM(CO)₃

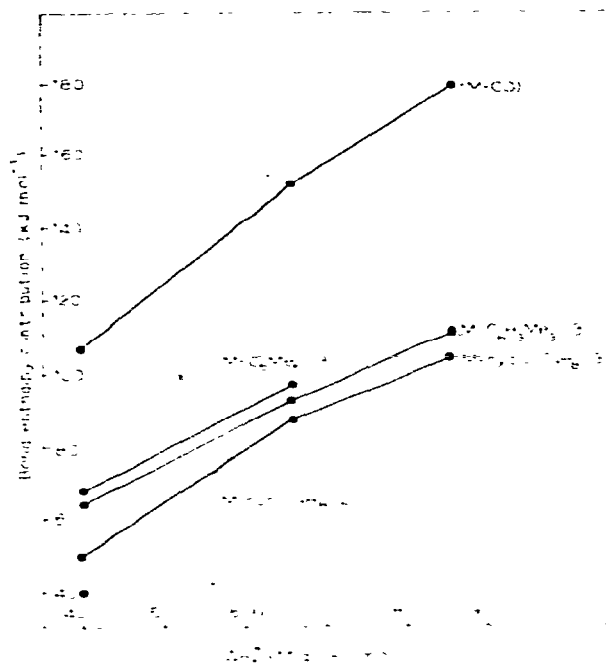| Compound	ΔH_9 (kJ mol⁻¹)
(Hexamethylbenzene)Cr(CO)₃	+19.7
(Hexamethylbenzene)Mo(CO)₃	−25.0
(Mesitylene)Cr(CO)₃	+17.6
(Mesitylene)Mo(CO)₃	−25.0
(Mesitylene)W(CO)₃	−66.5
(Cycloheptatriene)Cr(CO)₃	−35.1
(Cycloheptatriene)Mo(CO)₃	−52.7
(Cycloheptatriene)W(CO)₃	−99.6

Fig. 1.

The main results of the present investigation are presented graphically in Fig. 1 and 2. In Fig. 1, the bond enthalpy contributions $\bar{D}(\text{M—CO})$ are plotted against $\Delta H_f^0(\text{M, g})$ (M = Cr, Mo, W), with similar plots of $1/3\bar{D}(\text{M—L})$ against $\Delta H_f^0(\text{M, g})$ for the aromatic ligands (L = mesitylene and hexamethylbenzene)
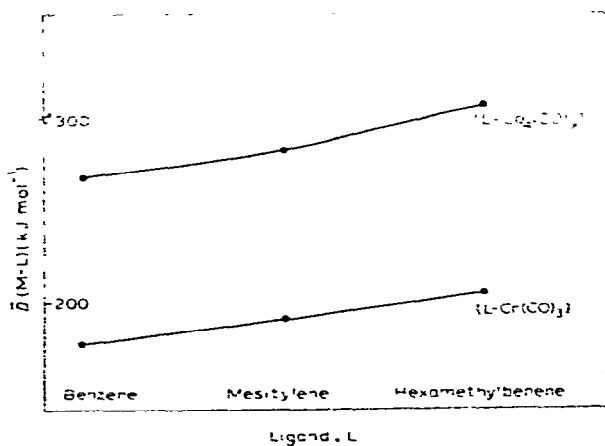

Fig. 2.

and for L = cycloheptatriene. The dotted line sketches the plot of $1/2\bar{D}(M—L)$ against $\Delta H_f^0(M, g)$, for L = norbornadiene (M = Cr, Mo).

We draw attention to the following trends:

(a) The bond enthalpy contributions, $\bar{D}(M—L)$ and $\bar{D}(M—CO)$, appear to be more sensitive to change of M from Cr to Mo, than for change from Mo to W. This may reflect the increasingly diffuse character of the metal d-orbitals with increasing atomic number, in that the principal contribution to the bonding involves $Mnd \rightarrow L\pi^*$ charge transfer.

(b) The enthalpy contribution of the bond between M and CO (the best π-acceptor ligand) seems rather more sensitive to change in M than is the comparative bond enthalpy contribution from bonding of M with aromatic ligands (which are better donors but worse acceptors than CO).

(c) There is an indication that the enthalpy contribution of the bond between an aromatic ligand and M is less sensitive to changes in M than for a bond between M and a non-conjugated cyclic polyolefin.

(d) We would estimate that the enthalpy contributions of olefin—Cr and olefin—Mo should lie in the range 45—55 kJ mol^{-1} (for Cr) and 86—95 kJ mol^{-1} (for Mo). These values are relavant in relation to current investigations on the catalytic metathesis of olefins, i.e.:
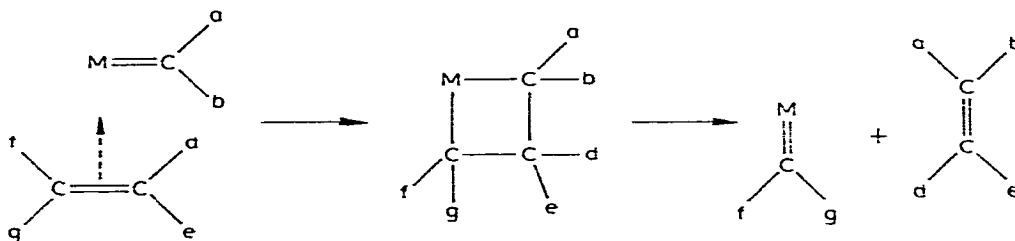

Figure 2 shows the similarity of the increases in $\bar{D}(M—L)$ for M = Cr and $[Co_4(CO)_9]$, as L changes from benzene $\rightarrow$ mesitylene $\rightarrow$ hexamethylbenzene.

Acknowledgements

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