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Thermochemistry of η^3-Allyltricarbonyliodoiron, Tricarbonyl (η^4-cyclooctatetraene)iron and Tetracarbonyldiiodoiron. The Enthalpy Contributions of Allyl-iron and Cyclooctatetraene-iron Bonds †

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Summary

Microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and iodination have led to values for the standard enthalpies of formation of the following crystalline compounds (values given in kJ mol^{-1}) at 298K : [(η^3-C_3H_5) Fe(CO)$_3$I] = -(428±10); [(η^4-C_8H_8)Fe(CO)$_3$] = -(237±12); [Fe(CO)$_4$I$_2$] =-(722±8). Separate measurements by the vacuum-sublimation microcalorimetric technique gave the following values for the enthalpy of sublimation at 298K (kJ mol^{-1}): [(η^3-C_3H_5)Fe(CO)$_3$I] = (84.5±4); [(η^4-C_8H_8)Fe(CO)$_3$] = (87±4); [Fe(CO)$_4$I$_2$] = (86.0±4). From these and other data, the bond enthalpy contributions of the various metal-ligand bonds in the gaseous metal complexes were evaluated as follows: [(η^3-C_3H_5)-Fe] 176; [(η^4-C_8H_8)-Fe] 180; Fe-I 177 kJ mol^{-1}.

The question of the transferability of the enthalpy contributions of iron-ligand bonds between organoiron complexes is discussed with the aid of structural and thermochemical data. It is concluded that the transfer of bond enthalpy contributions is valid within the scheme which relates iron-carbon bond lengths to iron-carbon bond enthalpies.

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† No reprints available.

Introduction

An earlier study [1] reported thermal decomposition and related studies on a number of olefin and diene complexes of iron carbonyls, from which values were obtained for the bond strengths (bond enthalpy contributions) of iron-olefin bonds in these complexes. The present work extends this type of investigation to include the compound $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$ and $[(\eta^4\text{-}C_8H_8)Fe(CO)_3$

Experimental

Calorimeter

The thermal measurements were made using a Calvet twin-cell microcalorimeter (Setaram, Lyon), adapted to the drop calorimetric technique [2]. Heats of sublimation were measured by using the microcalorimetric vacuum sublimation method [3].

Compounds

Samples of (η^3-allyl)tricarbonyliodoiron and of tricarbonyl(η^4-cyclooctatetraene)iron were prepared as described by King [4,5]. Tetracarbonyldiiodoiron was prepared according to Hieber and Bader [6]. The purity of each compound was established by microanalysis and by spectroscopic measurements (IR, NMR, mass) which were in agreement with published values.

Auxiliary data

All heat quantities are given in joules (J) or in kilojoules (kJ). The following auxiliary heat of formation data (kJ mol^{-1}) were used in evaluating the experimental results: ΔH_f^o (CO,g) = −(110.524±0.17) [7]; $\Delta H_f^o(I_2,g)$ = (62.44±0.04) [8]; $\Delta H_f^o(FeI_2,c)$ = −(116.3±8); ΔH_f^o(Fe,g) = (416.3±4) [7]; ΔH_f^o(I,g) = (106.8±0.04) [8]; $\Delta H_f^o(Fe(CO)_5,g)$ = −(723.8±8) [9]; ΔH_f^o(cyclooctatetraene, g) = (297.7±1.4) [10]; $\Delta H_f^o(C_3H_5I,g)$ = (95.4±4) [10]; ΔH_f^o(hexa-1,5-diene, g) = (84.1±1.2) [10]; ΔH_f^o(allyl,g) = (169.9±4) [11]; $\Delta H_f^o(C_5H_{10}I_2,g)$ ~98 (estimated, assuming that the enthalpy of addition of I_2(g) to hexa-1,5-diene (g) is the same as for the addition of I_2(g) to but-1-ene, for which ΔH(iodination) = −50.2 kJ mol^{-1} [10]). The value of $\Delta H_f^o(FeI_n(n<2.0),c)$ was assumed equal to $n[\Delta H_f^o(FeI_2,c)]/2$.

To reduce measured ΔH^T values to ΔH^{298}, (H^T-H^{298}) values for Fe(c) were taken from Hultgren, Orr, Andersen and Kelly [12], for FeI_2(c) from the JANAF tables [8], and for the hydrocarbons from Stull, Westrum and Sinke [13].

Results

(1) η^3-Allyltricarbonyliodoiron

The vacuum sublimation method was applied over the temperature range 348-357K, the samples subliming readily without decomposition. Thermal decomposition accompanied sublimation at temperatures in the range 385-390K, and thermal decomposition appeared to be complete at temperatures >415K. The solid residue from thermal decomposition analysed as FeI, and we presume that decomposition follows the equation:

$$[(\eta^3C_3H_5)Fe(CO)_3I]\ (c) \rightarrow FeI(c) + 3CO(g) + \tfrac{1}{2}\ \text{hexa-1,5-diene}\ (g) \quad .....(1)$$

Table 1 summarizes results from vacuum sublimation (VS) and thermal decomposition (TD) measurements.

TABLE 1 Sublimation and Thermal Decomposition of $[(\eta^3\text{allyl})Fe(CO)_3I]$

$\frac{T}{K}$	Method	$(C_3H_5)Fe(CO)_3I$ mg.	ΔH^*_{obs} kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
348	VS	2.795	98.1	87.8
349	VS	3.125	91.2	80.0
357	VS	2.845	97.9	85.7
418	TD	3.135	102.0	75.7
421	TD	3.140	98.7	71.8

The mean value from VS measurements gives $\Delta H^{298}_{sub} = (84.5\pm4)$ kJ mol^{-1}, and that from TD measurements, $\Delta H^{298}_{dec} = (73.8\pm4)$ kJ mol^{-1} corresponds to ΔH^0_f $[(\eta^3-C_3H_5)Fe(CO)_3I]$ (c) = $-(421.5\pm7)$ kJ mol^{-1}

The iodination of $[(\eta^3-C_3H_5)Fe(CO)_3I]$ was studied at temperatures in the range 455-462K. Excess iodine remaining in the reaction vessel after the end of the experiment was sublimed from the vessel by evacuation, trapped, and the amount determined by titration. The involatile solid residues (FeI_n) were analysed for iodine content separately. The iodine balance provided only a rough measure of iodine consumed in the reaction by the allyl ligand, since the small manipulative losses were estimated. The overall iodination reaction was assumed to follow the equation:-

$$(C_3H_5)Fe(CO)_3I\ (c,\ 298) + \tfrac{1}{2}(\underline{n} + \underline{m} - 1)\ I_2\ (g,T) \rightarrow FeI_{\underline{n}}\ (c,T) + 3CO(g,T) + \underline{m}C_3H_5I\ (g,T) + \tfrac{1}{2}(1-\underline{m})\ C_6H_{10}\ (g,T) \qquad (2)$$

values of $\underline{n}$ and $\underline{m}$ being obtained from iodine analysis and the iodine balance. (The term $\underline{m}\ C_3H_5I$ includes both allyl iodide and 5,6-di-iodo hex-1-ene which may be formed by addition of iodine to hexa-1,5-diene).

Results from the iodination experiments are summarized in Table 2, where ΔH^*_{obs} is the measured enthalpy of reaction (2), and H^{298}_{obs} refers to the same reaction carried out isothermally at 298K. The ΔH^o_f values for $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$ listed in column (a) are derived assuming that $\underline{m}(C_3H_5I,g)$ was exclusively allyl iodide; those in column (b) were obtained on the assumption that the C_3H_5I product was exclusively the di-iodohexene, $C_6H_{10}I_2$.

TABLE 2 Iodination of $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$

$\frac{T}{K}$	$\frac{(C_3H_5Fe(CO)_3I)}{mg.}$	$\frac{I_2}{mg.}$	$\underline{n}$	$\underline{m}$	$\frac{\Delta H^*_{obs}}{kJ\ mol^{-1}}$	$\frac{\Delta H^{298}_{obs}}{kJ\ mol^{-1}}$	$\frac{\Delta H^o_f}{kJ\ mol^{-1}}$ (a)	(b)
455	3.230	10.125	2.0	0.6	32.0	-4.2	-419.6	-448.3
456	3.030	11.470	1.9	0.4	36.6	0.4	-419.3	-438.1
459	3.000	7.295	2.0	0.5	43.8	6.4	-432.4	-456.0
462	3.075	7.515	2.0	0.5	30.9	-7.4	-418.6	-442.2
462	3.085	6.965	2.0	0.3	23.5	-14.6	-415.8	-430.0
					Mean values :		-421.1	-442.9

The mean values (column (a)) is in close agreement with that obtained from thermal decomposition studies. The mean value (column (b)) represents a lower limit to ΔH^o_f, and is based on an extreme assumption. An intermediate value, weighted towards the column (a) mean, is preferred by us, ΔH_f^o = -(428±10) kJ mol^{-1}.

(2) Tricarbonyl(η^4-cyclooctatetraene)iron

Vacuum sublimation measurements at 386 K gave ΔH_{obs} = (109±3) kJ mol^{-1}, corresponding to ΔH_{sub}^{298} -(87±4) kJ mol^{-1}. Thermal decomposition studies were made at temperatures in the range 460-513K; decomposition led to the deposition of a bright metallic mirror on the walls of the reaction vessel, and appeared to be complete at temperatures >480 K. Typical results at the higher range of temperatures are listed in Table 3.

TABLE 3. Thermal Decomposition of $[(\eta^4\text{-}C_8H_8)Fe(CO)_3]$

T / K	$(C_8H_8)Fe(CO)_3$ / mg.	ΔH^*_{dec} / kJ mol^{-1}	ΔH_{dec}^{298} / kJ mol^{-1}
488	1.600	243	192
488	1.425	253	201
513	1.895	274	215

The mean ΔH_{dec}^{298} = (203±11) kJ mol^{-1} corresponds to $\Delta H_f^o[(\eta^4\text{-}C_8H_8)Fe(CO)_3](c)$ = -(237±12) kJ mol^{-1}.

(3) Tetracarbonyldiiodoiron

Thermal decomposition measurements were made at temperatures in the range 455-457 K by dropping samples into the argon-filled hot-zone, and also into the hot-zone containing iodine vapour. Decomposition appeared to be complete at these temperatures, and the solid residue analysed as FeI_2. Results are summarised in Table 4, where ΔH^*_{dec} refers to the process

$$Fe(CO)_4I_2(c,298) \rightarrow FeI_2(c,T) + 4CO(g,T) \qquad ....(3)$$

The mean ΔH_{dec}^{298} (163.3±1 kJ mol^{-1}), combined with the given ΔH_f^o values for CO(g) and FeI_2(c), leads to $\Delta H_f^o(Fe(CO)_4I_2,c)$ = -(721.7±8) kJ mol^{-1}, in good agreement with that based on solution calorimetric measurements (ΔH_f^o = -(723±8)

TABLE 4. Thermal decomposition of $[Fe(CO)_4I_2]$

T K	$Fe(CO)_4I_2$ mg.	ΔH^*_{dec} kJ mol^{-1}	ΔH^{298}_{dec} kJ mol^{-1}
455	3.560	196.0	164.3
457	3.030	195.3	163.2
457	3.250	194.4	162.3

kJ mol^{-1}) by Hieber and co-workers [14,15] as listed in the compilation of thermochemical data by Glyshko and Medvedev [9].

Attempts to measure ΔH_{sub} of $[Fe(CO)_4I_2]$ by the vacuum-sublimation microcalorimetric technique were not successful at temperatures $\geqslant$380 K, there being substantial thermal decomposition within the hot-zone. At lower temperatures in the range 355-358 K, the extent of thermal decomposition accompanying sublimation was much reduced, amounting to ca. 5-6% of the sample introduced. Results are summarized in Table 5, the mean ΔH^{298}_{sub} (corrected for the thermal decomposition) being (86.0±4) kJ mol^{-1}.

TABLE 5. Sublimation of $[Fe(CO)_4I_2]$

T K	$Fe(CO)_4I_2$ mg.	ΔH^*_{obs} kJ mol^{-1}	ΔH^{298} kJ mol^{-1}	% decomp.	ΔH^{298}_{sub}(corr) kJ mol^{-1}
358	2.900	106.5	94.4	6.0	89.8
356	2.985	101.5	89.8	6.0	85.2
355	3.085	98.7	87.2	5.4	83.0

Discussion

Table 6 lists the values $\Delta H^o_f(c)$ and $\Delta H^o_f(g)$ here obtained, and the values $\Delta H_{disrupt}$ at 298 K, corresponding to the processes:

$$[Fe(\eta^3\text{-}C_3H_5)(CO)_3](g) \rightarrow Fe(g) + C_3H_5(g) + 3CO(g) + I(g) \qquad \text{.... (4a)}$$

$$[Fe(\eta^4\text{-}C_8H_8)(CO)_3](g) \rightarrow Fe(g) + C_8H_8(g) + 3CO(g) \qquad \text{.... (4b)}$$

and

$$[Fe(CO)_4I_2](g) \rightarrow Fe(g) + 4CO(g) + 2I(g) \qquad \text{.... (4c)}$$

TABLE 6. Enthalpies of disruption, $\Delta H_{disrupt}$

Compound	$\Delta H^o_f(c)$ / kJ mol^{-1}	$\Delta H^o_f(g)$ / kJ mol^{-1}	$\Delta H_{disrupt}$ / kJ mol^{-1}
$[Fe(\eta^3\text{-}C_3H_5)(CO)_3I]$	-(428±10)	-(344±11)	(705±11)
$[Fe(\eta^4\text{-}C_8H_8)(CO)_3]$	-(237±12)	-(150±13)	(532±14)
$[Fe(CO)_4I_2]$	-(722±8)	-(636±9)	(824±10)

Accepting that the bond enthalpy contribution to $\Delta H_{disrupt}$ from Fe-CO remains the same as in $Fe(CO)_5$, (where $\bar{D}$(Fe-CO) = (117.5±2) kJ mol^{-1} [1]), the contribution from (Fe-cyclooctatetraene) amounts to (180±15) kJ mol^{-1}. This compares closely with those measured previously [1] in other olefin-iron complexes.

The bond enthalpy contribution, $\bar{D}$(allyl-Fe) in $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$ may be evaluated if we assume that the contribution $\bar{D}$(Fe-I) is unchanged from its value in $[Fe(CO)_4I_2]$. On this basis,

$$\Delta H_{disrupt}[Fe(CO)_4I_2] = 4\bar{D}(Fe\text{-}CO) + 2\bar{D}(Fe\text{-}I) = (824\pm10)\ kJ\ mol^{-1}$$

and

$$\Delta H_{disrupt}[(\eta^3\text{-}C_3H_5)Fe(CO)_3I] = 3\bar{D}(Fe\text{-}CO) + \bar{D}(Fe\text{-}I) + \bar{D}(C_3H_5\text{-}Fe)$$
$$= (705\pm11)\ kJ\ mol^{-1}$$

giving

$$\bar{D}(C_3H_5\text{-}Fe) + \bar{D}(Fe\text{-}CO) = (293\pm11)\ kJ\ mol^{-1}$$

and, (with $\bar{D}$(Fe-CO) = (117.5±2) kJ mol^{-1}), $\bar{D}$(allyl-Fe) ~(176±11) kJ mol^{-1}. The corresponding bond enthalpy contribution, $\bar{D}$(Fe-I) is (177±7) kJ mol^{-1}.

Alternatively, one might start from the assumption that $\bar{D}$(Fe-I) in $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$ and in $[Fe(CO)_4I_2]$ is the same as in FeI_2(g) (284 kJ mol^{-1})

[9], in which case $\bar{D}$(Fe-CO) is calculated to be 64 kJ mol^{-1} and $\bar{D}$(Fe-allyl) = 229 kJ mol^{-1}. Such large differences in the calculated enthalpy contributions of the ligands in [(η^3-C_3H_5)Fe(CO)$_3$I] (which arise from the different assumptions made) suggest that the role of the formal oxidation state of the iron atom needs to be considered more seriously. Accordingly, we have reviewed all the structural information available for organo-iron compounds to date [16] in order to establish certain general results concerning iron-carbon bond lengths.

The atomic radius of Fe(0) is estimated [17] to be 137 pm from the Fe-N bond length (204 pm) in [Fe(CO)$_4$pyr]. This may be compared with the radius (126 pm) derived from the interatomic distance in metallic iron [18] and the Pauling radius (117 pm) of iron [19]. The corresponding radius of Fe(II) can be estimated from the many σ-bonded alkyl compounds [16] of iron. Accepting the usual carbon radii [77 (sp^3), 68(sp^2), 60 pm (sp)], the average value of the radius, r[Fe(II)] = 132 pm. This value should be compared with the radius of the low spin iron(II) ion, which is 61 pm [20]. We note that the length of a purely ionic ionic iron(II)-iodide bond is estimated as 282 pm (r(I$^-$) = 221 pm [19]). The average length of the iron(II)-iodine bonds which have been determined is 265 pm [16].

Substitution of carbon monoxide in Fe(CO)$_5$ by dienes causes r(Fe-CO) to decrease from an average value of 182 pm [21] to a value in the range 176-179 pm. The average Fe-CO bond length does not change significantly between [(η^4-diene)Fe(CO)$_3$] and [(η^4-diene)$_2$Fe(CO)] complexes. Formal oxidation to Fe(II) (as, for example, in [(η^5-C_5H_5)Fe(CO)$_2$X]) results in a further decrease in r(Fe-CO) to 172-176 pm, which can be accounted for by the smaller radius of Fe(II) compared with Fe(0).

The iron-carbon distances in π-complexes of monoolefin, enyl, diene and dienyl ligands fall within very limited ranges in each case [16]. The average val of these distances are shown in Table 7.
Using the appropriate radius for the iron atom (Fe(0) in monoolefin and diene compounds, Fe(II) in enyl and dienyl compounds) the average value of the effective carbon radius in these Fe-C bonds is 77 pm. This indicates that for all types

TABLE 7. Average iron-carbon distance in π-bonded organo-iron compounds, $[(\pi\text{-L})_m\text{FeQ}_n]$ [16]

Ligand, L	Average distance (Fe-C) pm.	
Monoolefin		216
Enyl	206	215
Diene	206	214
Dienyl	209	

of organic π-bonded ligand (which contain sp^2-hybridised carbon atoms in the ligating site of the free molecule) the iron-carbon distance is effectively constant and that the carbon radius is that of an sp^3-hybridised atom, irrespective of whether the iron atom is formally iron(0) (d^8) or iron(II) (d^6).

On this evidence, the transfer of the Fe-CO bond enthalpy contribution between $Fe(CO)_5$ and $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$ appears to be justified. To transfer the Fe-I bond enthalpy contribution from $FeI_2(g)$ would seem unjustifiable, in view of the very large difference in radius of Fe(II) from that of low spin iron(II) ion. Iron(II) iodide has the CdI_2-type structure in which infinite 2-dimensional layers are held together by van der Waals forces [22]. Within each layer, each iron atom is surrounded by four iodine atoms. We assume that the van der Waals forces are reduced in the liquid state, so that taking $\Delta H_f^o(FeI_2,\ell) = -82.7$ kJ mol^{-1} [8], the average $\bar{D}$(Fe-I) in liquid FeI_2 is 178 kJ mol^{-1}, which is very close to the value obtained here (177 kJ mol^{-1}).

The only previous estimate of the enthalpy contribution of a metal (η^3-allyl) bond appears to be that of Ashcroft and Mortimer [23] from measurements of the heat of thermal decomposition of $[(\eta^3\text{-}C_3H_5)PdCl]_2$. The reported value, $\bar{D}$(Pd-allyl) ~237 kJ mol^{-1} is considered minimal in view of approximations made in evaluating the Pd-Cl bond enthalpy contribution in the dimer molecule. It is noteworthy that D(Pd-allyl) > D(Fe-allyl); where comparison can be made, iron usually forms stronger bonds (e.g., FeO (406±12) > PdO (280±30); FeAu (188)>PdAu (151 kJ mol^{-1})), but this is not always so (e.g. PdGe (259±17)>FeGe (205±30); PdSi (322±15)>FeSi (288±21 kJ mol^{-1}) [24].

The bond enthalpy contribution $\bar{D}$(Fe-allyl) is compared with the contributions of other organic ligand-iron bonds in Table 8, in respect of a parameter $\bar{D}/\underline{n}$. The value of $\underline{n}$ was obtained assuming that the iron atom in each complex has the noble gas electron configuration so that, in $Fe(CO)_5$ for example, each Fe-CO bond has a number of bonding electrons $\underline{n}$ = 18/5 = 3.6, with a formal bond order 1.8. Correspondingly in ferrocene, the cyclopentadienyl-iron bonding is associated with 18/2 = 9 bonding electrons. Once again, the formal bond order of each Fe-C bond is 1.8. The number of bonding electrons $\underline{n}$ associated with the allyl-iron bonding in $[(\eta^3\text{-}C_3H_5)Fe(CO)_3I]$ is obtained to comply with the derivation of $\bar{D}$(Fe-allyl) as follows:

$$D(\text{Fe-allyl}) = \Delta H_D[(\eta^3\text{-}C_3H_5)Fe(CO)_3I] - \tfrac{1}{2}\Delta H_D[Fe(CO)_4I_2] - \tfrac{1}{5}\Delta H_D[Fe(CO)_5]$$

leading to

$$\underline{n}(\text{Fe-allyl}) = 18-18/2-18/5 = 5.4$$

TABLE 8 $\bar{D}/n$ values for M-L bonds

Compound	Bond	$\bar{D}$(kJ mol^{-1})	$\underline{n}$	$\bar{D}/\underline{n}$(kJ mol^{-1})	Ref.
$Fe(CO)_5$	Fe - CO	117.5	3.6	32.6	[1]
$Fe(\eta^5\text{-}C_5H_5)_2$	Fe - C_5H_5	297	9	33.0	[25]
$Fe(\eta^4\text{-}C_6H_8)_2(CO)$	Fe - C_6H_8	192	7.2	26.7	[1]
$Fe(\eta^4\text{-}C_8H_8)(CO)_3$	Fe - C_8H_8	180	7.2	25.0	this work
$Fe(\eta^3\text{-}C_3H_5)(CO)_3I$	Fe - C_3H_5	176	5.4	32.6	this work
$Fe(\eta^2\text{-}C_2H_4)(CO)_4$	Fe - C_2H_4	97	3.6	26.9	[1]
$Mo(CO)_6$	Mo - CO	152	3.0	50.7	[26]
$Mo(\eta^6\text{-}C_6H_3Me_3)(CO)_3$	Mo - C_9H_{12}	280	9	31.1	[26]
$Mo(\eta^5\text{-}C_5H_5)_2H_2$	Mo - C_5H_5	354	7	50.6	[27]
$Mo(\eta^2;\eta^2\text{-}C_7H_8)(CO)_4$	Mo - C_7H_8	187	6	31.2	[26]

As Table 8 shows the values $\bar{D}/\underline{n}$ for the ligands CO, $\eta^5\text{-}C_5H_5$ and $\eta^3\text{-}C_3H_5$ are larger than for olefin or arene ligands, implying that the ligand bonding power is greater in the former. Whether this greater bonding power is due to better donor or acceptor capability of these ligands, cannot be decided from values of $\bar{D}/\underline{n}$ alone.

An alternative approach to the interpretation of the same data considers the ligands as $\underline{q}$ electron donors where $\underline{q}$ = 2 (monoolefin), 4(enyl,diene) and 6 (dienyl, arene) in the generally accepted sense [28]. Table 9 shows the enthalpy contributions of the various organic ligands in respect of a parameter $\bar{D}/\underline{q}$.

TABLE 9. $\bar{D}/\underline{q}$ values for M-L bonds

	L	$\underline{q}$	$\bar{D}$(kJ mol^{-1})	$\bar{D}/\underline{q}$
a) Iron				
dienyl	$C_5H_5^-$	6	297	49.5
diene	C_8H_8	4	180	45.0
	C_6H_8	4	192	48.0
enyl	$C_3H_5^-$	4	176	44.0
monoolefin	C_2H_4	2	97	48.5
	CO	2	117.5	58.8
b) Molybdenum				
arene	$C_6H_3Me_3$	6	280	45.0
dienyl	$C_5H_5^-$	6	354	59.0
diene	C_7H_8	4	187	46.8
	CO	2	152	76.0

In this scheme, the average enthalpy contribution per electron pair, $2\bar{D}/\underline{q}$ for organo-iron compounds is 94 kJ mol^{-1} and does not change very much from one organic ligand to another. The contribution per electron pair is once again larger for CO. The data for organo-molybdenum compounds (Table 9b) suggests an enthalpy contribution per electron pair for neutral arene and diene ligands with respect to molybdenum(0) which is similar to that for organo-iron compounds. The larger contribution from a dienyl ligand relates to a compound of molybdenum(IV), and the comparison may be unrealistic in this case.

Finally, we note an implication of our results in respect of the isomerisation of coordinated dienes. Studies of the isomerisation of [(η^4-cyclooctatriene)Fe(CO)$_3$] to [(η^4-cis-bicyclo[4.2.0]octa-2,4-diene)Fe(CO)$_3$] have indicated that a mechanism for the process which involves the sequence of dissociation - isomerisation - recombination is unlikely, because the free energy change (10 kJ mol^{-1}) estimated for the dissociation step is too low [29]. Assuming that a metal-ligand bond enthalpy contribution can be identified with a specific dissociation step, the result we obtain here, that $\bar{D}$(Fe-C_8H_8) = 180 kJ mol^{-1}, supports this view.

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