Thermochemical Studies on (Acac)M(Olefin)$_2$ (M = Rh(I), Ir(II))

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The enthalpies of reaction of the crystalline complexes (acac)M(olefin)$_2$ (M = Rh(I), Ir(I); olefin = ethylene, propylene, vinyl chloride, vinyl acetate, methyl acrylate and styrene) with CO gas, according to the reaction (acac)M(olefin)$_2$(s) + 2CO(g) → (acac)M(CO)$_2$(s) + 2 olefin(g) have been determined by differential scanning calorimetry. From these results the enthalpies for the reaction in the gasphase have been derived. The Ir–ethylene bond is estimated at about 37 kcal mol^{-1} which means that this bond is stronger than the Rh–ethylene bond (31 kcal mol^{-1}). The influence of the substituent, which is present in the olefin, on the M–olefin bond depends on whether M = Rh or M = Ir.

Introduction

Thermochemical data of transition metal-olefin compounds are scarcely known; in particular, the strength of the metal–olefin bond has not been studied in any detail. Hartley [1] has reviewed thermodynamic data for transition metal-olefin compounds most of which were determined in solution. However, very few thermodynamic data of such complexes have been determined in the solid or in the gas phase. Cu– and Ag–olefin complexes have been investigated by measuring dissociation pressures [2, 3] and Fe–olefin complexes were studied by measuring disruption reactions [4]. The Ir–olefin bond in [IrX-(CO)(PPh$_3$)$_2$(olefin)] has been investigated by differential scanning calorimetry (DSC) [5] while pyrolysis of π-C$_5$H$_5$Rh(C$_2$H$_4$)$_2$ in the gas phase afforded a maximum value for the Rh–(C$_2$H$_4$) bond [6].

In our laboratory several thermochemical studies have been carried out in order to obtain more information about the transition metal–ligand bond strength [7, 8]. In particular, we are interested in the metal–olefin bond strength and in the way in which this bond is influenced by the metal and by substituents on the olefin in complexes of the type (acac)M(CH$_2$=CHX)$_2$ (acac = acetylacetonate; M = Rh(I), Ir(I); CH$_2$=CHX = ethylene (ET), propylene (PR), vinyl chloride (VCl), vinyl acetate (VA), methyl acrylate (MA) and styrene (ST)).

Differences in the metal–olefin bond enthalpy contributions (E) can be determined from enthalpies of reaction (1):

$$(acac)M(olefin)_2s) + 2CO(g) \rightarrow$$
$$(acac)M(CO)_2(s) + 2 \text{ olefin}(g) \qquad (1)$$
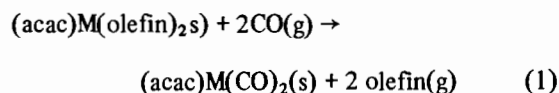
and the heats of sublimation of the respective metal complexes.

In this article we report the results of a study involving thermogravimetric (TG) and DSC measurements on the reaction of the solid compounds (acac)-M(CH$_2$=CHX)$_2$ with CO and on the decomposition of these complexes in N$_2$ atmosphere. The enthalpies of reaction (1) have been determined and the differences in E(metal–olefin) will be discussed.

Experimental

Preparation of the Complexes

(acac)Rh(ET)$_2$ and (acac)Ir(ET)$_2$ were prepared according to literature methods [9, 10]. The remaining complexes (acac)Rh(CH$_2$=CHX)$_2$ and (acac)Ir(CH$_2$=CHX)$_2$ were synthesized via a displacement reaction of ET in (acac)Rh(ET)$_2$ or (acac)Ir-(ET)$_2$ by an excess of olefin. A detailed description of the synthesis and characterization of these complexes has been presented in a previous paper [11].

Thermochemical Measurements

Thermogravimetry (TG) was carried out using a Mettler Thermoanalyser type 1, with NiCr/Ni thermocouples for simultaneous DTA. The heating rate was 4 deg min^{-1}; the gas flow was 5 l h^{-1}. The typical sample size was 10 mg. Sub-ambient temperature measurements were performed by a Mettler furnace provided with a cooling gas inlet.

Reaction enthalpies were measured with a Dupont 990 differential scanning calorimeter (DSC). The heating rate was 5 deg min^{-1}; the gas flow was 2 l h^{-1}. The typical sample size varied from 1–5 mg. In order to maintain a good contact with the purge gas, open sample pans were used. Sub-ambient temperatures were performed with a Dupont cooling accessory

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TABLE I. Thermogravimetry of the Complexes (acac)M(olefin)$_2$ in N$_2$ Atmosphere.

Complex	Melting Point[a,b] (°C)	Decomposition Temp.[b] (°C)	Percentage Residue	Calculated Original Percentage Metal
(acac)Rh(ET)$_2$	78	78	40	39.9
(acac)Rh(PR)$_2$	38	38	37	36.0
(acac)Rh(VCl)$_2$	43	60	44	31.5
(acac)Rh(VA)$_2$	100	100	37	27.5
(acac)Rh(MA)$_2$	82	82	34	27.5
(acac)Rh(ST)$_2$	74	74	42	25.1
(acac)Rh(CO)$_2$	–	86[c]	0	
(acac)Ir(ET)$_2$	110	110	51	55.3
(acac)Ir(PR)$_2$	31	31	71	51.2
(acac)Ir(VCl)$_2$	40	56	48	46.2
(acac)Ir(VA)$_2$	100	100	57	41.5
(acac)Ir(MA)$_2$	60	60	54	41.5
(acac)Ir(ST)$_2$	122	122	59	39
(acac)Ir(CO)$_2$	–	100[c]	0	

[a]Determined by the simultaneous DTA signal. [b]Except (acac)Rh(VCl)$_2$, (acac)Ir(VCl)$_2$, (acac)Rh(CO)$_2$ and (acac)Ir(CO)$_2$, all complexes melt with decomposition. [c]The compounds sublime, the temperature given is the temperature at which 1% of the compound has sublimed.

consisting of a metal block which contained liquid nitrogen. Each reaction enthalpy was determined with 10 to 15 samples and the apparatus was calibrated during each series by the enthalpy of fusion of freshly distilled Hg (ΔH_f(Hg) = 6.79 cal g^{-1}).

In order to prevent condensation of water on the DSC cell, the sample was always heated to above-ambient temperatures. In several cases the base line was obtained by heating the sample first in N$_2$ atmosphere, then over the same temperature traject in CO atmosphere. After the reaction the products were cooled again to obtain a base line in CO atmosphere.

All exchange reactions on the thermal balance and in the DSC apparatus were performed by cooling the sample first below the temperature at which reaction with CO occurs, then changing the purge gas from N$_2$ to CO, after which the sample was heated at a constant rate. Specific heat data were obtained with the DSC apparatus, which was calibrated with sapphire.

The uncertainties given are standard deviations of the mean.

Spectroscopic Measurements

^{1}H-NMR measurements were performed on a Varian T-60 apparatus; infrared spectra were obtained on a Beckman 4250 spectrophotometer.

Results

TG in N$_2$ Atmosphere

In Table I results of thermogravimetry under N$_2$ atmosphere are presented together with the melting points which were determined by the simultaneously recorded DTA signal.

The compounds melt with decomposition, except for (acac)Rh(VCl)$_2$, (acac)Ir(VCl)$_2$, (acac)Rh(CO)$_2$ and (acac)Ir(CO)$_2$. The latter two compounds sublime without decomposition. The decomposition reactions are exothermal and start with slow rates for (acac)Rh(PR)$_2$, (acac)Rh(MA)$_2$ and all Ir complexes. (acac)Rh(ET)$_2$ decomposed quantitatively into Rh metal, whereas the other complexes afforded residues which consisted of charred products after being heated up to 500 °C. As the residue percentage from (acac)Ir(ET)$_2$ is lower than the Ir percentage in the complex the compound must have sublimed partly. The Ir compounds gave a higher percentage of charred product than the corresponding Rh compounds.

TG in CO Atmosphere

All complexes react with CO according to exchange reaction (1) at sub-ambient temperatures, except for (acac)Ir(ET)$_2$ which reacts at 22 °C. Thus, in order to follow these reactions by TG, the samples were cooled in N$_2$ atmosphere below their reaction temperature with CO before heating them in CO atmosphere.

In Table II the TG results in CO atmosphere are given. The observed weight losses as well as the spectroscopic results (IR: ν(CO); ^{1}H-NMR: olefinic protons) show that, except for (acac)Rh(ST)$_2$, a quantitative reaction took place.

According to the shape of the DTA and TG curves the complexes can be divided into three groups:

TABLE II. Thermogravimetry of the Complexes (acac)M-(olefin)$_2$ in CO Atmosphere.

Complex	Reaction Temperature (°C)		Weight Loss (%)	
	T_i^a	T_f^a	Calc.	Found
(acac)Rh(ET)$_2$	-90	-50	0.03	0.8
(acac)Rh(PR)$_2$			9.83	9.7[b]
(acac)Rh(VCl)$_2$	-50	-32	21.09	21.2
(acac)Rh(VA)$_2$	-18	$+38$	31.04	30.8
(acac)Rh(MA)$_2$	-88	$+30$	31.04	30.4
(acac)Rh(ST)$_2$	-54	$+100$	37.11	34.0
(acac)Ir(ET)$_2$	$+22$	$+193^c$	99.7[c]	99.8[c]
(acac)Ir(PR)$_2$	-105	-64	7.49	8.0
(acac)Ir(VCl)$_2$			16.57	16.1[b]
(acac)Ir(VA)$_2$	-88	31	25.06	23.2
(acac)Ir(MA)$_2$	-72	30	25.06	24.0
(acac)Ir(ST)$_2$	-68	92	30.48	29.8

[a]T_i = initial temperature, T_f = final temperature.
[b]Determined by weighting of DSC samples. [c]After evaporation of the product, see text.

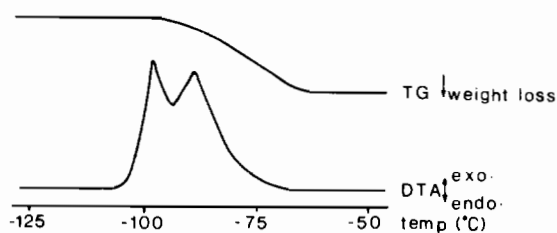1. (acac)Rh(ET)$_2$, (acac)Rh(PR)$_2$ and (acac)Ir(PR)$_2$.

Figure 1. Thermogravimetric (TG) curve and DTA curve of (acac)Ir(PR)$_2$ in CO atmosphere.

In Figure 1 the DTA curve shows an exothermal peak while the expected weight loss is shown by the TG curve (the behaviour of (acac)Rh(PR)$_2$ has been deduced from the DSC results by weighting each sample before and after the exchange reaction).
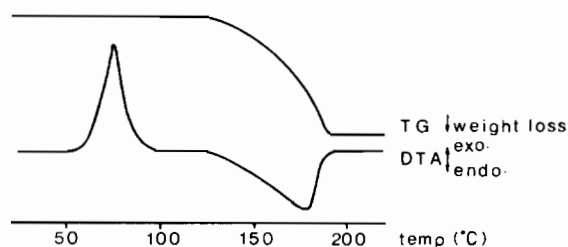
2. (acac)Ir(ET)$_2$.

Figure 2. Thermogravimetric (TG) curve and DTA curve of (acac)Ir(ET)$_2$ in CO atmosphere.

Figure 2 indicates that the exchange reaction, which is apparent from an exothermal DTA peak, is immediately followed by evaporation of the product, (acac)Ir(CO)$_2$. From Table I it can be concluded that (acac)Ir(ET)$_2$ does not evaporate, because in N$_2$ atmosphere significant weight loss did not occur before the melting point was reached.

3. (acac)Rh(VCl)$_2$, (acac)Rh(VA)$_2$, (acac)Rh(MA)$_2$, (acac)Rh(ST)$_2$ (acac)Ir(VCl)$_2$, (acac)Ir(VA)$_2$, (acac)-Ir(MA)$_2$ and (acac)Ir(ST)$_2$.
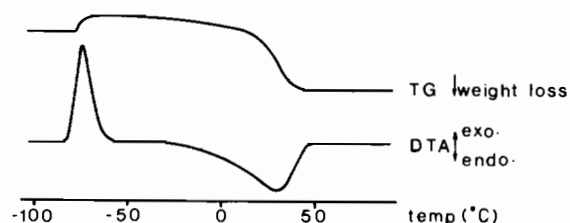

Figure 3. Thermogravimetric (TG) curve and DTA curve of (acac)Rh(MA)$_2$ in CO atmosphere.

Figure 3 shows that directly at the beginning of the reaction, which is shown by a sharp exothermal peak in the DTA curve, a rapid weight increase occurs, after which a broad endothermal peak appears in the DTA curve, accompanied by a weight decrease. The weight increase is very small for (acac)Rh(VCl)$_2$ and (acac)Ir(VCl)$_2$, but corresponds to about 2 mol CO per mol (acac)M for the other complexes. The endothermal DTA peak is absent in the curve of (acac)Rh(VCl)$_2$, but corresponds to about the enthalpy of evaporation of 2 mol of olefin in the case of (acac)Ir(VA)$_2$ and (acac)Rh(MA)$_2$. These results indicate that the initial reaction involves a rapid exchange reaction with CO, which is followed by a slow evaporation of the free olefin. The slow rate of evaporation is caused by the low temperatures at which the reaction took place. For the other complexes of group 3 both weight increase and endothermal peak are smaller because evaporation of the olefin starts already during the exchange reaction with CO.

DSC in CO Atmosphere

In Table III the reaction enthalpies and reaction temperatures of the exchange reaction (1) are reported.

On the DSC apparatus all complexes behave in the same way as on the thermobalance, except for (acac)Rh(VA)$_2$ which behaves like (acac)Ir(ET)$_2$. However, the reaction temperatures on the DSC apparatus are higher, which probably is caused by different sample size, heating rate and different gas flow conditions.

On changing heating rate, sample size and particle size the exothermal and endothermal peaks of the group 3 thermograms shift more or less with respect

TABLE III. DSC Data of the Complexes $(acac)M(olefin)_2$ in CO Atmosphere.

Complex	T_i^a (°C)	T_p^a (°C)	T_c^a (°C)	$T_{c'}^a$ (°C)	T_f^a (°C)	$\Delta H(1)$ kcal mol^{-1}
$(acac)Rh(ET)_2$	−85	−64			−46	−12.8 ± 0.4
$(acac)Rh(PR)_2$	−137	−118[b]			−70	−13.7 ± 0.8
$(acac)Rh(VCl)_2$	−65	−1			+29	−14.4 ± 0.7
$(acac)Rh(VA)_2$	−2	+35		+66	+142[c]	−6.8 ± 2[d]
$(acac)Rh(MA)_2$	−58	−54	−49			−3.8 ± 0.8
$(acac)Rh(ST)_2$						0 ± 3[e]
$(acac)Ir(ET)_2$	+34	+62		+73	+150[c]	−17.7 ± 1.1[d]
$(acac)Ir(PR)_2$	−106	−90[b]			−66	−19.6 ± 1.2
$(acac)Ir(VCl)_2$	−100	−96	−96		−83	−15.0 ± 1.3
$(acac)Ir(VA)_2$	−76	−62	−44		−5	−14.2 ± 1.1
$(acac)Ir(MA)_2$	−66	−48	−40		−1	−12.3 ± 1.3
$(acac)Ir(ST)_2$	−85	−34	−16		42	−13.6 ± 1.3

[a]T_i = initial temperature, T_p = peak temperature, T_c = base line crossing temperature when ligand evaporates, $T_{c'}$ = base line crossing temperature when $(acac)M(CO)_2$ evaporates, T_f = final temperature; see also Fig. 1, Fig. 2 and Fig. 3.   [b]Double peak. [c]The product, $(acac)M(CO)_2$, has been evaporated.   [d]Corrected for the sublimation enthalpy of $(acac)M(CO)_2$.   [e]The reaction was not stoichiometric.

to each other. As it was not possible to separate both peaks, the best base line was obtained when both peaks were maximal.

It has already been noted that, in the case of $(acac)Rh(VA)_2$ and $(acac)Ir(ET)_2$, the products $(acac)Rh(CO)_2$ and $(acac)Ir(CO)_2$ start to evaporate directly after the exchange reaction (1). As it was not possible to separate the peaks for sublimation and exchange reaction respectively, the total effect has been measured. The results have been corrected for the sublimation enthalpies of the dicarbonyl compounds which were determined in separate experiments under the same conditions. However, the correction resulted in the introduction of a large standard deviation for the reaction enthalpy.

In Table IV specific heat data for two complexes are given.

Discussion

All olefin complexes react with CO. The thermograms of $(acac)Rh(VA)_2$ and $(acac)Ir(ET)_2$ (Fig. 2) show that the compounds that evaporate are $(acac)$-$Rh(CO)_2$ and $(acac)Ir(CO)_2$ respectively. From the observed weight losses (Table II), in combination with results of spectroscopic investigations of the compounds before and after the reaction with CO, it can be concluded that all olefin complexes react stoichiometrically according to reaction (1). The combined results given in Tables I and II show that none of the olefin complexes evaporated during the reaction. However, Table II shows that in the case of $(acac)Rh(ST)_2$ the reaction is not stoichiometric.

Since the lattice energies of the crystalline complexes are dependent on the olefin or CO group present in the complex, the reaction enthalpies in Table III cannot directly be related to the metal–olefin or metal–carbonyl bond dissociation energies (E). Therefore the enthalpies of sublimation of these complexes were determined, which results have been published quite recently [12].

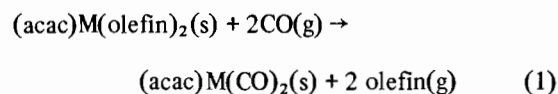The reaction enthalpies in the gas phase $\Delta H(4)$ were obtained according to the following reaction scheme:

$$(acac)M(olefin)_2(s) + 2CO(g) \rightarrow$$

$$(acac)M(CO)_2(s) + 2 \text{ olefin}(g) \qquad (1)$$

TABLE IV. Specific Heat Data for Complexes*.

Complex	a cal mol^{-1}	b cal deg^{-1} mol^{-1}	Accuracy cal mol^{-1}	Experimental Range (°C)
$(acac)Rh(CO)_2$	51.4	0.125	±0.3	−40–+25
$(acac)Rh(ET)_2$	56.6	0.173	±0.5	−35–+20

*$Cp = a + bt$, t in deg C.

TABLE V. Enthalpies of the Reaction[a] between the Complexes (acac)M(olefin)$_2$ and CO in Solid and Gaseous State; Sublimation Enthalpies of the Complexes (acac)M(olefin)$_2$ and (acac)M(CO)$_2$.

Complex	$\Delta H(1)^b$ kcal mol^{-1}	$\Delta H(2)^{b,c}$ kcal mol^{-1}	$\Delta H(4)^b$ kcal mol^{-1}
(acac)Rh(ET)$_2$	-12.8 ± 0.4	23.4 ± 0.9	-15.6 ± 1.2
(acac)Rh(PR)$_2$	-13.7 ± 0.8	20.6 ± 0.4	-13.7 ± 1.1
(acac)Rh(VCl)$_2$	-14.4 ± 0.7	28.0 ± 1.7	-21.8 ± 2.0
(acac)Rh(VA)$_2$	-6.8 ± 2	29.0 ± 0.8	-15.2 ± 2.3
(acac)Rh(MA)$_2$	-3.8 ± 0.8	26.7 ± 1.1	-9.9 ± 1.5
(acac)Rh(CO)$_2$		20.6 ± 0.7^d	
(acac)Ir(ET)$_2$	-17.7 ± 1.1	19.8 ± 1.0	-15.5 ± 1.6
(acac)Ir(PR)$_2$	-19.6 ± 1.2	21.5 ± 0.3	-19.1 ± 1.3
(acac)Ir(VCl)$_2$	-15.0 ± 1.3	21.4 ± 1.0	-14.4 ± 1.7
(acac)Ir(VA)$_2$	-14.2 ± 1.1	28.8 ± 0.7	-21.0 ± 1.3
(acac)Ir(MA)$_2$	-12.3 ± 1.3	28.0 ± 1.2	-18.3 ± 1.8
(acac)Ir(CO)$_2$		22.0 ± 0.3^d	

[a]It is assumed that Kirchoff corrections are small, so reaction enthalpies will be the same at 25 °C. [b]$\Delta H(1)$: enthalpy of the reaction (acac)M(olefin)$_2$(s) + 2CO(g) → (acac)M(CO)$_2$(s)+ 2 olefin(g). $\Delta H(2)$: enthalpy of the reaction (acac)M(olefin)$_2$(s) → (acac)M(olefin)$_2$(g). $\Delta H(4)$: enthalpy of the reaction (acac)M(olefin)$_2$(g) + 2CO(g) → (acac)M(CO)$_2$(g) + 2 olefin(g). [c]From ref. 12. [d]Refers to $\Delta H(3)$: enthalpy of the reaction (acac)M(CO)$_2$(s) → (acac)M(CO)$_2$(g).

$$(acac)M(olefin)_2(s) \rightarrow (acac)M(olefin)_2(g) \quad (2)$$

$$(acac)M(CO)_2(s) \rightarrow (acac)M(CO)_2(g) \quad (3)$$

$$(acac)M(olefin)_2(g) + 2CO(g) \rightarrow$$

$$(acac)M(CO)_2(g) + 2 \text{ olefin (g)} \quad (4)$$
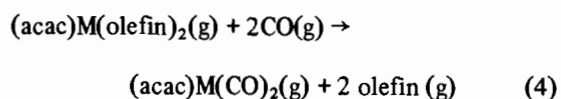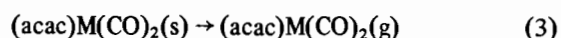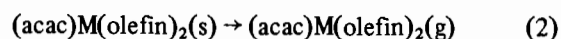
In Table V the values for $\Delta H(1)$, $\Delta H(2)$, $\Delta H(3)$ and $\Delta H(4)$ are given.

As the groups contributing to the specific heat are nearly the same before and after the reaction with CO, the Kirchoff corrections will be small. From Table IV and from literature data [13] it can be calculated that the Kirchoff correction for the reaction (acac)Rh(ET)$_2$(s) + 2CO(g) $\xrightarrow{\Delta H(1)}$ (acac)Rh(CO)$_2$-(s) + 2ET(g) from the mean reaction temperature (-70 °C) to 25 °C will be 0.05 ± 0.06 kcal mol^{-1}. Data for the other reactants and products are hardly available in the temperature range at which the reactions occur. For these reactions no Kirchoff corrections have been made.

All values of $\Delta H(4)$ are negative, so all values for E(M–olefin) are lower than for E(M–CO). As a result of the summation of ΔH values, each having a considerable standard deviation, the total standard deviation in $\Delta H(4)$ is high. The fact that the differences in $\Delta H(4)$ are of the same order of magnitude as the standard deviation hampers comparison of all results.

In toluene solution E(Rh–ET) – E(Rh–PR) and E(Rh–ET) – E(Rh–VCl) amount to 1.4 ± 0.9 kcal mol^{-1} and 0.8 ± 0.8 kcal mol^{-1} respectively [14]. When it is assumed that solvation effects cancel, these results do not agree with our results of $-1.0 \pm$ 0.8 kcal mol^{-1} and 3.1 ± 1.2 kcal mol^{-1} respectively.

From thermal decomposition of Rh$_4$(CO)$_{12}$ and Rh$_6$(CO)$_{16}$ the (Rh–CO) bond enthalpy contribution is estimated at 39 kcal mol^{-1} [15]. Gas phase pyrolysis of π-C$_5$H$_5$Rh(ET)$_2$ indicates a maximum value of about 31 kcal mol^{-1} for E(Rh–ET) in that compound [6]. The difference, 8 kcal mol^{-1}, agrees with our value for E(Rh–CO) – E(Rh–ET) = ½(ΔH(4)) = 7.8 ± 0.6 kcal mol^{-1}.

If one assumes that the metal–ligand bond enthalpy contributions are transferable from one compound to another, as has already been done for the calculation of the (M–CO) bond enthalpy contributions [15, 16] then the (Ir–ET) bond enthalpy contribution can be calculated. The Ir–(CO) bond enthalpy contribu-

TABLE VI. Bond Enthalpy Contributions[a] for (M–CO) and (M–ET); M = Rh(I), Ir(I).

E(Rh–CO) = 39 kcal mol^{-1} [b]	E(Rh–Et) = 31 kcal mol^{-1} [d]
E(Ir–CO) = 45 kcal mol^{-1} [c]	E(Ir–Et) = 37 kcal mol^{-1} [e]

[a]As there are several assumptions in this calculation, no uncertainties are quoted; they can be calculated from the sources in literature (ref. 15, 16, this work). [b]Ref. 15. [c]Ref. 16. [d]Ref. 6. [e]This work.

TABLE VII. Bond Enthalpy Contributions E' (M–olefin) Relative to E(M–ET)[a].

Olefin	E' (Rh–olefin) (kcal mol^{-1})	E'(Ir–olefin) (kcal mol^{-1})
ET	0	0
PR	$0.9_5 \pm 0.8$	-3.6 ± 1.0
VCl	-3.1 ± 1.2	1.1 ± 1.2
VA	0.2 ± 1.3	-5.5 ± 1.0
MA	$2.8_5 \pm 1.0$	-2.8 ± 1.2

[a]E'(M–olefin) = E(M–olefin) − E(M–ET).

tion is estimated at 45 kcal mol^{-1} from the thermal decomposition of $Ir_4(CO)_{12}$ [16]. Together with E(Ir–CO) − E(Ir–ET) = 7.8 ± 0.8 kcal mol^{-1} a value of approximately 37 kcal mol^{-1} is calculated for the (Ir–ET) bond enthalpy contribution.

In Table VI data for E(M–CO) and E(M–ET) are compiled.

From Table VI it can be concluded that the Ir–olefin bond is stronger than the Rh–olefin bond. This conclusion has also been drawn from spectroscopic results [11].

The influence of group X in the olefin, $CH_2=CHX$, can be seen from Table VII where the differences $E'(M–(CH_2=CHX)) = E(M–(CH_2=CHX)) − E(M–(CH_2=CH_2)) = \frac{1}{2}\{\Delta H(4)(CH_2=CHX) − \Delta H(4)(CH_2=CH_2)\}$ are compiled.

The influence of the substituents on the strength of the metal–olefin bond can be divided into a steric factor and an electronic factor. In general, any substituent on a double bond has an unfavourable steric effect on the metal–olefin bond enthalpy [1]. One would expect all olefins to give a larger reaction enthalpy $\Delta H(4)$ than ET, except those with a strong electronic effect which is able to overcome the steric effect.

From Table VII it can be seen that, in spite of the large standard deviation, E'(Rh–PR) > E'(Rh–VCl) and E'(Ir–PR) < E'(Ir–VCl) which means that, as Cl and CH_3 have comparable steric factors, an electron donating CH_3 group increases E(Rh–olefin) and an electron withdrawing Cl substituent increases E(Ir–olefin). This can be explained by assuming that in the Dewar–Chatt–Duncanson model [17] σ-donation is more important in the Rh–olefin bond and π-backbonding is more important in the Ir–olefin bond. However, this conclusion is not in agreement with our spectroscopic investigations on these compounds. From vibrational data on the olefinic frequencies $\nu(C=C)$, $\delta(CH_2)_{scis}$ and/or $\delta(CH)_{bend}$ and from ^{13}C-NMR results we have concluded that the type of bonding of olefins with different substituents to Rh(I) or Ir(I) is highly similar [11]. However, this

similarity is not found in this work possibly because σ-donation and π-backbonding contribute in a different way to the spectroscopic and thermodynamic parameters.

Conclusion

By measuring reaction enthalpies of crystalline compounds it is possible to determine differences in bond dissociation energies. The influence of olefinic substituents on the Rh–olefin and Ir–olefin bond are not similar as would be expected from spectroscopic studies. The Ir–ethylene bond could be estimated at about 37 kcal mol^{-1} which is stronger than the Rh–ethylene bond which is 31 kcal mol^{-1}.

Acknowledgments

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