Thermochimica Acta, 30 (1979) 293–302
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CALORIMETRIC INVESTIGATION OF THE REACTION OF 1,5-CYCLOOCTADIENE WITH COMPLEXES OF THE TYPE (acac)M(olefin)$_2$ [M = Rh(I), Ir(I)]

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(Received 13 June 1978)

ABSTRACT

The enthalpies of reaction of the complexes (acac)M(olefin)$_2$ (acac = acetylacetonate, M = Rh(I), Ir(I); olefin = ethylene, propene, vinyl chloride, vinyl acetate, methyl acrylate and styrene) with 1,5-cyclooctadiene in *n*-heptane, according to the reaction $[(\text{acac})\text{M}(\text{olefin})_2 + 1{,}5\text{COD} \rightarrow (\text{acac})\text{M}(1{,}5\text{COD}) + 2\ \text{olefin}]_{n\text{-heptane}}$ have been determined by solution calorimetry. From these results the influence of substituent R in the olefin CH_2CHR on the M–(CH_2CHR) displacement enthalpy has been derived. It is concluded that π back-bonding is slightly more important in the Ir–olefin bond than in the Rh–olefin bond. Furthermore, the data show that, as a result of steric factors which inhibit the approach of solvent molecules, solvation enthalpies are not additive.

INTRODUCTION

Transition metals play an important role in catalysis and therefore the nature of the metal–olefin bond is of great interest. Especially thermochemical data can give more insight in the nature and the strength of the metal–olefin bond. Thermochemical studies have been reviewed by Hartley[1] and by Pettit and Barnes[2]. Generally, these studies are not very accurate since most data have been obtained from the temperature dependence of stability constants.

More accurate measurements by means of calorimetry have been reported by Partenheimer et al.[3–7] for complexes of Ag(I), Pd(II), Pt(II) and Rh(I) with cycloolefins. Recently, Ni(O)–olefin complexes have been investigated by the same methods[8].

In the Amsterdam laboratory the nature of the metal–olefin bond has been

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investigated by spectroscopy[9-12]. These studies revealed that the Rh(I)– and Ir(I)–olefin bonds are highly similar in character, but different from the Pt(II)–olefin bond. In a recent paper we reported data concerning the metal–olefin bond enthalpy contributions (E) obtained from DSC and vapour pressure measurements for reaction (1)[13, 14]

$$(\mathrm{acac})\mathrm{M}(\mathrm{olefin})_2(\mathrm{g}) + 2\,\mathrm{CO}(\mathrm{g}) \rightarrow (\mathrm{acac})\mathrm{M}(\mathrm{CO})_2(\mathrm{g}) + 2\,\mathrm{olefin}(\mathrm{g}) \qquad (1)$$

where M = Rh(I), Ir(I). These results, however, showed that most probably the Rh– and Ir–olefin bonds are different in character. In view of the limited accuracy of these data we remeasured the relative metal–olefin bond enthalpy contributions by solution calorimetry which in general leads to data with a high accuracy.

In this article the enthalpies of reaction (2)

$$[(\mathrm{acac})\mathrm{M}(\mathrm{olefin})_2 + \mathrm{COD} \rightarrow (\mathrm{acac})\mathrm{M}(\mathrm{COD}) + 2\,\mathrm{olefin}]_{n\text{-heptane}} \qquad (2)$$

(acac = acetylacetonate; M = Rh(I), Ir(I); olefin = ethylene (ET), propene (PR), vinyl chloride (VCl), vinyl acetate (VA), methyl acrylate (MA), styrene (ST); COD = 1,5-cyclooctadiene) are reported. The influence of the metal and of the substituent R in CH_2CHR on the metal–olefin displacement enthalpies are calculated and the results are compared with results obtained for the gas phase reaction (1).

EXPERIMENTAL

Preparation of the complexes

$(\mathrm{acac})\mathrm{Rh}(\mathrm{ET})_2$ and $(\mathrm{acac})\mathrm{Ir}(\mathrm{ET})_2$ were prepared according to literature methods[15, 16]. The other complexes $(\mathrm{acac})\mathrm{M}(\mathrm{olefin})_2$ were synthesized via a displacement reaction of ET in $(\mathrm{acac})\mathrm{Rh}(\mathrm{ET})_2$ or $(\mathrm{acac})\mathrm{Ir}(\mathrm{ET})_2$ by an excess of olefin. A detailed description of the synthesis and characterisation of these complexes has been presented in a previous paper[11]. *n*-Heptane (Merck, zur synthese) and 1,5-cyclooctadiene (Merck, zur synthese) were distilled and stored over molecular sieves (Merck 4A) prior to use.

Calorimeter

Enthalpies of reaction and solution were measured in a calorimeter which is a revised version of the type previously described[17]. The calorimeter is of the isoperibol type and consists of a 250 cm^3 glass Dewar vessel. The environment is kept constant within ±0.002 K at 298.15 K. The inner part of the reaction chamber contains a heater, a thermistor, a platinum stirrer, a cooler and a sample container. The sample container consists of a glass tube provided with a Teflon bottom which is leak-tight by means of O-rings. Sampling is performed by pushing the bottom out of the tube, which has an effective volume of 5 cm^3, with a glass-coated tungsten wire at the beginning of the dissolution. It was checked that heat effects from this action can be neglected. The temperature sensitivity of the apparatus is $\pm 2 \times 10^{-6}$ K. The energy equivalent of the calorimeter is determined after each measurement.

Since in general, short main periods did not occur, the corrected temperature increment was obtained by a computer program that accounted for the temperature changes according to Newtons law during the pre- and post-periods. The calorimeter was tested by the dissolution of Tris(NBS Standard Reference Material No. 724) in 200 cm^3 of 0.1 M HCl.

$\Delta H_{\text{soln}}(298.15\ \text{K}) = -(58.73 \pm 0.09)\ \text{cal}^{*}\ \text{g}^{-1}$
(NBS-value $\Delta H_{\text{soln}}(298.15\ \text{K}) = -(58.74 \pm 0.06)\ \text{cal g}^{-1}$

For the ^{1}H-NMR measurements a Varian T60 apparatus was used.

TABLE 1

ENTHALPY OF REACTION OF A MASS m_1 OF (acac)Rh(olefin)$_2$, WITH AN EQUIMOLAR MASS OF COD IN 200 CM^{-3} OF n-HEPTANE AT 298.15 K

Olefin	g_1 *m[(acac)Rh(olefin)$_2$] (g)*	g_2 *m[COD] (g)*	$\varepsilon\theta^0$ *(cal)*	$\Delta\theta$ *(θ^0)*	$-\Delta h_3$ *(cal g^{-1})*
ET	0.09715	0.08445	8.803	0.0537	8.11
	0.10142	0.08824	8.945	0.0550	8.10
					8.11 ± 0.01
PR	0.08680	0.07460	9.233	0.1635	20.60
	0.08996	0.07397	9.185	0.1726	20.69
					20.65 ± 0.09
VCl	0.09449	0.07298	8.673	0.1626	17.81
	0.09836	0.07593	8.835	0.1715	18.28
					18.05 ± 0.47
VA	0.10649	0.08996	9.161	0.1308	14.40
	0.10983	0.08034	8.920	0.1461	14.59
					14.50 ± 0.19
MA	0.10909	0.07796	9.018	0.1079	11.59
	0.11305	0.07475	9.011	0.1145	11.59
					11.59 ± 0.0
ST	0.12057	0.07291	9.036	0.1752	15.39
	0.11898	0.07435	9.053	0.1722	15.43
					15.41 ± 0.04

[a] Δh_1 represents: $[(\text{acac})\text{Rh}(\text{olefin})_2]_{n\text{-heptane}} + (1 + x)\ \text{COD(l)} \rightarrow [(\text{acac})\text{Rh}(\text{COD}) + 2\ \text{olefin} + x\ (\text{COD})]_{n\text{-heptane}}$

Δh_2 represents: $\text{COD(l)} \xrightarrow{n\text{-heptane}} [\text{COD}]_{n\text{-heptane}}$

Δh_3 represents: $[(\text{acac})\text{Rh}(\text{olefin})_2 + \text{COD} \rightarrow (\text{acac})\text{Rh}(\text{COD}) + 2\ \text{olefin}]_{n\text{-heptane}}$

$-\Delta h_3 = (\Delta h_1 - \Delta h_2)\ g_1^{-1};\ \Delta h_1 = \varepsilon\Delta\theta;\ \Delta h_2 = -\ 3.73\ g_2.$

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[*] Throughout this paper 1 cal = 4.184 J.

TABLE 2

ENTHALPY OF SOLUTION OF A SPECIFIED SOLUTE OF A MASS m IN 200 CM^3 OF n-HEPTANE AT 298.15 K

Solute	m *(g)*	$\varepsilon\theta^0$ *(cal)*	$\Delta\theta$ *(θ^0)*	$-\Delta h$ *(cal g^{-1})*	$-\Delta H$ *(kcal mole^{-1})*
COD	0.08532	8.707	−0.0365	−3.72	
	0.07918	9.086	−0.0326	−3.74	
				−3.73 ± 0.01	−0.406 ± 0.001
VA	0.09011	8.844	−0.1597	−15.67	
	0.08147	8.773	−0.1415	−15.24	
				−15.46 ± 0.30	−1.33 ± 0.03
(acac)Rh(ET)$_2$	0.09715	8.960	−0.2912	−26.86	
	0.10142	9.090	−0.2991	−26.81	
				−26.84 ± 0.04	−6.93 ± 0.01
(acac)Rh(VA)$_2$	0.10649	8.879	−0.3077	−25.66	
	0.10983	9.017	−0.3062	−25.14	
				−25.40 ± 0.37	−9.50 ± 0.1

RESULTS

The enthalpies of solution and reaction of liquid COD in a solution of (acac)Rh(olefin)$_2$ in n-heptane have been measured (reaction (3)). In order to obtain the enthalpy of the totally solvated reaction (reaction (2), Tables 1 and 5) the enthalpy of solution of COD in n-heptane has also been measured (reaction (4), Table 2).

$$[(\text{acac})\text{Rh}(\text{olefin})_2]_{n\text{-heptane}} + (1+x)\,\text{COD}(1) \rightarrow [(\text{acac})\text{Rh}(\text{COD}) + 2\text{olefin} + x\,\text{COD}]_{n\text{-heptane}} \quad (3)$$

$$(1+x)\text{COD}(1) + \xrightarrow{n\text{-heptane}} [(1+x)\text{COD}]_{n\text{-heptane}} \quad (4)$$

$$[(\text{acac})\text{Rh}(\text{olefin})_2 + \text{COD} \rightarrow (\text{acac})\text{Rh}(\text{COD}) + 2\ \text{olefin}]_{n\text{-heptane}} \quad (2)$$

In some cases the solution of the Rh-complexes appeared to be slightly opalescent after the measurement, which may be caused by oxidation of the complex. The solutions of the Ir-complexes, however, sometimes became turbid during the measurement and this influenced the reproducibility. Obviously the solutions of the Ir-complexes are less air stable than the solutions of the Rh-complexes. The lower stability towards oxidation of the Ir-complexes is also shown by the fact that the decomposition in air of solid (acac)Ir(PR)$_2$ takes place within a couple of hours, whereas solid (acac)Rh(PR)$_2$ is air stable. It was expected that the reactivity of the Ir-complexes towards oxidation would be enhanced in solution and therefore the enthalpy of solution of solid (acac)Ir(olefin)$_2$ in a solution of COD in n-heptane has

TABLE 3

ENTHALPY OF SOLUTION OF A MASS m OF (acac)Ir(olefin)$_2$ IN 200 CM^3 n-HEPTANE AT 298.15 K

Olefin	*m[(acac)Ir(olefin)$_2$]* *(g)*	$\varepsilon\theta^0$ *(cal)*	$\Delta\theta$ *(θ^0)*	$-\Delta h$ *(cal g^{-1})*
ET	0.11133	8.965	−0.2385	−19.21
	0.11543	8.920	−0.2427	−18.75
	0.10883	8.949	−0.2346	−19.29
				−19.08 ± 0.34
VCl	0.11131	9.242	−0.1758	−14.60
	0.11710	8.978	−0.1903	−14.59
				−14.60 ± 0.01
VA	0.09551	9.094	−0.2055	−19.57
	0.10095	9.085	−0.2057	−18.51
				−19.04 ± 1.06
MA	0.10510	9.193	−0.2070	−18.11
	0.10337	9.213	−0.1940	−17.29
				−17.70 ± 0.82
ST	0.12306	9.386	−0.1823	−13.90
	0.11139	9.023	−0.1713	−13.88
				−13.89 ± 0.02

TABLE 4

ENTHALPY OF SOLUTION-REACTION OF A MASS m OF (acac)Ir(olefin)$_2$ IN 200 CM^3 n-HEPTANE CONTAINING CA. 0.075 g COD

Olefin	*m[(acac)Ir(olefin)$_2$]* *(g)*	$\varepsilon\theta^0$ *(cal)*	$\Delta\theta$ *(θ^0)*	$-\Delta h$ *(cal g^{-1})*
ET	0.11049	9.074	−0.1575	−12.93
	0.11608	9.065	−0.1642	−12.82
	0.11669	8.967	−0.1667	−12.76
				−12.83 ± 0.10
VCl	0.11126	9.049	−0.0554	−4.51
	0.11159	8.903	−0.0568	−4.53
				−4.52 ± 0.02
VA	0.09320	9.111	−0.0903	−8.83
	0.09872	9.150	−0.0962	−8.92
				−8.88 ± 0.05
MA	0.10961	9.213	−0.1122	−9.43
	0.09517	9.056	−0.0975	−9.28
				−9.35 ± 0.15
ST	0.12207	9.103	−0.0090	−0.67

TABLE 5

ENTHALPY OF REACTION OF ONE MOLE (acac)M(olefin)$_2$ WITH ONE MOLE COD IN *n*-HEPTANE AT 298.15 K

Olefin	*(acac)Rh(olefin)$_2$ ΔH (kcal mole^{-1})*	*(acac)Ir(olefin)$_2$ ΔH (kcal mole^{-1})*
ET	-2.15 ± 0.10	-2.17 ± 0.10
PR	-5.89 ± 0.02	
VCl	-5.88 ± 0.10	-4.19 ± 0.01
VA	-5.41 ± 0.05	-4.72 ± 0.3
MA	-4.32 ± 0.003	-3.87 ± 0.3
ST	-6.31 ± 0.10	-6.53 ± 0.2

been measured (reaction (5), Table 4). In order to obtain the enthalpy of the totally solvated reaction (reaction (2), Table 5) it was necessary to determine the enthalpy of solution in *n*-heptane for all complexes (acac)Ir(olefin)$_2$ (reaction (6), Table 3). In this way the time during which (acac)Ir(olefin)$_2$ was solved in *n*-heptane was much shorter than for (acac)Rh(olefin)$_2$, while the complex (acac)Ir(COD) is much more air stable. Furthermore, weighing and filling of the (air-tight) sample container with (acac)Ir(olefin)$_2$ was performed in a glove box and oxygen free solvents were used. The design of the calorimeter, however, prevented operation without air contact. The solutions of (acac)Ir(ET)$_2$ were slightly opalescent after the experiment (reaction (6)) but all other solutions were clear; (acac)Ir(PR)$_2$ was too unstable to give reproducible results.

$$\text{(acac)Ir(olefin)}_2\text{(c)} + [(1 + x)\ \text{COD}]_{n\text{-heptane}} \rightarrow [\text{(acac)Ir(COD)} + 2\ \text{olefin} + x\ \text{COD}]_{n\text{-heptane}} \quad (5)$$

$$\text{(acac)Ir(olefin)}_2\text{(c)} \xrightarrow{n\text{-heptane}} [\text{(acac)Ir(olefin)}_2]_{n\text{-heptane}} \quad (6)$$

$$[\text{(acac)Ir(olefin)}_2 + \text{COD} \rightarrow \text{(acac)Ir(COD)} + 2\ \text{olefin}]_{n\text{-heptane}} \quad (2)$$

In a discussion of the solvation effects, the enthalpies of solutions of VA, (acac)Rh(ET)$_2$ and (acac)Rh(VA)$_2$ have been used (Table 2).

Reaction (2) has been monitored by ^{1}H-NMR. Because of the sensitivity of the ^{1}H-NMR apparatus the concentrations were higher. When a stoichiometric quantity of COD was added to a solution of (acac)M(olefin)$_2$ the components reacted according to reaction (2) within a few seconds, which was shown by the fine structure of the uncoordinated olefin, $\delta'H_\gamma$ of the (acac)M-moiety and the peak integrals. The complexes (acac)M(ET)$_2$ showed, however, an evolution of gaseous ET directly after adding the COD. Since the top of the calorimeter contains connections that are not totally gas-tight some experiments were performed in order to determine the rate of escape of the gaseous olefin out of the solution. ^{1}H-NMR spectra showed that the concentration of solutions of the olefins ET, PR and VCl in CCl$_4$ standing in an open round bottom is halved by degassing in 90 min, 4 h and over 3 days, respectively. In the experiments the concentrations of these (saturated) solutions were about tenfold of those in the calorimeter.

DISCUSSION

The complexes (acac)Rh(olefin)$_2$ and (acac)Ir(olefin)$_2$ have been characterized by elemental analysis, ^{1}H- and ^{13}C-NMR and IR/Raman spectroscopy[11]. Crystallographic data for (acac)Rh(ET)$_2$ revealed that the (acac)Rh-moiety is lying in a plane while the ethylene molecules are standing perpendicular to this plane[18]. Molecular weight determinations of (acac)Ir(ET)$_2$ showed that the complex is monomeric[16]. COD as ligand was chosen since reaction (2) was expected to be complete ("chelate effect"[4]); this was confirmed by ^{1}H-NMR. Since the calorimetric measurements were completed in about 20 min it can be assumed that a negligible amount of olefin escapes from the solution during the measurement[19]. Accordingly, it has been concluded that the data in Table 5 represent reaction (2) which shows an exchange reaction carried out in a dilute solution of *n*-heptane. *n*-Heptane is a poor solvating solvent without any specific interactions with the reacting compounds so according to Drago[21] the reaction enthalpy of reaction (2) is supposed to be equal to the reaction enthalpy in the gas phase.

This assumption means that in scheme 1 the solvation terms cancel, i.e. $\Delta H_3 = \Delta H_4$ when $\Delta H_1 + \Delta H_2 = \Delta H_5 + \Delta H_6$.

$$\begin{tikzcd}
\text{(acac)M(olefin)}_2\text{(g)} \arrow[d, "\Delta H_1"] & + 2\,\text{ET(g)} \arrow[d, "\Delta H_2"] \arrow[r, "\Delta H_3"] & \text{(acac)M(ET)}_2\text{(g)} \arrow[d, "\Delta H_5"] & + 2\,\text{olefin(g)} \arrow[d, "\Delta H_6"] \\
\text{[(acac)M(olefin)}_2 & + 2\,\text{ET} \arrow[r, "\Delta H_4"] & \text{(acac)M(ET)}_2 & + 2\,\text{olefin]}_{n\text{-heptane}}
\end{tikzcd}$$

Scheme 1

From the enthalpies of solution and sublimation[13, 20] it can be calculated that for (acac)Rh(VA)$_2$ $\Delta H_1 + \Delta H_2 = -23.5 \pm 1.0$ kcal mole^{-1} and $\Delta H_5 + \Delta H_6 = -30.4 \pm 1.0$ kcal mole^{-1}; for (acac)Ir(VA)$_2$ $\Delta H_1 + \Delta H_2 = -24.0 \pm 1.5$ kcal mole^{-1} and $\Delta H_5 + \Delta H_6 = -27.2 \pm 1.1$ kcal mole^{-1}. For these complexes $\Delta H_1 + \Delta H_2$ is considerably less exothermic than $\Delta H_5 + \Delta H_6$. This may be caused by the bulkiness of R in the olefin CH$_2$CHR by which parts of R and of the (acac)M-moiety become less solvated[22]. Further comparison according to scheme 1 is not possible because of lack of data, but estimations for the Ir-complexes show that for VCl $\Delta H_1 + \Delta H_2 \sim \Delta H_5 + \Delta H_6$, and that for MA $\Delta H_1 + \Delta H_2$ is less exothermic than $\Delta H_5 + \Delta H_6$.

The reaction enthalpy in the gas phase, ΔH_3, can also be calculated from the enthalpies of reaction (1) which we have determined previously by DSC and vapour pressure measurements[14]. There is, however, a large discrepancy between the results from DSC-vapour pressure measurements and those from solution calorimetry-vapour pressure measurements, e.g. ΔH_3 (scheme 1) for (acac)Rh(VA)$_2$

TABLE 6

RELATIVE DISPLACEMENT ENTHALPIES[a] D(M-olefin) IN KCAL MOLE^{-1}

Olefin	*(acac)Rh(olefin)$_2$*	*(acac)Ir(olefin)$_2$*	*tr-PtCl$_2$ (py)(olefin)*[b]	*tr-PdCl$_2$ (py)(olefin)*[c]
ET	0	0	0	0
PR	-1.87 ± 0.05			
VCl	-1.87 ± 0.05	-1.01 ± 0.05		
VA	-1.63 ± 0.05	-1.28 ± 0.05		
MA	-1.09 ± 0.05	-0.85 ± 0.05		
ST	-2.08 ± 0.05	-2.18 ± 0.05	-4.5 ± 0.3	-0.2 ± 0.3
cis-Butene			-2.4 ± 0.3	$+1.4 \pm 0.3$

[a] For Rh and Ir $D(\text{M–olefin}) = \frac{1}{2}\Delta H(8) = \frac{1}{2}\{\Delta H(2)(\text{CH}_2\text{CHR}) - \Delta H(2)(\text{ET})\}$; for Pt and Pd $D(\text{M–olefin}) = \Delta H(9)$; $[\text{MCl}_2(\text{py})(\text{CH}_2\text{CHR}) + \text{ET} \rightarrow \text{MCl}_2(\text{py})(\text{ET}) + \text{CH}_2\text{CHR}]_{\text{solvens}}$ (ref. 9).
[b] From ref. 7.
[c] From ref. 6.

$(\Delta H_3)_{\text{soln.cal.-vap.pr}} = 3.6 \pm 0.4$ kcal mole^{-1}, $(\Delta H_3)_{\text{DSC-vap.pr.}} = 0.4 \pm 2.0$ kcal mole^{-1} for (acac)Ir(VA)$_2$: $(\Delta H_3)_{\text{soln.cal.-vap.pr.}} = 0.6 \pm 0.5$ kcal mole^{-1}, $(\Delta H_3)_{\text{DSC-vap.pr.}} = -11.0 \pm 1.6$ kcal mole^{-1}. (Since the enthalpies of vaporisation cancel, the uncertainties given do not contain this source). These large discrepancies may be due to either the errors in the calorimetric measurements or to the errors in the DSC measurements, which are not only dependent on the accuracy of the apparatus but also on the assumptions that have been made in the evaluation of these data (e.g. stoichiometry, decomposition, Kirchhoff's corrections, DSC baseline).

For a discussion concerning the dependance of the nature of the metal–olefin bond on the substituent R in the olefin CH$_2$CHR it is more convenient to consider the relative displacement energies $D(\text{M–CH}_2\text{CHR})$[4].

$$[(\text{acac})\text{M}(\text{CH}_2\text{CHR})_2 + 2\,\text{ET} \rightarrow (\text{acac})\text{M}(\text{ET})_2 + 2\,\text{CH}_2\text{CHR}]_{n\text{-heptane}} \qquad (8)$$
$$D(\text{M–CH}_2\text{CHR}) = \tfrac{1}{2}\Delta H(8) = \tfrac{1}{2}\{\Delta H(2)(\text{CH}_2\text{CHR}) - \Delta H(2)(\text{ET})\}$$

In Table 6 the data for D(M–olefin) and some literature data, determined by calorimetric methods, are given. From Table 6 it can be seen that $D(\text{Pd–}cis\text{-butene}) > 0$ and $D(\text{Pt–}cis\text{-butene}) < 0$ so methyl groups, which are electron-donors, enhance the Pd–olefin bond strength, this in spite of the negative influence that every substituent R has on the metal–olefin bond strength[1]. According to the Dewar–Chatt and Duncanson model for the description of the metal–olefin bond[23a,b] the σ-contribution is more important than the π-contribution for Pd(II) and vice versa for Pt(II). The phenyl group in ST is electron-donating[12] so the same can be concluded from $D(\text{Pd–ST}) > D(\text{Pt–ST})$. Probably because of steric influences D(Pd–ST) is negative[24]. Rh(I) and Ir(I) are isoelectronic with Pd(II) and Pt(II) and likewise $D(\text{Rh–ST}) > D(\text{Ir–ST})$, although the difference is small.

The negative sign is probably also determined by electronic factors and accordingly in both metals π back-bonding is more important than σ-bonding. D(Rh–ST) > D(Ir–ST); D(Rh–VCl) < D(Ir–VCl) and D(Rh–MA) < D(Ir–MA); ST is an electron-donor and MA and VCl are electron-acceptors (relative to ET)[12] so probably π back-bonding is more important in the Ir–olefin bond than in the Rh–olefin bond. This was also found from spectroscopic data[25, 26]. According to spectroscopic data[12] VA is an electron-donor, so it is expected that D(Ir–VA) < D(Rh–VA). However, spectroscopic and calorimetric investigations on Ni(O)–olefin complexes showed that while the electron-withdrawal properties of the olefin were relatively inductive in nature, the overall bond strengths were more closely related to resonance effects[8].

The data for D(M–olefin) have been investigated in order to test various spectroscopic parameters that have been thought to reflect the metal–olefin bond strength such as the summed percentage lowering of the coupled olefinic frequencies $\nu(C{=}C)$, $\delta(CH_2)_{scis.}$ and $\delta(CH)_{bend}$, and the ^{13}C-NMR shifts[11]. The differences between the values for $D(M{-}CH_2CHR)$, however, are small and of about the same magnitude as the corrections for the solvation enthalpy. Therefore it is not surprising that no simple correlations have been found. On the other hand, a comparison of the role of the metal for these isostructural complexes is not hampered by solvation enthalpy corrections. Both thermochemical and spectroscopic methods show the larger importance of π back-bonding in the Ir–olefin bond compared to the Rh–olefin bond.

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