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Vibrational and NMR Spectroscopic Studies on (β-diket)Rh(substituted olefin)$_2$. The Influence of the β-diketone

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Spectroscopic studies (IR, Raman, ^{1}H and ^{13}C NMR) on the complexes (β-diket)Rh(olefin)$_2$ (β-diket = dpm, tfac, dbm; olefin = ethylene, propene, vinyl chloride, vinyl acetate, methyl acrylate, styrene) have been carried out. The influence of the β-diketone ligand on the Rh–olefin bond supports the view that metal-to-olefin π back-bonding is predominant. The ^{1}H NMR spectra of the (β-diket)Rh(olefin)$_2$ complexes show that δH_γ depends on the nature of both the substituents on the β-diketone and on the olefin.

Introduction

Several spectroscopic studies have been reported in the literature discussing the metal–olefin bond. Powell *et al.* [1, 2] have shown that the summed percentage lowering (SPL) of the frequencies of ν(C=C) and $\delta(CH_2)_{scis}$ in ethylene complexes is proportional to the metal–olefin bond strength. Pt(II) and Ni(0) complexes with olefins of the type CH_2-CHR have been investigated by ^{13}C NMR [3, 4]. In this laboratory the M–(CH_2CHR) bond in the complexes *trans*-$PtCl_2(CH_2CHR)(L)$, (acac)Rh(CH_2-$CHR)_2$ and (acac)Ir($CH_2CHR)_2$ has been investigated by vibrational (Raman and IR) and ^{13}C NMR spectroscopy [5–7] and by thermochemical methods [8]. It has been found that the Rh– and Ir–olefin bonds were highly similar but different from the Pt–olefin bond. In (β-diket)Ir(COD) and (β-diket)Ir(CO)$_2$ the influence of substituents of the β-diketone on the Ir–olefin bond has been investigated by ^{1}H, ^{13}C NMR and IR spectroscopy [9–11]. In order to find out how substituents on the β-diketone influence the metal–olefin bond, we recorded the vibrational and ^{1}H and ^{13}C NMR spectra of (β-diket)Rh(olefin)$_2$ (β-diket = 2,2,6,6-tetramethyl-3,5-heptanedionate (dpm), 1,1,1 trifluoro-2,4-pentanedionate(tfac) and 1,3-diphenyl-1,3-propanedionate(dbm); olefin = ethylene(ET), propene(PR), vinyl chloride(VCl), vinyl acetate(VA), methyl acrylate(MA) and styrene(ST)) and of (β-diket)Rh(CO)$_2$. These data were compared with those for the complexes (acac)-Rh(olefin)$_2$ which we described in a recent paper [5].

Experimental

General

Infrared spectra of the solid compounds (KBr pellets) were recorded on a Beckman 4250 spectrophotometer. Raman spectra of the solid compounds were obtained on a Coderg PH 1 spectrophotometer. The 6471 Å line of a CRL 52 Kr$^+$ laser was used as the exciting line. The proton decoupled ^{13}C NMR spectra were measured in $CDCl_3$ at 20 MHz on a Varian CFT 20 spectrometer. For most compounds 30,000 pulses (A.T. = 0.8 sec, P.D. = 2.0 sec) were necessary. ^{1}H NMR spectra were obtained in $CDCl_3$ on a Varian T 60 spectrometer.

All reactions were performed under an atmosphere of dry, oxygen free nitrogen. The silicagel was from Merck (0.063–0.200 mm). In many cases colloidal particles were formed which coloured the silicagel grey or black. The complexes [RhCl(ET)$_2$]$_2$, (acac)-Rh(ET)$_2$ and (dbm)Rh(ET)$_2$ were prepared according to literature methods [12, 13]. The preparation of (hfac)Rh(ET)$_2$, (tfac)Ir(ET)$_2$ and (hfac)Ir(ET)$_2$ afforded the compounds in very low yields which hampered extensive spectroscopic studies similar to those carried out for the other complexes.

The analyses (Table I) were carried out at the Institute for Organic Chemistry TNO, Utrecht, The Netherlands

Syntheses of the (β-diket)Rh(olefin)$_2$ Complexes

(tfac)Rh(ET)$_2$

To a mixture of 5.82 g (15 mmol) of [RhCl-(ET)$_2$]$_2$, ether (100 ml) and 3.63 ml (30 mmol) of H(tfac), 3.36 (30 mmol) of K-tert-butoxide was added at 0 °C. After four hours stirring the mixture was filtered off. The residue was washed several times with ether. The ether fractions were combined and the solvent was evaporated. The reddish solid was dissolved in 100 ml pentane and forced through a

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TABLE 1. Analytical Data for (β-diket)Rh(olefin)$_2$.

Olefin	(dpm)Rh(olefin)$_2$					(tfac)Rh(olefin)$_2$					(dbm)Rh(olefin)$_2$				
	%C		%H		state	%C		%H		state	%C		%H		state
	calc.	found	calc.	found		calc.	found	calc.	found		calc.	found	calc.	found	
ET	52.64	52.68	7.95	7.96	yellow crystals	34.64	34.20	3.88	3.66	orange cr.	59.70	59.66	5.01	4.99	yellow cr.
PR	55.14	53.82	8.44	8.33	yellow/white cr.	61.47	60.98	5.65	5.81	yellow oil	61.47	60.92	5.65	5.61	yellow cr.
VCl	43.82	44.03	6.13	6.20	light yellow oil	28.37	a	2.65	a	red oil	50.58	50.70	3.80	3.90	yellow cr.
VA	49.79	49.84	6.82	6.84	light yellow cr.	36.47	36.50	3.77	3.79	dark yellow cr.	55.43	55.69	4.65	4.81	yellow cr.
MA	49.79	50.11	6.82	6.94	orange cr.	36.47	36.40	3.77	3.95	orange-red powder	55.43	55.83	4.65	4.84	yellow cr.
ST	65.58	65.11	7.13	7.24	yellow cr.	54.33	54.78	4.34	4.39	red cr.	69.67	69.78	5.09	5.21	yellow cr.

[a] This complex was unstable.

layer of silicagel. The solution was concentrated and at −80 °C small orange crystals were obtained. The yield was 6.5 g (66%).

(dpm)Rh(ET)$_2$

To a mixture of 4.73 g (12 mmol) of [RhCl(ET)$_2$]$_2$ ether (60 ml) and 4.93 mol (24 mmol) of H(dpm), which was cooled to −25 °C, a solution of 5 g of KOH in 15 ml of water was added dropwise. Another 60 ml of ether was added and the mixture was kept at 0 °C while stirring for one hour. The ether and aqueous layers were separated. The ether solution was filtered, the ether was evaporated and the solid residue was dissolved in pentane. The solution was forced through a layer of silicagel. At −40 °C small yellow crystals were obtained. The yield was 7.2 g (88%).

(β-diket)Rh(olefin)$_2$; olefin = MA, VA, ST

These complexes were prepared by dissolving (β-diket)Rh(ET)$_2$ in the freshly distilled liquid olefin, which reacted immediately. The excess olefin was evaporated and the remaining solid was dissolved in pentane. The solution was forced through a layer of silicagel and at low temperatures (−20 to −80 °C) crystals were isolated. (tfac)Rh(MA)$_2$ was unstable in solution and decomposed into a yellow solid which was insoluble in pentane.

(β-diket)Rh(PR)$_2$ and (β-diket)Rh(VCl)$_2$

At −80 °C equal amounts of CH_3Cl and PR, or at −40 °C VCl, were condensed on the complex (β-diket)Rh(ET)$_2$ till all crystals were dissolved. The mixture was stirred at room temperature in an open round bottom until the olefin (and CH_3Cl) had evaporated. The procedure was repeated twice. The remaining solid or oil was dissolved in pentane, forced through a layer of silicagel, after which the solution was concentrated. Crystals were obtained at low temperature (−20 to −80 °C) except for (dpm)Rh(PR)$_2$ which remained as an oil. The yellow crystals of (tfac)Rh(VCl)$_2$ formed a red oil at room temperature. (dpm)Rh(PR)$_2$ and (tfac)Rh(VCl)$_2$ are unstable.

(β-diket)Rh(CO)$_2$

These complexes were obtained by passing CO through a solution of (β-diket)Rh(ET)$_2$ in hexane for one hour.

Results and Discussion

Vibrational Spectra

According to the bond model of Dewar, Chatt and Duncanson [14] the double bond character of an olefin decreases upon coordination. This decrease is

TABLE II. Frequencies and Percentage Lowerings of the Vibrational Bands I, II and III[a,b,c,d,e].

	ET					PR							VA						
	I		II		SPL	I		II		III		SPL	I		II		III		SPL
free	1623		1342			1648		1415		1297			1647		1386		1295		
dpm	1512	*6.84*	1225	*8.72*	*15.6*	1502	*8.86*	1397	*1.27*	1246	*3.93*	*14.1*	1499	*8.99*	1364	*1.59*	1248	*3.63*	*14.2*
acac	1513	*6.78*	1231	*8.27*	*15.1*	1503	*8.80*	1395	*1.41*	1246	*3.93*	*14.1*	1497	*9.11*	1373	*0.94*	1243	*4.02*	*14.1*
tfac	1515	*6.65*	1231	*8.27*	*14.9*	1508	*8.50*	1398	*1.20*	1245	*4.01*	*13.7*	1499	*8.99*	1366	*1.44*[f]	1250	*3.47*	*13.9*[f]
															1362	*1.73*			*14.2*

	VCl							ST							MA						
	I		II		III		SPL	I		II		III		SPL	I		II		III		SPL
free	1612		1374		1281			1632		1414		1305			1633		1402		1283		
dpm	1459	*9.49*	1309	*4.73*	1229	*4.06*	*18.3*	1515	*7.17*	1401	*0.92*	1256	*3.75*	*11.8*	1501	*8.08*	1398	*0.29*	1236	*3.66*	*12.0*
acac	1466	*9.05*	1316	*4.22*[g]	1242	*3.12*	*16.4*	1513	*7.29*	1403	*0.78*	1253	*3.98*	*12.1*	1498	*8.27*	1394	*0.57*	1245	*2.96*	*11.8*
tfac	1464	*9.18*	1309	*4.73*	1230	*3.98*	*18.2*	1516	*7.11*	1402	*0.85*	1257	*3.68*	*11.6*	1508	*7.65*	1394	*0.57*	1245	*2.96*	*11.2*

[a] Bands I, II and III represent the coupled modes ν(C=C), $\delta(CH_2)_{scis}$ and $\delta(CH)_{bend}$ [6]. [b] Only Raman data were used. However, it was not possible to obtain Raman spectra of the dark red complexes (dpm)Rh(CO)$_2$ and (tfac)Rh(CO)$_2$. [c] Percentage lowerings are in italics, SPL = summed percentage lowering. [d] Data for the free olefins are from ref. 6, 16 and ref. therein. [e] Data for the complexes (acac)Rh(olefin)$_2$ from ref. 5. [f] Two bands are possible, one of these belongs to the (tfac)Rh moiety. [g] Assignment different from that in ref. 5, the bands that could not be assigned (*e.g.* 1316 cm^{-1} for (acac)Rh(VCl)$_2$ and 1300 cm^{-1} for (acac)Ir(VCl)$_2$) will probably be band II. See text.

reflected in ν(C=C). This vibration, however, is coupled to $\delta(CH_2)_{scis}$ and/or $\delta(CH)_{bend}$ depending on the type of olefin [15].

Powell *et al.* [1, 2] have shown that the summed percentage lowering (SPL) of ν(C=C) and $\delta(CH_2)_{scis}$ in M-ET d^8 complexes is a measure for the decrease in double bond character. For a monosubstituted olefin the $\delta(CH)_{bend}$ has to be included in the summation of ν(C=C) and $\delta(CH_2)_{scis}$ [16] which also has been done for our complexes.

The infrared spectra of the compounds are complicated because many modes of both the (β-diket)Rh moiety (*e.g.* νCC, νCO) and of the olefin absorb in the same frequency region. On the other hand, in the Raman spectra bands belonging to the ring vibrations are weak compared to the olefinic bands I, II and III which are assigned to the coupled modes ν(C=C), $\delta(CH_2)_{scis}$ and/or $\delta(CH)_{bend}$. This assignment is based on the comparison of the Raman and infrared spectra with those of the (acac)Rh(olefin)$_2$ and (acac)Ir(olefin)$_2$ series [5] and with those of (β-diket)Rh(CO)$_2$.

In Table II the positions of the three bands I, II and III and the SPL are given for the series (dpm)-Rh(olefin)$_2$ and (tfac)Rh(olefin)$_2$ together with previous results for (acac)Rh(olefin)$_2$.

In the case of the (dbm)Rh(olefin)$_2$ series only vibrations of the (dbm)Rh moiety were observed. No difference was found between both olefins in the spectra of the asymmetric (tfac)Rh(olefin)$_2$ series.

The position of band II in (β-diket)Rh(VCl)$_2$ is difficult to assign because the (acac)Rh, (acac)Ir and (tfac)Rh moieties possess a band at a frequency (1366–1370 cm^{-1}) where also band II of VCl is expected [5]. However, neither the (dpm)Rh moiety nor (dpm)Rh(VCl)$_2$ show a band in this region, which implies that the band at about 1310 cm^{-1} will probably be band II. Accordingly the SPL seems to be rather high in the case of VCl.

Generally the order of the SPL is dpm > acac > tfac, but it is discontinuous for (acac)Rh(VCl)$_2$ and (acac)Rh(ST)$_2$ which might indicate that the influence of the substituent on the β-diketone on the SPL (uncertainty estimated at about 0.1%) depends on the nature of the olefin. In general the electron releasing t-Bu groups in dpm cause an increase and the electron withdrawing CF$_3$ group in tfac a decrease of the SPL.

Table III shows that the difference in $\bar{\nu}$(CO) between (tfac)Rh(CO)$_2$ and (dpm)Rh(CO)$_2$ is of the same order as for (acac)Rh(CO)$_2$ and (acac)Ir(CO)$_2$, so it seems likely that this is also the case for the π back-bonding. The difference in SPL between (tfac)-Rh(olefin)$_2$ and (dpm)Rh(olefin)$_2$ is, however, much smaller (0.2 to 0.8%) than between (acac)Rh(olefin)$_2$ and (acac)Ir(olefin)$_2$ (1.1 to 3.0%) which difference has been attributed to an increase of both σ- and π-

TABLE III. ν(CO) Frequencies of (β-diket)M$(CO)_2$[a].

	ν(CO)	(cm^{-1} in hexane)
(dpm)Rh$(CO)_2$	2078(s)	2009(s)
(acac)Rh$(CO)_2$	2082(s)	2011(s)
(tfac)Rh$(CO)_2$	2091(s)	2021(s)
(acac)Ir$(CO)_2$	2073(s)	1999(s)

[a] This work, partly also published by Bonati *et al.* [11, 17].

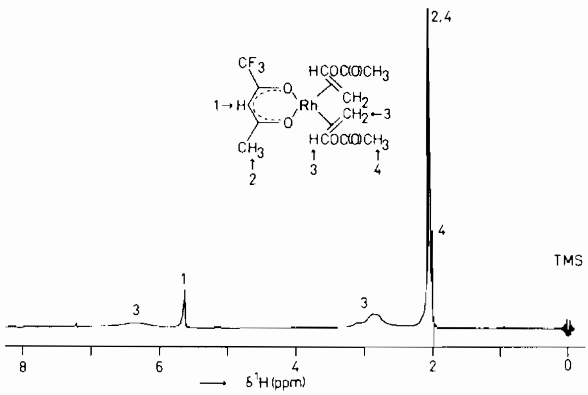

Figure 1. ^{1}H NMR spectrum of (tfac)Rh$(VA)_2$ in $CDCl_3$ at 25 °C.

back-bonding [5]. So in going from tfac to dpm mainly the π-back-bonding seems to be enhanced.

^{1}H NMR Spectra

At 25 °C the (β-diket)Rh$(ET)_2$ ^{1}H NMR spectra (Table IV) show one resonance for the olefinic protons. The other olefinic complexes give broad resonances (Table IV, Fig. 1) for the olefinic protons, caused by proton coupling and the presence of a large number of isomers as could be concluded from ^{13}C NMR spectra (*vide infra*) and from the ^{1}H spectra of (β-diket)Rh$(PR)_2$ and (β-diket)Rh$(ST)_2$ (three PR-methyl and two β-diket-methyl signals respectively). No ^{103}Rh–^{1}H coupling was observed.

The olefinic resonances are broad, which in some cases prevented their detection. Although the other olefinic resonances given in Table IV are not assigned, it can be seen that the chemical shifts of the olefinic protons depend on the type of β-diketone. The order of the upfield shift upon coordination is dpm ~ acac > tfac > dbm for all olefins, which indicates that differences in charge on the respective (β-diket) ring are transmitted to the olefin. Phenyl rings can act either as electron donor or as an acceptor [18] but from the order in shift of the olefinic protons it can be concluded that in the complexes (dbm)Rh(olefin)$_2$ they must act as electron acceptor.

Table IV shows that the influence of the olefin on the (β-diket) ring is reflected in δH_γ, which decreases according to CO > MA > VCl > ET > VA > PR > ST, the maximum difference amounting to 0.48 ppm. In Fig. 2 δH_γ is plotted against the e-value of the olefins, which is a measure for the polarization of the olefinic bond by the substituent. An electron accepting substituent causes a high e-value, an electron donating substituent a lower one [19].

For all β-diketones the plots are linear and do not depend on the solvent although the shifts differ. Apparently shifts of δH_γ are caused by the charge transmitted from the olefin to the (β-diket) ring via

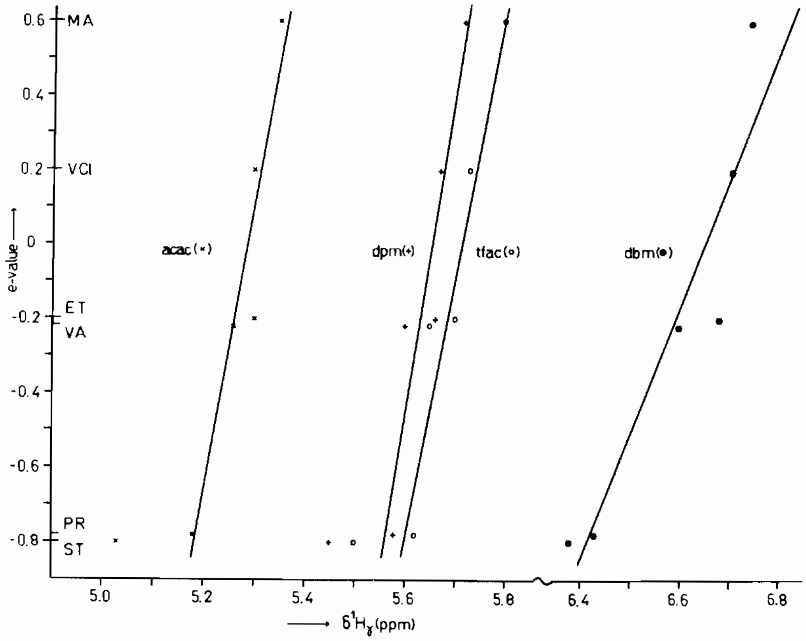

Figure 2. Plot of e-value of the olefin (ref. 19) *versus* δ^1H_γ (ppm) of the complexes (β-diket)Rh(olefin)$_2$.

TABLE IV. Proton spectra of (β-diket)Rh(olefin)$_2$ in CDCl$_3$[a].

	(dpm)Rh(olefin)$_2$				(acac)Rh(olefin)$_2$				tfacRh(olefin)$_2$				dbmRh(olefin)$_2$			
	(dpm)	ring	olefin		(acac)	ring	olefin		(tfac)	ring	olefin		(dbm)	ring		
	H_γ	methyl	olefinic[b]	other	H_γ	methyl	olefinic[b]	ohter	H_γ	methyl	olefinic[b]	other	H_γ	phenyl[c]	olefinic	other[b]
ET	5.66	1.13	2.92		5.30	1.97	2.90		5.70	2.10	3.00		6.68	7.45	3.12	
PR	5.58	1.10	3.13	1.55	5.18	1.87	3.23	1.50	5.62	2.03	3.37	1.50	6.43	7.42	3.50	1.67
			3.08	1.45			3.03	1.40			3.15	1.42			3.30	1.57
			2.87	1.40			2.90	1.33			3.03	1.40			3.15	1.52
			2.75				2.65				2.73				2.98	
VCl	5.67	1.13	3.40		5.30	1.98	3.42		5.73	2.15	3.47		6.71	7.42		
VA	5.60	1.10	2.87	2.05	5.26	1.93	2.88	2.08	5.65	2.08[d]	2.88	2.08[d]	6.60	7.42	2.98	2.05
				2.00				2.05				2.03				1.98
MA	5.72	1.10	3.95	3.67	5.35	1.98	3.93	3.68	5.80	2.20	4.00	3.70	6.75	7.47	4.47	3.65
				3.63								3.66			4.17	
ST	5.45	1.00	3.73	7.17	5.03	1.76	3.70	7.18	5.50	1.93	3.86	7.30	6.38	7.37	3.90	e
		0.97	3.50			1.72	3.50			1.88	3.65				3.68	
			3.23				3.18				3.32				3.37	
CO	5.88	1.15			5.47	1.98			5.98	2.17			6.80	7.40		

[a] The chemical shifts were measured at room temperature relative to TMS and are reported in the δ scale. [b] Broad resonances; the amount of resonances is not always complete, therefore only the resonances that occur for each β-diketone are reported. [c] The phenyl resonances are positioned in two multiplets from 7.1 to 8.0 ppm; here the most intense peak is reported. [d] Resonances coincide. [e] Not possible to determine because of overlap with the (dbm) ring resonances.

TABLE V. Carbon-13 NMR of (β-diket)Rh(olefin)$_2$ in CDCl$_3$[a].

	olefin								(β-diket) ring									
	δC_1				δC_2				δCO			δCH			δCH_3		δtBu	δCF_3[c]
	free[b]	dpm	tfac	dbm	free[b]	dpm	tfac	dbm	dpm	tfac	dbm	dpm	tfac	dbm	dpm	tfac	dpm	tfac
ET	122.8	59.3	60.6	59.9	122.8	59.3	60.6	59.9	196.2	194.0	181.3	89.2	94.5	93.3	28.5	28.4	40.6	118.4
PR	115.0	62.0	61.9	61.6	131.1	72.4	75.0	74.0	195.3	193.2	180.9	89.2	94.5	93.3	28.8	28.3	40.7	118.4
VCl	117.4	59.5	61.0	60.0	126.1	79.2	83.2	82.6	196.2	194.6	181.1	89.6	95.0	93.2	28.6	28.5	40.8	118.2
VA	96.4	43.7	44.1	44.5	141.7	97.5	98.5	98.5	195.7	194.5	181.0	89.2	94.8	93.1	28.3	28.3	40.6	d
MA	129.9	61.4	62.5	62.2	128.7	61.4	62.5	62.2	196.1	194.5	181.0	89.4	94.9	93.0	28.4	28.2	40.6	117.8
ST	112.3	50.0	54.4	55.3	135.8	73.4	75.6	74.4	195.1	192.8	181.0	89.2	94.2	93.6	28.5	28.9	40.6	d

[a] The chemical shifts were measured at room temperature relative to TMS, using $\delta_{TMS} = \delta_{CDCl_3} - 76.9$ ppm. The given shifts are mean positions, see text. [b] Ref. 20. [c] $^1J(^{13}C-^{19}F) = 284$ Hz for all complexes. [d] Not found.

the metal. Accordingly, CO, which is known to be a very good π-acceptor, leaves the lowest charge on the ring while ST gives the highest one.

Deviations from linearity are found for the complexes (dbm)Rh(olefin)$_2$ and (β-diket)Rh(ST)$_2$. Bonati *et al.* [11] concluded that conjugation of the phenyl rings with the chelated ring makes back donation more difficult. So in the complex (dbm)Rh(MA)$_2$ back donation may be smaller than expected from the e-value. Probably the phenyl ring in ST also prevents the acceptance of charge via back bonding which may explain the high field position of the Hγ resonance for the ST complexes.

The proton shifts of the methyl groups in (acac)Rh(olefin)$_2$, (tfac)Rh(olefin)$_2$ and (dpm)Rh(olefin)$_2$ show the same trend as δH_γ although the differences are much smaller. This order is also found for the shift of the most intense peak of the multiplet arising from the phenyl protons in the (dbm)Rh(olefin)$_2$ complexes.

^{13}C *NMR Spectra*

The ^{13}C NMR resonances of the carbon atoms of the (β-diket) ring (Table V) are only slightly influenced by the nature of the olefin and no relation could be found between $\delta^{13}C_\gamma$ and the e-value of the olefin.

The olefinic resonances in (β-diket)Rh(ET)$_2$ are broad (halfwidth 20 Hz at 25 °C) and ^{103}Rh–^{13}C coupling (14 Hz) could not always be observed. The other complexes showed several broad resonances for each olefinic carbon atom because of the large number of isomers [5]. Since tfac is asymmetric, the spectra of (tfac)Rh(PR)$_2$ and (tfac)Rh(VA)$_2$ showed even more resonances, due to the larger amount of possible isomers.

The data for the olefinic carbon atoms in Table V represent the weighted mean of all resonances. Except for the MA complexes, where δC_1 and δC_2 were not sufficiently separated, the resonance at lower field belongs to the substituted olefinic carbon atom C$_2$ and the resonance at higher field to C$_1$ [6].

In Table VI the mean chemical shifts of the olefinic carbon atoms are given together with the mean upfield shifts upon coordination, $\delta^{13}(C_2–C_1)$ and the difference of the latter two quantities compared to the complexes (acac)Rh(olefin)$_2$.

The influence of substituents on the (β-diket) ring on the olefinic resonances is small. Generally the order of the mean upfield shift of the carbon resonances is dpm > acac > dbm > tfac which has also been found for (β-diket)Ir(COD) [9]. The VA complexes do not agree with this order. However, in view of the uncertainty in the calculation of $\delta^{13}C_{mean}$ values it can not be concluded whether or not the VA complexes deviate from the other olefin complexes.

The order of the upfield shift of the olefinic protons is tfac > dbm, whereas the order of the olefinic

TABLE VI. Mean Shifts of Olefinic Carbon Atoms and Chemical Shift Differences After Coordination (in ppm).

	$\delta^{13}C_{mean}$[a]					$\Delta\delta^{13}C_{mean}$[c]				$\Delta\delta^{13}C_{mean} - \Delta\delta^{13}C_{mean}^{(acac)}$			$\delta^{13}(C_2–C_1)$					$\delta^{13}(C_2–C_1) - \delta^{13}(C_2–C_1)_{(acac)}$		
	free	dpm	acac[b]	tfac	dbm	dpm	acac	tfac	dbm	dpm	tfac	dbm	free	dpm	acac	tfac	dbm	dpm	tfac	dbm
VA	119.0	70.6	70.2	71.3	71.5	48.4	48.8	47.7	47.5	–0.4	–1.1	–1.3	45.3	55.1	55.5	54.4	54.0	–0.4	–1.1	–1.5
VCl	121.8	69.4	71.2	72.1	71.3	52.4	50.6	49.7	50.5	+1.8	–0.9	–0.1	8.7	18.7	21.3	22.2	22.6	–2.6	+0.9	+1.3
PR	124.0	67.2	67.2	68.5	67.8	56.8	56.8	55.5	56.2	0	–1.3	–0.4	18.1	11.0	11.6	13.1	12.4	–0.6	+1.5	+0.8
ST	124.0	61.7	64.1	65.0	64.9	62.3	59.9	59.0	59.1	+2.4	–0.9	–0.8	23.5	19.2	19.7	21.2	19.1	–0.5	+1.5	–0.6
ET	122.8	59.3	59.4	60.6	59.9	63.5	63.4	62.2	62.9	+0.1–	–1.2	–0.3	0	0	0	0	0	0	0	0
MA	129.3	61.4	61.4	62.5	62.2	67.9	67.7	66.8	67.1	+0.2	–0.9	–0.6	–1.2							

[a] $\delta^{13}C_{mean} = ½(\delta^{13}C_1 + \delta^{13}C_2)$. [b] From ref. 5. [c] $\Delta\delta^{13}C_{mean} = \delta^{13}C_{mean}(ligand) - \delta^{13}C_{mean}(complex)$.

carbon atoms is dbm > tfac. This difference can be caused by anisotropy effects exerted by the two phenyl rings on the protons [9]. However, the largest value of this anisotropy effect is estimated to be about 0.05 ppm [9] whereas for the ET, PR and MA complexes the difference in mean olefinic proton shift between (dbm)Rh(olefin)$_2$ and (tfac)Rh(olefin)$_2$ is more than 0.1 ppm and thus exceeds this maximum value. This cannot be explained.

From the ^{13}C spectra of some PR complexes it was suggested that $\delta^{13}(C_2–C_1)$ decreases with increasing π back-bonding and increases with increasing σ-bonding [21]. We found [5] that PR and ST showed an increase of $\delta^{13}(C_2–C_1)$ when they were coordinated to Pt(II) and a decrease when they were coordinated to Rh(I) and Ir(I). VCl and VA, however, showed an increase in $\delta^{13}(C_2–C_1)$ when coordinated to Pt(II), Rh(I) and Ir(I).

Table VI shows that for PR, ST and VCl $\delta^{13}(C_2–C_1)$ decreases according to tfac > acac > dpm. As $\delta^{13}(C_2–C_1)$ decreases with an electron donating substituent and increases with an electron accepting substituent on the **β-diketone** this confirms that $\delta^{13}(C_2–C_1)$ is sensitive to an increasing π back-bonding and/or a decreasing σ-donation.

According to the relationship between δH_γ and the e-value it can be expected that VA and VCl, compared to PR and ST, have (i) stronger π back-bonding to the metal or (ii) have a weaker σ bond or (iii) have both. From this it can be concluded that for VA and VCl, compared to PR and ST, $\delta^{13}(C_2–C_1)$ should decrease upon coordination. The fact that $\delta^{13}(C_2–C_1)$ increases may originate from an ionic resonance structure [3] although this should be reflected in δH_γ, or from steric influences which, however, should be the same for VCl and PR.

In comparison to the complexes (acac)Rh(olefin)$_2$, $\delta^{13}(C_2–C_1)$ for the complexes (dbm)Rh(olefin)$_2$ is more complex, but, as already concluded from the relationship between δH_γ and the e-value, the metal–olefin bond in these complexes is not only dependent on the polarisation of the olefin.

Conclusions

The NMR parameters as well as the SPL of the coupled modes $\nu(C{=}C)$, $\delta(CH_2)_{scis}$ and/or $\delta(CN)_{bend}$ show that the π back-bonding component in the complexes (β-diket)Rh(olefin)$_2$ decreases according to dpm > acac > dbm ~ tfac. There is a linear relation between δH_γ and the polarisation in the C=C bond of the olefin, which is reflected by its e-value. The irregularities in this relationship and in $\delta^{13}(C_2–C_1)$ for the complexes (dbm)Rh(olefin)$_2$ and the irregularities in the SPL may indicate that the influence of the substituents on the β-diketone depends on the nature of the olefin.

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