

Vibrational and NMR Spectroscopic Studies on (acac)*M*(substituted olefin)₂ (*M* = Rh(I), Ir(I))

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*Spectroscopic studies (IR, Raman and ¹³C NMR) on the complexes (acac)*M*(olefin)₂ (*M* = Rh(I), Ir(I); olefin = ethylene, propylene, vinyl chloride, vinyl acetate, methyl acrylate and styrene) have been carried out and are used to interpret the bonding between the metal and the olefin. The metal-olefin bond is stronger for Ir than for Rh but the influence of the substituent on the olefin is the same.*

Introduction

Reports have recently appeared on the influence of substituents on the olefinic group on the bonding between a metal atom and a substituted olefin. Cooper *et al.* [1] and Meester *et al.* [2, 3] have reported vibrational and NMR spectroscopic data for a large number of Pt(II)-olefin complexes, while Tolman *et al.* [4] have published ¹³C NMR data for Ni(0) compounds.

In this laboratory work is being carried out on the correlation of thermochemical data concerning the metal-ligand bond with vibrational (IR and Raman) and NMR data (¹³C) [5]. In particular, we are interested in complexes of the type (acac)*M*(CH₂=CHX)₂ (*M* = Rh(I), Ir(I); CH₂=CHX = ethylene (ET), propylene (PR), vinyl chloride (VCl), vinyl acetate (VA), methyl acrylate (MA) and styrene (ST)), and also their relation to the dicarbonyl complexes, (acac)*M*(CO)₂. In this article the vibrational and NMR spectroscopic data are reported and used for a discussion of the metal-olefin bond. In a following article the thermochemical data will be reported and discussed in the light of the present findings.

Experimental

Preparations

Olefin complexes

(acac)Rh(ET)₂ and (acac)Ir(ET)₂ were prepared according to literature methods [6, 7]. The other complexes were obtained by displacement of ET in the

complexes (acac)Rh(ET)₂ or (acac)Ir(ET)₂ by an excess of olefin, following a procedure described by Cramer [8]. With the exception of PR the undiluted olefin was used as the solvent. In order to prevent polymerisation, the liquid olefin was distilled directly before use. After reaction, the excess of olefin was removed under vacuum and the resulting oil or solid dissolved in ether or pentane. The solution was forced through a layer of silicagel (Merck 0.063–0.200 mm). At low temperature (–20 to –80 °C) crystals were obtained and isolated by filtration. All reactions were carried out under dry, oxygen-free nitrogen.

All complexes are bright yellow as a powder, but they darken to orange when the crystals become larger. The PR and VCl complexes easily form oils. The complexes could be kept without decomposition for about a month at –20 °C except for (acac)Ir(PR)₂ which decomposes within a week.

Dicarbonyl complexes

The complexes (acac)Rh(CO)₂ and (acac)Ir(CO)₂ were not prepared according to literature methods [9, 10] but by passing CO through a solution of (acac)-*M*(ET)₂ in hexane for one hour. The precipitate was filtered off and recrystallised from warm hexane.

The analytical data are listed in Table I.

Spectroscopic Measurements

Infrared spectra of the solid compounds (KBr pellets) were recorded on a Beckman 4250 spectrophotometer. Raman spectra of the solid compounds were obtained using a Coderg PH1 spectrophotometer with dc detection. The 6471 Å line of a CRL 52 Kr⁺ laser was used as the exciting line. The dicarbonyl complexes and (acac)Ir(VCl)₂ decomposed in the laser beam, even at –190 °C. Raman spectra of solutions gave poor results. ¹³C NMR spectra were measured in CDCl₃ at 20 MHz on a Varian CFT 20 spectrometer with full proton decoupling. For most compounds 40,000 pulses (A.T. = 1 sec, P.D. = 0.8 sec) were necessary to give reasonable spectra. ¹³C chemical shifts were measured relative to CDCl₃ and are reported in ppm downfield from TMS using δ_{TMS} = δ_{CDCl₃} – 76.9 ppm.

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TABLE I. Analytical Data for (acac)M(olefin)₂ and (acac)M(CO)₂.

Olefin	(acac)Rh(olefin) ₂						(acac)Ir(olefin) ₂					
	%C		%H		%O		%C		%H		%O	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
ET	41.88	41.82	5.86	5.90	12.40	12.32	31.12	31.17	4.35	4.37	9.21	9.38
PR	46.16	45.89	6.69	6.75	11.18	11.69	35.19	35.25	5.10	5.01	—	—
VCl ^a	33.06	33.12	4.01	4.04	10.22	10.05	25.97	26.04	3.15	3.32	7.69	7.84
VA	41.73	41.73	5.12	5.15	25.57	25.39	33.69	33.84	4.13	4.19	20.71	20.63
MA	41.73	41.70	5.12	5.20	25.57	25.60	33.69	34.00	4.13	4.28	20.71	20.55
ST	61.47	61.48	5.65	5.81	—	—	50.49	50.48	4.64	4.74	6.48	6.54
CO	32.58	32.45	2.73	2.69	24.80	24.79	24.21	24.04	2.03	2.08	18.43	18.48

^a For (acac)Rh(VCl)₂; % Cl: calc. 21.68; found 21.63.

For (acac)Ir(VCl)₂; % Cl: calc. 17.03; found 16.79.

Results

Vibrational Results

The infrared and Raman data for the Rh and Ir complexes in the region 1200–1600 cm⁻¹ are collected in Tables II and III respectively. A typical Raman spectrum is shown in Fig. 1.

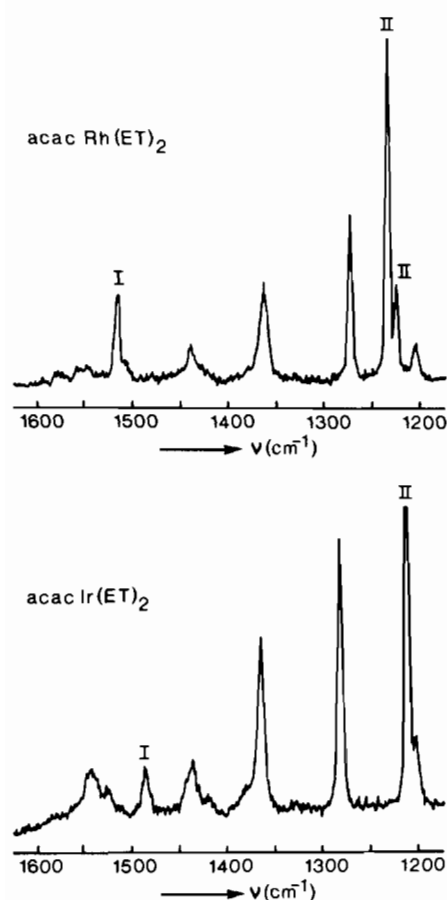


Figure 1. Raman spectra of (acac)M(ET)₂ for the solid state.

By comparing the spectra of different olefin complexes both with each other and with spectra of (acac)Rh(CO)₂ and (acac)Ir(CO)₂ it was established that only three vibrations of the olefin shift significantly upon coordination. The frequencies in italics belong to the acetylacetonate ring. The three bands which shift belong to the coupled modes $\nu(\text{C}=\text{C})$, $\delta(\text{CH}_2)_{\text{scis}}$ and $\delta(\text{CH})_{\text{bend}}$, and are labelled I, II and III in accordance with the notation of Powell *et al.* [11].

NMR Results

The ¹³C NMR data of the complexes are given in Table IV and a typical spectrum is shown in Fig. 2. The shifts of the carbon atoms of the acetylacetonate ring do not show appreciable variation with olefin and the shifts of the olefin-substituent carbon atoms do not change greatly upon coordination. The C₂ and C₄ carbon atoms of the acetylacetonate ring occur as doublets or multiplets in some cases. It is assumed that the resonance at lower field belongs to the substituted olefinic carbon atom C₂ and the resonance at higher field belongs to C₁ [3]. In the case of MA δC_1 and δC_2 were not sufficiently separated, since the resonances were broad. For the same reason off-resonance spectra did not give additional information. At room temperature, the olefinic carbon atoms show rather broad ¹³C resonances with a halfwidth varying from 20 Hz in the ET complexes to 50 Hz in the ST complexes, regardless of the metal. The spectra of the complexes of PR, VA and VCl clearly show more than one resonance for each olefinic carbon atom, which, in the case of (acac)Rh(PR)₂, is probably due to the presence of two isomers [13].

When cooled to -60 °C, the olefinic carbon resonances in (acac)Rh(VCl)₂ sharpened and six doublets for each olefinic carbon atom were found. These doublets are due to the ¹⁰³Rh-¹³C coupling which varies from 14.9 to 17.2 Hz. At -60 °C the C₂

TABLE II. Vibrational Data of (acac)Rh(olefin)₂ and (acac)Rh(CO)₂ (1200–1600 cm⁻¹),^{a,b,c}.

ET	PR		VCI		VA		MA		ST		CO	
	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR
1576(vs)	1576(vw)	1581(vs)		1578(vs)					1601(sh, m)		1601(vs)	1582(s)
1558(vs)	1552(vw)		1565(sh)	1566(vw)	1564(vs)		1564(vs)		1587(s)	1569(vs)		1562(vs)
1526(vs)		1548(sh)		1524(vs)	1523(vs)		1524(vs)		1529(vs)		1513(vs)	1525(vs)
1506(sh)	1510(sh, w)	1503(sh)		1497(s)	1497(m)		1505(sh)		1488(s)			
1438(sh)	1442(m)	1450(sh, m)	1463(m)	1466(m)			1490(sh)		1450(m)			
1426(s)		1430(m)	1432(m)	1437(w)	1427(s)		1437(s)		1447(m)		1446(w)	
1373(sh)		1396(sh)					1396(s)		1430(br)		1403(s)	1428(m)
1363(vs)	1365(vs)	1387(vs)	1377(s)	1369(vs)	1374(vs)		1366(s)		1400(sh)			
		1364(s)	1362(sh)	1362(m)	1365(sh)		1366(s)		1379(vs)		1366(vw)	1380(vs)
			1312(m)	1316(m)					1330(m)		1330(m)	1363(vs)
1270(s)	1274(s)	1272(s)	1277(m)	1281(s)	1291(w)		1277(s)		1274(s)		1296(s)	1276(s)
1236(s)	1235(vs)	1245(m)	1236(w)	1241(vs)	1272(s)		1242(sh)		1251(m)			
1225(m)	1227(m)				1244(s)		1230(m)		1253(vs)			
1203(m)	1206(w)	1200(m)	1201(w)	1201(w)	1205(vs)		1200(vs)		1201(m)			1202(m)

^a IR spectra were recorded as KBr pellets; Raman spectra were recorded for the solid compounds. ^b vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. ^c The bands in italics are assigned to the acetylacetonate ring.

TABLE III. Vibrational Data of (acac)Ir(olefin)₂ and (acac)Ir(CO)₂ (1200–1600 cm⁻¹),^{a,b,c}.

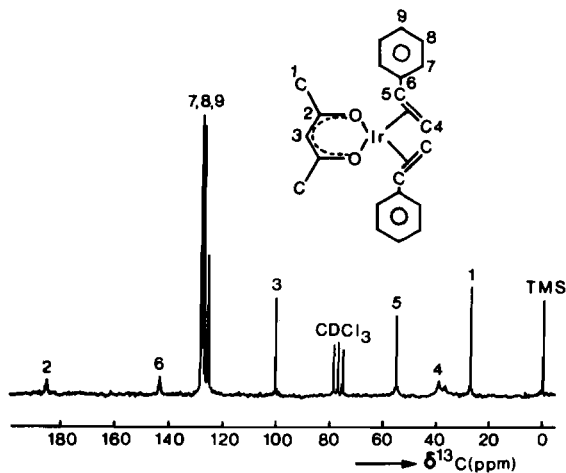
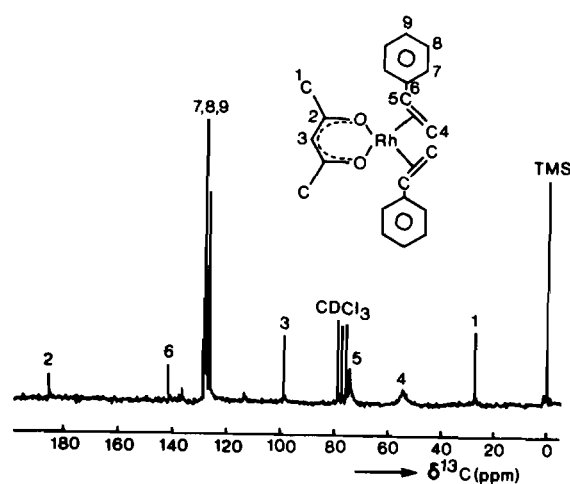
ET	PR		VCI		VA		MA		ST		CO	
	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR
<i>1576</i> (sh)		<i>1570</i> (vs)	<i>1584</i> (vw)	<i>1568</i> (vs)		<i>1573</i> (vs)				<i>1604</i> (m)	<i>1605</i> (vs)	
<i>1554</i> (vs)		<i>1555</i> (m)					<i>1557</i> (vs)		<i>1560</i> (vs)		<i>1566</i> (w)	<i>1566</i> (vs)
<i>1538</i> (vs)	<i>1542</i> (m)	<i>1540</i> (sh)	<i>1539</i> (vs)	<i>1538</i> (vs)			<i>1533</i> (vs)		<i>1526</i> (vw)	<i>1533</i> (vs)		<i>1538</i> (vs)
	<i>1524</i> (w)	<i>1529</i> (s)									<i>1505</i> (s)	
<i>1487</i> (sh, w)	<i>1486</i> (m)	<i>1485</i> (w)	<i>1490</i> (m)		<i>1475</i> (s)		<i>1481</i> (s)		<i>1485</i> (s)	<i>1504</i> (m)		
				<i>1455</i> (w)					<i>1458</i> (w)	<i>1448</i> (w)		
<i>1430</i> (m)	<i>1436</i> (m)	<i>1430</i> (m)	<i>1432</i> (m)	<i>1433</i> (w)	<i>1430</i> (s)		<i>1437</i> (s)		<i>1430</i> (br)			<i>1430</i> (m)
		<i>1392</i> (sh)	<i>1392</i> (w)				<i>1398</i> (s)		<i>1395</i> (m)			<i>1400</i> (m)
		<i>1378</i> (s)		<i>1370</i> (s)	<i>1375</i> (vs)		<i>1391</i> (s)			<i>1393</i> (sh)		<i>1383</i> (m)
<i>1368</i> (s)	<i>1364</i> (s)	<i>1361</i> (m)	<i>1362</i> (s)		<i>1363</i> (vs)		<i>1363</i> (sh)		<i>1370</i> (m)	<i>1372</i> (vs)		<i>1370</i> (m)
							<i>1354</i> (m)			<i>1331</i> (w)		
				<i>1300</i> (sh)						<i>1312</i> (w)		<i>1314</i> (m)
<i>1281</i> (s)	<i>1282</i> (vs)	<i>1279</i> (s)	<i>1280</i> (s)	<i>1288</i> (s)	<i>1280</i> (s)		<i>1283</i> (s)		<i>1289</i> (m)	<i>1282</i> (s)		<i>1278</i> (m)
		<i>1261</i> (sh)								<i>1263</i> (vw)		<i>1266</i> (w)
										<i>1248</i> (sh)		
										<i>1241</i> (m)		
											<i>1248</i> (m)	
<i>1216</i> (s)	<i>1212</i> (vs)											
<i>1205</i> (s)	<i>1203</i> (s)	<i>1200</i> (m)	<i>1203</i> (w)				<i>1197</i> (s)		<i>1200</i> (m)	<i>1200</i> (w)		<i>1208</i> (w)

^a IR spectra were recorded as KBr pellets; Raman spectra were recorded for the solid compounds. ^b vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. ^c The bands in italics are assigned to the acetylacetonate ring.

TABLE IV. Carbon-13 NMR of (acac)M(olefin)₂, M = Rh, Ir, in CDCl₃^a.

Olefin	δC ₁						δC ₂						δCO		δCH		δCH ₃	
	Free ^b		Rh		Ir		Free		Rh		Ir		Rh	Ir	Rh	Ir	Rh	Ir
ET	122.8	59.4	40.9	122.8	59.4	40.9	122.8	59.4	40.9	186.4	186.7	98.9	100.9	27.1	27.4			
PR	115.0	61.4	46.7 ^c	131.1	73.0	54.6 ^c	131.1	73.0	54.6 ^c	185.7	185.6 ^c	98.7	101.2 ^c	27.1	27.4 ^c			
VCl	117.4	60.5	41.0	126.1	81.8	60.7	126.1	81.8	60.7	186.6	186.8	99.1	101.2	27.0	26.8			
VA	96.4	42.4	27.9	141.7	97.9	78.2	141.7	97.9	78.2	186.3	186.6	99.1	101.1	26.9	27.1			
MA	129.9	61.4	42.0	128.7	61.4	42.0	128.7	61.4	42.0	186.2	187.1	98.9	101.1	26.8	27.2			
ST	112.3	54.2	38.3	135.8	73.9	55.1	135.8	73.9	55.1	185.5	185.2	98.4	100.3	26.9	27.0			

^a The chemical shifts were measured at room temperature relative to TMS, using $\delta_{\text{TMS}} = \delta_{\text{CDCl}_3} - 76.9$ ppm. The given shifts are mean positions, see text. ^b Ref. 12. ^c Spectra at -40 °C.

Figure 2. ¹³C NMR spectra of (acac)M(ST)₂ in CDCl₃.

and C₄ carbon atoms of the acetylacetonate ring give six resonances for (acac)Rh(VCl)₂. This agrees with the ten isomers, eight of which form four enantiomeric pairs, as described by Herberhold *et al.* [14].

For the above reasons shifts of the olefinic carbon atoms in Table IV represent the weighted mean of all resonances. ¹⁰³Rh–¹³C coupling at room temperature is also clearly observed in the ET, PR and VA spectra.

The mean upfield shifts of the olefinic carbon atoms upon coordination varies from 49–68 ppm for the Rh compounds, which does not agree with the upfield shift of 86 ppm for (acac)Rh(ET)₂ reported by Bodner *et al.* [15].

For the Ir compounds the mean upfield shifts upon coordination are 67–87 ppm. To our knowledge only Bonnaire *et al.* [16] have published ¹³C NMR data on Ir(I)–olefin complexes. These were of the type (β-diketone)Ir(1,5-COD) (see Table VI).

The proton spectra of the complexes exhibited very broad resonances for the olefinic protons being barely observable. These spectra were only used for identification purposes.

Discussion

Complexes are reported of the type (acac)M(olefin)₂ (M = Rh, Ir), of which (acac)Ir(PR)₂, (acac)Ir(VCl)₂, (acac)Ir(VA)₂, (acac)Ir(MA)₂ and (acac)Ir(ST)₂ were prepared for the first time.

According to the known structure of (acac)Rh(ET)₂ [17] the (acac)Rh group is nearly planar and the olefinic groups are perpendicular to this plane. Molecular models show that for the other olefins steric hindrance can be expected.

The bond model of Dewar, Chatt and Duncanson [18] shows that the double bond character of the olefin will decrease upon coordination. A measure for this weakening of the double bond is the lowering in frequency of $\nu(\text{C}=\text{C})$ which is, however, coupled to the modes $\delta(\text{CH}_2)_{\text{scis}}$ and/or $\delta(\text{CH})_{\text{bend}}$ depending on the olefin [3].

Powell *et al.* [11, 19] have shown that the summed percentage lowering of the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)_{\text{scis}}$ in ET complexes is a measure for this decrease in

TABLE V. Frequencies and Percentage Lowerings of the Vibrational Bands I, II and III^{a,b,c,d}.

ET	PR			VA									
	summed %	I	II	III	summed %	I	II	III	summed %				
free		1623	1342	1648	1415	1297	1647	1386	1295				
Rh	8.3	1513	6.8	1503	8.8	1395	1497	9.1	1373	0.9	1243	4.0	14.0
Ir	9.7	1486	8.4	1490	9.6	1392	1476	10.4	1375 ^e	0.8	1243	4.0	15.2
VCI													
VCI	ST			MA									
	summed %	I	II	III	summed %	I	II	III	summed %				
free		1612	1374	1281	1632	1414	1305	1633	1402	1283			
Rh	0.4	1466	9.1	1369 ^g	0.4	1241	1513	7.3	1403	0.8	1253	4.0	12.1
Ir	0.3	1455 ^f	9.7	1370 ^{f,g}	0.3	1223 ^f	1505	7.8	1400	1.0	1248	4.4	13.2

^a Bands I, II and III represent the coupled modes $\nu(\text{C}=\text{C})$, $\delta(\text{CH}_2)_{\text{scis}}$ and $\delta(\text{CH})_{\text{bend}}$ [3]. ^b Raman data are used. ^c The percentage lowerings are in italics. ^d Data for the free olefins, also in order to select the bands that shift upon coordination, are from ref. 3, 20 and ref. therein. ^e Band probably hidden. ^f IR data are used. ^g These bands are probably hidden. The bands at 1316 cm^{-1} (Rh) and 1300 cm^{-1} (Ir) could not be assigned, but the percentage lowerings would differ greatly from the other olefins if they were assigned to band II.

double bond character, while the summed percentage lowering of $\nu(\text{C}=\text{C})$, $\delta(\text{CH}_2)_{\text{scis}}$ and $\delta(\text{CH})_{\text{bend}}$ has to be considered for a monosubstituted olefin [3]. It has also been shown that this total percentage lowering of frequencies, when the olefin is coordinated to different d⁸ metals, is proportional to the metal-olefin bond strength [19].

In Table V the percentage lowerings of band I, II and III and the summed percentage lowerings are given. In Table VI $\delta^{13}\text{C}_{\text{mean}}$ of the olefinic carbon atoms is given for the free olefins and for the olefins after coordination to Rh and Ir, together with $\Delta\delta^{13}\text{C}_{\text{mean}}$. The total percentage lowering upon coordination to Ir is 1.1% (ST) to 3.0% (ET) higher than upon coordination to Rh, which means that the Ir-olefin bond is stronger than the Rh-olefin bond.

This is in agreement with the ¹³C NMR data which show that upfield coordination shifts of the olefinic carbons are 16.5 (PR) to 20.8 (VCI) ppm higher for Ir compared with Rh. In this respect, however, it has to be considered that the nature of the metal may also influence the ¹³C NMR shifts [21].

From Table VII it can be seen that $\nu(\text{CO})$ for (acac)Ir(CO)₂ is only 11 cm^{-1} lower than for (acac)Rh(CO)₂. As $\nu(\text{CO})$ mostly reflects the amount of π back-bonding [22], the proportion of π back-bonding does not increase very much on going from Rh to Ir. The observed increase in metal-olefin bond strength on going from Rh to Ir can, therefore, only partly be caused by a stronger π -bond and implies a stronger σ -bond in the Ir complexes, which has also been suggested on the basis of metal-chlorine frequencies [23].

Since different substituents on the olefin are expected to influence the ratio of σ - and π -bonding in the metal-olefin bond, a comparison between the results from different olefins bonded to the same metal, in order to establish the electronic and steric influences of the substituents, cannot easily be made. Nevertheless, it can be seen that the sequence of the total percentage lowering in the Rh series, ET>PR>VA>VCI>ST>MA, is nearly the same as in the Ir series, i.e. ET>PR>VA>VCI>MA>ST. If the ratios of σ - and π -bonding components in the Rh complexes differed greatly from those in the Ir analogues, no such close agreement between these two series would have been expected.

The sequence of $\Delta\delta^{13}\text{C}_{\text{mean}}$ for the different olefins on coordination to Rh and Ir is different from the vibrational sequence i.e. MA>ET>ST>PR>VCI>VA. This is probably caused by the fact that the σ and π contributions affect the vibrational and ¹³C NMR results to a differing degree.

As already noted, steric factors may be more important than electronic factors in the bonding, but, on the other hand, the sequence of $\Delta\delta^{13}\text{C}_{\text{mean}}$ in Pt(II)-monoolefin complexes is the same as for the Rh and Ir complexes and this is also true for the

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

	$\delta^{13}\text{C}_{\text{mean}}^{\text{a}}$			$\Delta\delta^{13}\text{C}_{\text{mean}}^{\text{b}}$		$\delta^{13}(\text{C}_2-\text{C}_1)$			
	free	Rh	Ir	Rh	Ir	free	Rh	Ir	Pt ^c
VA	119.0	70.2	51.6	48.8	67.4	45.3	55.5	50.3	55.2
VCl	121.8	71.2	50.4	50.6	71.4	8.7	21.3	19.7	
PR	124.0	67.2	50.7	56.8	73.3	18.1	11.6	7.9	24.3
ST	124.0	64.1	46.7	59.9	77.3	23.5	19.7	16.8	31.8
ET	122.8	59.4	40.9	63.4	81.9	0	0	0	0
MA	129.3	61.4	42.0	67.7	87.3	-1.2			3.1
COD ^d	128.5	75	59.3	52.6	69.3				

^a $\delta^{13}\text{C}_{\text{mean}} = \frac{1}{2}(\delta^{13}\text{C}_1 + \delta^{13}\text{C}_2)$. ^b $\Delta\delta^{13}\text{C}_{\text{mean}} = \delta^{13}\text{C}_{\text{mean}}(\text{ligand}) - \delta^{13}\text{C}_{\text{mean}}(\text{complex})$. ^c Ref. 3. ^d Ref. 16.

TABLE VII. $\nu(\text{CO})$ Frequencies of $(\text{acac})\text{M}(\text{CO})_2$ (M = Rh, Ir)^a.

	$\nu(\text{CO})$ (cm ⁻¹ in hexane)	
$(\text{acac})\text{Rh}(\text{CO})_2$	2082(s)	2011(s)
$(\text{acac})\text{Ir}(\text{CO})_2$	2073(s)	1999(s)

^a This work, also published by Bonati *et al.* [9, 10].

vibrational sequence [3]. When the *trans* ligand L, in the complex *trans*-PtCl₂(olefin)(L) is varied, the latter sequence changes, which implies that the *trans* ligand has a greater influence on the results than does the metal.

In Table IV $\delta^{13}(\text{C}_2-\text{C}_1)$ is presented for the Rh and Ir compounds. Aris *et al.* [13] have obtained ¹³C NMR data for several PR complexes and have suggested that $\delta^{13}(\text{C}_2-\text{C}_1)$ becomes smaller when PR is coordinated to a good π -backdonating metal.

For the $(\text{acac})\text{M}(\text{olefin})_2$ complexes, however, $\delta^{13}(\text{C}_2-\text{C}_1)$ decreases on going from the free ligand to Rh and to Ir for PR and ST, but increases for VCl and VA so there exists no such general rule in this case.

In the case of the compounds *trans*-PtCl₂(olefin)(L) [3] there is always an increase of $\delta^{13}(\text{C}_2-\text{C}_1)$ upon coordination of the olefin, so the Pt(II)-olefin bond has a different character than the Ir(I)- or Rh(I)-olefin bonds.

Conclusions

The type of bonding of olefins with different substituents to Rh(I) or Ir(I) is highly similar and differs from the bonding to Pt(II). The Ir(I)-olefin bond is stronger than the Rh(I)-olefin bond and this is caused by an increase of both σ and π metal-olefin bonding.

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