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Spectral characteristics of products formed by reaction between Rhacac(PPh_3)(CO) and methyl iodide

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Abstract

^{13}C, ^{31}P and ^{1}H NMR spectra revealed that in reaction mixtures Rhacac(PPh_3)(CO) and MeI there were present two methylcarbonyl (MC) complexes of Rh^{III}. These were presumably isomers of Rhacac(PPh_3)(CO)(Me)I: MC-I (δ ^{13}C 185.3 ppm, ^{1}J(C–Rh) 64.0 Hz, ^{2}J(C–Rh–P) 18.1 Hz; δ ^{31}P 33.7 ppm, ^{1}J(P–Rh) 124.4 Hz; δ ^{1}H (Me–Rh) 1.36 ppm, ^{2}J(H–C–Rh) 1.9 Hz, ^{3}J(H–C–Rh–P) 2.1 Hz) and MC-II (δ ^{13}C 185.6 ppm, ^{1}J(C–Rh) 62.5 Hz, ^{2}J(C–Rh–P) 11.0 Hz; δ ^{31}P 28.4 ppm, ^{1}J(P–Rh) 117.4 Hz δ ^{1}H (Me–Rh) 1.65 ppm, ^{2}J (H–C–Rh) 1.9 Hz, ^{3}J(H–C–Rh–P) 3.8 Hz). The third product is an acetyl complex, presumably the dimer [Rhacac(PPh_3)(MeCO)I]$_2$ (δ ^{13}C 212.4 ppm, ^{1}J(C–Rh) 28.0 Hz, ^{2}J(C–Rh–P) ~ 7 Hz; δ ^{31}P 37.6 ppm, ^{1}J(P–Rh) 153.0 Hz; δ ^{1}H (MeCO) 2.94 ppm, ^{2}J(H–C–C) 5.9 Hz). The MC-I complex is able to transform partially into MC-II. Oxidative addition of MeI to Rhacac ($AsPh_3$)(CO) and to Rhoxq(PPh_3)(CO) (hoxq = 8-hydroxyquinoline; oxq its residue) yielded similar methylcarbonyl and acetyl complexes. All species present in the reaction mixtures are identified spectroscopically without isolation.

Key words: Rhodium; Oxidative addition; Nuclear magnetic resonance; Acetylacetonato; Carbonyl; Phosphine

1. Introduction

In a previous publication [1] we briefly outlined addition reactions of methyl iodide (MeI) to acetylacetonatodicarbonylrhodium(I), Rhacac$(CO)_2$, and to its phosphine derivative, Rhacac(PPh_3)(CO). In the first case the oxidative addition of MeI yields an acyl complex of Rh^{III} that we have isolated and described tentatively as a dimer with iodide bridges, [Rhacac (MeCO)(CO)I]$_2$. The assumption was supported later by X-ray and spectral data [2]. The final product of the second reaction was presumed to be a methylcarbonyl complex of Rh^{III}, Rhacac(PPh_3)(CO)(Me)I. In a later study [3] on kinetics of the reaction Rhacac(PPh_3)(CO) + MeI the composition of the final product was corroborated. The authors [3] also observed, at an earlier stage of the reaction, a carbonyl insertion across the Rh–Me bond with the intermediate formation of an acetyl complex.

Reactions of planar rhodium(I) complexes with methyl iodide continue to be of interest [4–29 and references therein]. In this paper we present the results of a study of NMR spectra of products that coexist in the reaction mixtures Rhacac(PPh_3)(CO) + MeI and assign the ^{1}H, ^{13}C and ^{31}P resonances to the individual species. Preliminary data have already been reported [5].

2. Experimental section

All operations were performed under argon. Initial complexes Rhacac(PPh_3)(CO), Rhacac($AsPh_3$)(CO) and Rhoxq(PPh_3)(CO) were prepared by published procedures [30,31]. To obtain compounds containing ^{13}C-enriched carbon monoxide, 50%-enriched CO was bubbled through solutions in benzene of the respective complexes. Methyl iodide was doubly distilled just prior to use. IR and NMR spectra were measured in deuterochloroform solutions. Before use $CDCl_3$ was washed with water, dried over $CaCl_2$, distilled and kept under argon.

IR spectra were measured with a Specord-75 IR instrument using 0.01 cm thick cells with CaF_2 windows.

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^{13}C and ^{31}P NMR spectra were recorded with a Bruker AM-500 spectrometer operating in pulse mode at 125.759 and 202.458 Hz respectively. A relaxing agent $Cr(acac)_3$ was used in registering ^{13}C spectra. The chemical shifts were measured from internal standards, $CDCl_3$ solvent (δ ^{13}C 77.04 ppm) and tributhylphosphate (δ ^{31}P 0.45 ppm).

^1H NMR spectra were recorded on a Bruker HX 270 spectrometer. The solvent (residual $CHCl_3$ in $CDCl_3$) peak served as internal reference.

"Standard" samples of reaction mixtures were prepared as follows:

2.1. Rhacac(PPh_3)(CO) + MeI

0.049 g of Rhacac(PPh_3)(CO) were dissolved in 0.5 ml of CH_3I. The orange-red solution was kept for 1 h under argon at room temperature. The solvent was then removed *in vacuo*. The oily residue was triturated with hexane, which was decanted off. After performing the operation twice the residue was dried *in vacuo*. For spectral measurements the sample was dissolved in chloroform.

2.2. Rhoxq(PPh_3)(CO) + MeI

0.054 g of Rhoxq(PPh_3)(CO) was dissolved in 0.5 ml of CH_3I to obtain an orange-red solution. Further operations as described above were performed.

2.3. Rhacac($AsPh_3$)(CO) + MeI

0.058 g of Rhacac($AsPh_3$)(CO) were dissolved in 0.5 ml of CH_3I and further treated as above.

3. Results and discussion

Addition of methyl iodide to crystalline Rhacac(PPh_3)(CO) yields a homogeneous orange-red solution. The samples of reaction mixtures were prepared for spectroscopic studies as follows. After 1 h methyl iodide was distilled off *in vacuo* at room temperature, the residue washed with hexane, dried *in vacuo* and dissolved in chloroform. We designate further samples thus prepared as "standard".

The region of ν(CO) stretching vibrations for an IR spectrum of the standard sample is presented in Fig. 1(a). The strongest band with a maximum at 2062 cm^{-1} is due to stretching vibrations ν(CO) in a methylcarbonylrhodium(III) complex, and the less intensive band with a maximum at 1720 cm^{-1} corresponds to stretching vibrations ν(CO) in the –C(=O)Me group of an acetylrhodium(III) complex [3–5,13] (respective frequencies for [Rhacac(MeCO)(CO)I]$_2$ are 2080 and 1728 cm^{-1} [2]). A weak maximum at 1984 cm^{-1} is in the same place as the respective band of the initial Rhacac(PPh_3)(CO) complex. The spectrum of a Nujol mull

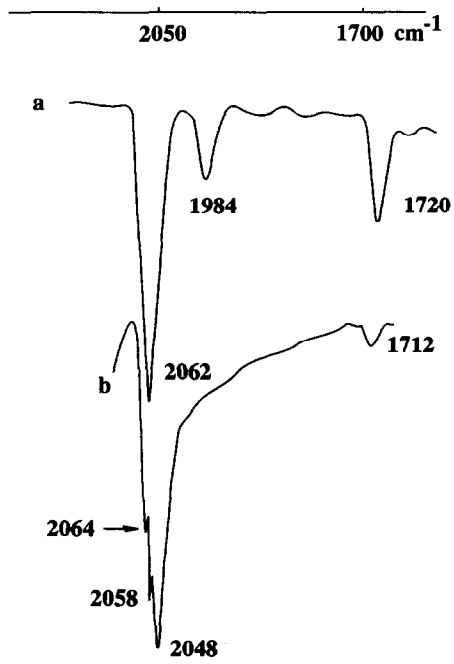


Fig. 1. IR spectra of reaction products Rhacac(PPh_3)(CO) + MeI ("standard" sample): (a) $CHCl_3$ solution; (b) Nujol mull.

of a similar polycrystalline sample (Fig. 1(b)) resembles the solution spectrum but the high frequency band has in this case a complicated contour due probably to the effect of crystalline state (in the spectra of some samples the splitting of the band did not occur). If the reaction mixture is kept for 24 h instead of 1 h and then treated in the standard way we observe a tendency of the carbonyl band (2062 cm^{-1}) to increase its intensity at the expense of the acetyl band (1720 cm^{-1}).

The studies of ^{13}C NMR spectra were performed with preparations of Rhacac(PPh_3)(CO) obtained with CO enriched in ^{13}C. The ^{13}C NMR spectrum of a

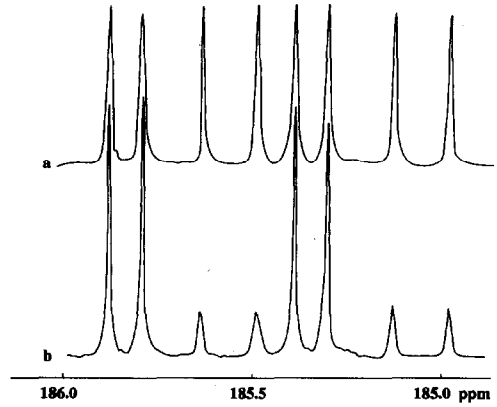


Fig. 2. ^{13}C NMR spectra (Rh ← CO region) of reaction products Rhacac(PPh_3)(CO) + MeI: (a) "standard" sample; (b) sample after multiple recrystallization.

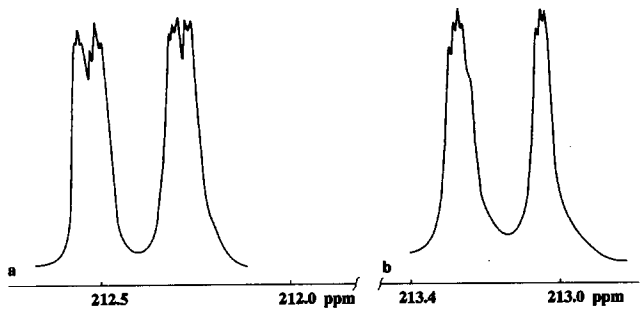
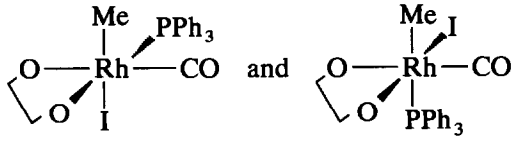


Fig. 3. ^{13}C NMR spectra (Rh–C(=O)Me region): (a) reaction products Rhacac(PPh$_3$)(CO) + MeI; (b) reaction products Rhacac (AsPh$_3$)(CO) ("standard" samples).

chloroform solution prepared by standard procedure is shown in Figs. 2(a) and 3(a). The region around δ 185 ppm (Fig. 2) corresponds to carbonyl groups bound to rhodium [32]; in this part of the spectrum appear eight signals that are easily separated in pairs according to spin-spin coupling values [^2J(C–Rh–P) is 11.0 Hz for the low field doublet of doublets, 18.1 Hz for the strong field doublet of doublets]. Larger separation between similar doublets (62.5 Hz; 64.0 Hz respectively) is due to ^{13}C–^{103}Rh coupling. Positions of the signals and the coupling constants (*cf.* ref. 32) allow unambiguous attribution of the resonances to isomers of Rhacac(PPh$_3$)(CO)(Me)I, two of the six possible for an octahedric complex, *e.g.*



(an isomer with *trans*-situated CO and PPh$_3$ is hardly probable).

A complicated signal near δ 212 ppm (Fig. 3(a)) can be assigned to an acetyl complex (*cf.* [2]). Due to spin–spin coupling with ^{103}Rh and ^{31}P it also appears as doublet of doublets [^1J(C–Rh) 28 Hz, ^2J(C–Rh–P) ~ 8 Hz]. In the spectrum of a triphenylarsine analogue (Fig. 3(b)) measured at similar conditions there appears only a doublet caused by coupling with rhodium nucleus. The components of the acetyl signal in both spectra are broadened and show badly resolved splitting due presumably to spin–spin coupling of ^{13}C with methyl protons [2]. Spectral parameters of a similar acetyl complex formed in reaction of methyl iodide with Rhoxq(PPh$_3$)(CO) are given in Table 1 (oxq is the residue of the 8-hydroxyquinoline).

Some spectra contain a group of weak signals centred at δ 189 ppm that belong to the initial Rhacac(PPh$_3$)(CO) (the spectrum of the respective individual compound is a doublet of doublets centred at δ ^{13}C 189.1 ppm; ^1J(C–Rh) 75.7 Hz; ^2J(C–Rh–P) 24.8 Hz [32]).

Repeated distilling of the solvent with subsequent dissolving of the residue in chloroform results in redistribution of the resonance intensities in the 185 ppm region, namely, four of the peaks grow at the expense of the other four. This means that one form of the phosphine-containing methylcarbonyl complex (which may be called MC-I) is transformed into the other (MC-II). This procedure was performed many times before registering the spectrum (Fig. 2(b)) that demonstrated how the ratio of MC-I and MC-II was strongly shifted to the latter. The data are used to attribute the signals presented in Table 1. Here also are given spectral parameters of compounds containing in the reaction mixture Rhoxq(PPh$_3$)(CO) + MeI. The IR

TABLE 1. ^{13}C and ^{31}P NMR spectral parameters of carbonyl and acetyl rhodium complexes.

Compound	Rh←CO			Rh–C(=O)Me			δ ^{31}P ppm	^1J(P–Rh) Hz	^2J(P–Rh–C) Hz
	δ ^{13}C ppm	^1J(C–Rh) Hz	^2J(C–Rh–P) Hz	δ ^{13}C ppm	^1J(C–Rh) Hz	^2J(C–Rh–P) Hz			
Rhacac(PPh$_3$)(CO)	189.1	75.7	24.8	–	–	–	48.9	175.7	24.8
Rhacac(PPh$_3$)(CO)(Me)I (MC-I)	185.3	64.0	18.1	–	–	–	33.7	124.4	18.7
Rhacac(PPh$_3$)(CO)(Me)I (MC-II)	185.6	62.5	11.0	–	–	–	28.4	117.4	?
[Rhacac(PPh$_3$)(MeCO)I]$_2$	–	–	–	212.4	28.0	~ 8.0	37.6	153.0	7.4
[Rhacac(CO)(MeCO)I]$_2$ [2]	180.3	67.5	–	210.9	~ 23	–	–	–	–
[Rh(CO)(MeCO)I$_3$]$^-$ [5]	117.1	54.0	–	216.4	18	–	–	–	–
Rhacac(AsPh$_3$)(CO)	187.9	72.3	–	–	–	–	–	–	–
Rhacac(AsPh$_3$)(CO)(Me)I (MC-I')	184.8	61.6	–	–	–	–	–	–	–
Rhacac(AsPh$_3$)(CO)(Me)I (MC-II')	184.9	63.0	–	–	–	–	–	–	–
[Rhacac(AsPh$_3$)(MeCO)I]$_2$	–	–	–	213.2	~ 26	–	–	–	–
Rhoxq(PPh$_3$)(CO)	190.7	72.3	22.6	–	–	–	41.1	164.6	22.9
Rhoxq(PPh$_3$)(CO)(Me)I (MC-I")	185.5	60.1	15.0	–	–	–	28.4	117.0	14.5
Rhoxq(PPh$_3$)(CO)(Me)I (MC-II")	184.9	61.0	6.6	–	–	–	25.6	120.2	7.4
[Rhoxq(PPh$_3$)(MeCO)I]$_2$	–	–	–	210.6	~ 28	–	32.8	146.1	6.2

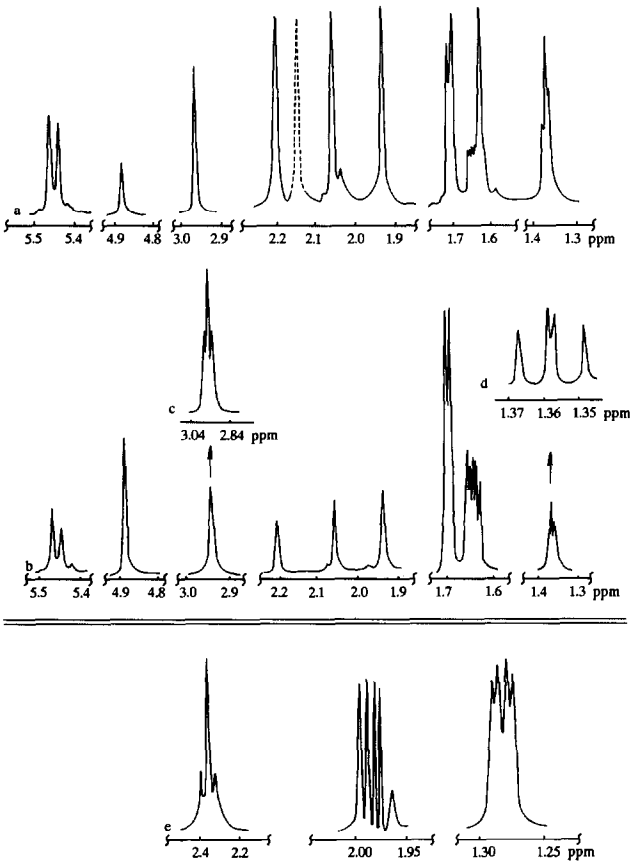


Fig. 4. ^{1}H NMR spectra of reaction products Rh(LL)(PPh$_3$)(CO) + MeI: (a) LL = acac ("standard" sample), dotted line = methyl resonance of MeI; (b) LL = acac, sample after multiple recrystallization; (c) sample enriched in ^{13}CO (methyl protons in acetyl group); (d) LL = acac (measured at higher resolution); (e) LL = oxq ("standard" sample).

data (a strong band at 2051 cm^{-1}, a weak band of initial complex at 1956 cm^{-1} and a band of medium intensity at 1710 cm^{-1}) and also the ^{13}C NMR spectrum indicate that in this system reaction products have formed similar to those resulting from interaction of Rhacac(PPh$_3$) (CO) with methyl iodide, namely, two forms of methylcarbonyl complex and an acetyl derivative. The structural similarity of products resulting from treating with methyl iodide either Rhacac(PPh$_3$)(CO) or Rhoxq(PPh$_3$)(CO) is reflected in the fact that the methylcarbonyl complex with larger δ ^{13}C possesses a notably smaller ^2J(C–Rh–P).

The ^{1}H NMR spectrum of a sample obtained from Rhacac(PPh$_3$)(CO) + MeI by the standard procedure is presented in Fig. 4(a); the region of phenyl protons of triphenylphosphine ligand is excluded. The group of low field signals (δ 5.5–4.8 ppm) is situated in the region of methine protons from β-diketonate ligands [33]. Respective signals of Rhacac(CO)$_2$ and Rhacac(PPh$_3$)(CO) appear at δ 5.59 and 5.43 ppm (our data). The remaining resonances, namely, a singlet at 2.95 ppm and a number of peaks in the 2.2–1.3 regions correspond to various protons from methyl groups belonging a) to acetylacetonate ligands of the three reaction products and probably also of the initial complex present in the reaction mixture, b) to acetyl ligand and c) to two methylcarbonyl complexes (MC-I and MC-II) where the methyl is bound directly to the metal atom. The signals were assigned using the following data:

1. In a symmetrical complex RhacacL$_1$L$_2$ with L$_1$ = L$_2$, equivalent protons of both methyl groups in the acac ligand give a single peak (for Rhacac(CO)$_2$ at δ 2.05 ppm [2]). At L$_1$ ≠ L$_2$ the acac methyls become non-equivalent and appear as separate signals, *e.g.*, δ 2.08 and 1.60 ppm for Rhacac(PPh$_3$)(CO) (*cf.* [33,34*]). Since all compounds present in the reaction mixture under study have different ligands in the plane common to the diketonate we should expect to see three pairs of acac methyl peaks from the three substances. Similar considerations apply in ref. [13].

2. The spectrum in Fig. 4(b) that belongs to a sample subjected to multiple recrystallization allows assignment of the signals from MC-II, which according to the ^{13}C NMR data is the main methylcarbonyl species; two singlets of non-equivalent acetylacetonate methyls at δ 1.71 and 1.72 ppm, methine proton of the same ligand at 4.87 ppm; a complicated peak pattern near 1.65 ppm which may be described as a doublet of doublets from methyl bonded to rhodium [splitting of the signal is due to spin-spin coupling with rhodium, ^2J(H–C–Rh) 1.88 Hz, and with phosphorus, ^3J(H–C–Rh–P) 3.76 Hz]. Similar ^{1}H NMR data for the methyl ligand in Rhacac[P(OPh)$_3$]$_2$(CH$_3$)I have been given [16]. The attribution of the signal and coupling constants was further corroborated by comparison with the arsine analogue of the complex (see point 6). The methyl signals of the acetylacetonate ligand nearly coincide thus indicating that the other ligands in the same plane, L$_1$ and L$_2$, are much alike.

3. We have treated Rhacac(PPh$_3$)(CO) with perdeuterated methyl iodide and in the ^{1}H NMR spectrum of the sample obtained (standard preparation) all the peaks of the spectrum Fig. 3a except the signals at δ 1.36, 1.65 and 2.95 ppm. The absence of the δ 1.65 resonance confirms its assignment to methyl bound to rhodium in the MC-II complex; it is thus reasonable to assume that the signal at 1.36 is produced by similar methyl group of the MC-I complex. The δ 2.95 ppm peak we assign to acetyl protons according to the data [4].

* Reference number with an asterisk indicates a note in the list of references.

4. The above assignment was confirmed by findings obtained by treating ^{13}C-enriched Rhacac(PPh$_3$)(CO) preparation with methyl iodide according to the usual procedure. The singlet at δ 2.95 appeared in the ^{1}H NMR spectrum surrounded by a doublet caused by proton coupling with ^{13}C nuclei in the acetyl groups formed in the reaction [^2J(H–C–C) 5.9 Hz], –^{13}C(=O)Me (Fig. 4(c)).

5. The signal with δ 1.36 ppm that we assigned to methyl ligand of the MC-I complex on account of its absence in the spectrum of sample obtained with methyl iodide-d_3 looked like a triplet (*cf.* Fig. 4(a),(b)) when it should have been a doublet of doublets). This suggests that coupling constants ^2J(H–C–Rh) and ^3J(H–C–Rh–P) have similar values, $\simeq$ 2 Hz, by coincidence (it is also observed in a methylcarbonyl complex formed by treating Rh(5,7-Cl,Cl-oxq)(PPh$_3$)(CO) with MeI [12]). Recording of the ^{1}H spectrum of a standard sample at higher resolution allowed separation of the "triplet" into doublet of doublets with ^2J(H–C–Rh) 1.88 Hz and ^3J(H–C–Rh–P) 2.07 Hz (Fig. 4(d)). It is interesting to note that the coupling constants to ^{103}Rh are similar in both MC-I and MC-II but the values of coupling constants to ^{31}P are noticeably different (2.07 and 3.76 Hz respectively). The data indicate that the main difference in the structure of the isomers lies in the relative positions of methyl and phosphine ligands.

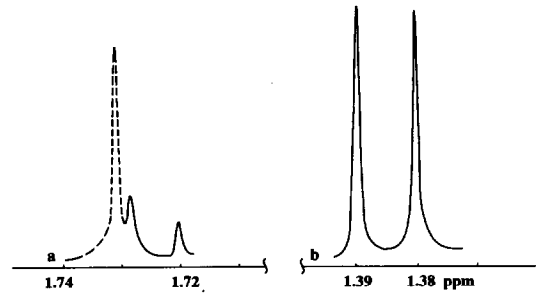


Fig. 5. ^{1}H NMR spectrum of reaction products Rhacac(AsPh$_3$)(CO) + MeI ("standard" sample): (a) resonance of methyl ligand protons in MC-I′ (dotted line = methyl resonance of acac); (b) resonance of methyl ligand protons in MC-II′.

6. The attribution of coupling constants with phosphorus observed in the signals at δ 1.36 and 1.65 ppm was by comparison with the respective spectra of analogous triphenylarsine complexes MC-I′ and MC-II′ prepared by standard procedure from Rhacac(AsPh$_3$)(CO). The resonances of methyls in MC-I′ and MC-II′ appeared here as doublets respectively at δ 1.39 ppm, ^2J(H–C–Rh) 1.89 Hz, and at δ 1.72 ppm, ^2J(H–C–Rh) 1.94 Hz. For assignment was used the relative intensity of signals (Fig. (5)).

Parameters of ^{1}H NMR spectra of the compounds present in the reaction mixture of Rhacac(PPh$_3$)(CO)

TABLE 2. ^{1}H NMR spectral parameters of carbonyl and acetyl Rh^I complexes.

Compound	δ^1H, ppm					Notes * Coupling constants, Hz
	Me (acac)	Me (acac)	H(C) (acac)	Me (Rh–Me)	Me (Rh–C(=O)–Me)	
Rhacac(CO)$_2$	2.05	2.05	5.59	–	–	
Rhacac(PPh$_3$)(CO)	2.08	1.60	5.43	–	–	
Rhacac(MeCO)(CO)I	2.22	2.04	5.61	–	2.61	
Rhacac(Me^{13}CO)(^{13}CO)I	2.21	2.04	5.60		2.62	2.62 s + d, ^1J(H–C) 6.27
Rhacac(CD$_3$CO)(CO)I	2.22	2.04	5.61			
Rhacac(PPh$_3$)(CO)(Me)I (MC-I)	2.06	1.93	5.47	1.36	–	1.36 dd, ^2J(H–C–Rh) 1.88, ^3J(H–C–Rh–P) 2.07
Rhacac(PPh$_3$)(CO)(Me)I (MC-II)	1.71	1.72	4.87	~ 1.65	–	1.65 dd, ^2J(H–C–Rh) 1.88, ^3J(H–C–Rh–P) 3.76
Rhacac(PPh$_3$)(MeCO)I	2.20	1.63	5.44	–	2.95	
Rhacac(PPh$_3$)(CO)(CD$_3$)I (MC-I)	2.06	1.93	5.47	–	–	
Rhacac(PPh$_3$)(CO)(CD$_3$)I (MC-II)	1.71	1.72	4.87	–	–	
Rhacac(PPh$_3$)(CD$_3$CO)I	2.20	1.63	5.44	–	–	
Rhacac(PPh$_3$)(^{13}CO)(Me)I (MC-I)	2.06	1.93	5.47	1.36	–	1.36 dd
Rhacac(PPh$_3$)(^{13}CO)(Me)I (MC-II)	1.72	1.71	4.87	1.65	–	1.65 dd
Rhacac(PPh$_3$)(Me^{13}CO)I	2.20	1.63	5.45	–	2.94	2.94 s + d, ^1J(H–C) 5.9
Rhacac(AsPh$_3$)(CO)(Me)I (MC-I′)	2.08	1.94	5.48	1.39	–	1.39 d, ^2J(H–C–Rh) 1.89
Rhacac(AsPh$_3$)(CO)(Me)I (MC-II′)	1.71	1.74	4.97	1.72	–	1.72 d, ^2J(H–C–Rh) 1.94
Rhacac(AsPh)(MeCO)I	2.20	1.73	5.47	–	2.93	
Rhoxq(PPh$_3$)(CO)(Me)I (MC-I″)	–	–	–	1.30	–	1.30 dd, ^2J(H–C–Rh) 2.07, ^3J(H–C–Rh–P) 2.92
Rhoxq (PPh$_3$)(CO)(Me)I (MC-II″)	–	–	–	2.00	–	2.00 dd, ^2J(H–C–Rh) 1.84, ^3J(H–C–Rh–P) 4.14
Rhoxq(PPh$_3$)(MeCO)I	–	–	–	–	2.35	
Rhoxq(PPh$_3$)(Me^{13}CO)I	–	–	–	–	2.36	2.36 s + d, ^1J(H–C) 5.60

* s = singlet, d = doublet, dd = doublet of doublets

with MeI, and of similar isotope-substituted derivatives and arsine analogues are presented in Table 2.

Table 2 also contains spectral parameters of compounds present in the reaction mixture Rhoxq(PPh$_3$)(CO) + MeI. The ^{1}H NMR spectrum of a sample prepared from the mixture by the standard procedure is shown in Fig. 4(e) (the initial rhodium complex was prepared with ^{13}C-enriched CO; the aromatic region of the spectrum is excluded). The methyl resonances of methylcarbonyl complexes MC-I″ and MC-II″ appear as well-resolved doublets of doublets: MC-II″ δ ^{1}H 1.30 ppm, ^2J(H–C–Rh) 2.07 Hz, ^3J(H–C–Rh–P) 2.92 Hz; MC-II″ δ ^{1}H 2.00 ppm; ^2J(H–C–Rh) 1.84 Hz, ^3J(H–C–Rh–P) 4.41 Hz. To assign the resonances we prepared a sample containing a preponderance of MC-II″ complex using the procedure of multiple dissolution in chloroform and removing of solvent as described previously. As expected, the ^{1}H signal from the acetyl group appeared as a quasi-triplet. The observed coupling constant ^2J(H–C–C), 5.6 Hz, was similar to that of the acetylacetonate analogue, 5.9 Hz.

The ^{31}P NMR spectrum of sample prepared (standard procedure) from Rhacac(PPh$_3$)(CO) + MeI contains four doublets. Multiple recrystallization of the standard sample yielded a preparation enriched with MC II; ^{13}C and ^{1}H spectra permitted attribution of the signals as follows: doublets at δ ^{31}P 33.7 ppm, ^1J(P–Rh) 124.4 Hz and at δ ^{31}P 28.4 ppm, ^1J(P–Rh) 117.4 Hz belong to MC-I and MC-II respectively. The doublet at δ ^{31}P 37.6 ppm, ^1J(P–Rh) 153.0 Hz was assigned to the acetyl complex since it has been demonstrated [6–8] that the ^1J(P–Rh) of acetyl rhodium(III) complexes was usually larger than that of the respective methyl derivatives.

The ^{31}P NMR spectrum of a ^{13}CO-enriched standard sample is presented in Fig. 6a. Whereas most of the signals appear as doublets with well resolved further splitting to a singlet surrounded by doublet due to the presence of ^{12}CO and ^{13}CO-containing complexes, the doublet at δ ^{31}P 28.4 looks like a doublet of unresolved broad peaks. The signal belongs to the MC-II complex; the expected splitting is presumably unobserved due to ligand exchange in the complex which is sufficiently quick to eliminate ^{31}P–^{13}C coupling but too slow for that of ^{31}P–^{103}Rh. A weaker signal at δ ^{31}P 48.9 ppm, ^1J(P–Rh) 175.7 Hz is that of the initial complex (according to our own data; *cf.* also [33]).

In ^{31}P NMR spectra recorded with more scans and thus with a better signal-to-noise ratio there appear

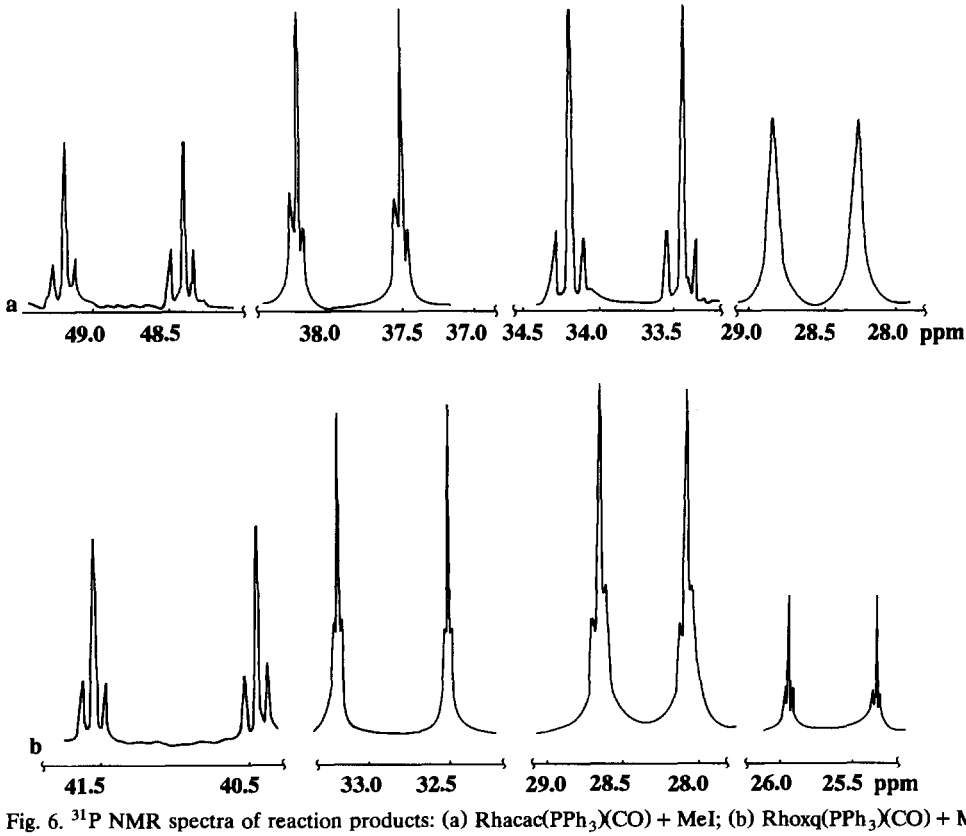


Fig. 6. ^{31}P NMR spectra of reaction products: (a) Rhacac(PPh$_3$)(CO) + MeI; (b) Rhoxq(PPh$_3$)(CO) + MeI

several smaller new doublets from unidentified products: δ ^{31}P 35.6 ppm, ^1J(P–Rh) 155.3 Hz; δ ^{31}P 38.9 ppm, ^1J(P–Rh) 154.9 Hz; δ ^{31}P 35.6 ppm, ^1J(P–Rh) 158.8 Hz. The coupling constants suggest that the signals belong to various acetyl complexes. Identification of the products needs further research beyond the scope of this study.

A similar ^{31}P NMR spectrum obtained from the reaction mixture Rhoxq(PPh_3)(CO) + MeI (with ^{13}C-enriched CO) is presented in Fig. 6b; respective spectral parameters are given in Table 1. The spectral characteristics of the two methylcarbonyl complexes are as follows: MC-I″ δ ^{31}P 28.4 ppm, ^1J(P–Rh) 117.0 Hz, ^2J(P–Rh–C) 14.5 Hz; MC-II″ δ ^{31}P 25.6 ppm, ^1J(P–Rh) 120.2 Hz, ^2J(P–Rh–C) 7.4 Hz. The ^2J(P–Rh–C) obtained are in sufficiently good agreement with the values taken from ^{13}C spectra (*cf.* Table 1). Other signals are assigned to acetyl complex [δ ^{31}P 32.8 ppm, ^1J(P–Rh) 146.1 Hz, ^2J(P–Rh–C) 6.5 Hz] and to residual initial Rhoxq(PPh_3)(CO)[δ ^{31}P 41.1 ppm, ^1J(P–Rh) 164.6 Hz, ^2J(P–Rh–C) 22.9 Hz (our data)]. Similar data for Rh^{I} complexes with halogen-substituted 8-hydroxyquinolines are given [6].

At greater resolution it was possible to observe further splitting of ^{31}P resonance belonging to MC-II″ probably due to spin-spin coupling with methyl ligand protons, ^3J(P–Rh–C–H) ~ 2 Hz. It is possible to distinguish similar splitting in the spectrum of the acetylacetonate complex MC-II registered at the same conditions. Both in systems Rhacac(PPh_3)(CO) + MeI and Rhoxq(PPh_3)(CO) + MeI the ^{31}P NMR spectra reveal that with longer contact between the reagents and long-term storage of isolated samples several new products are formed.

Study of ^{13}C, ^{1}H and ^{31}P NMR spectra of the reaction mixture Rhacac(PPh_3)(CO) + MeI has thus revealed that two isomers of methylcarbonyl complexes exist in the system. We hope that the data published here and spectral characteristics of the products will be of use in further research of the oxidative addition of methyl iodide to rhodium(I) β-diketonato and related complexes.

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