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Infrared and NMR, ^1H, ^{19}F, ^{31}P Studies of Rh(I) Complexes of the Formula: [Rh(β-diketone)$(CO)_x(P)_y$] ($x = 0, 1, 2; y = 0, 1, 2; x + y = 2$; P = PPh_3 or $P(OPh)_3$)

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Abstract

Products of substitution reactions of CO by PPh_3 and $P(OPh)_3$ in Rh(β-diketone)$(CO)_2$ complexes (where β-diketone: acetylacetone, thenoyltrifluoroacetone, trifluoroacetone, benzoyltrifluoroacetone, naphthoyltrifluoroacetone) were examined by IR and NMR. Reactions with PPh_3 produced the compounds containing one CO group, *i.e.* Rh(β-diketone)(CO)(PPh_3). In the case of asymmetric β-diketones, two isomers were observed in solution. The presence of free phosphine caused labilization of the coordination sphere of complexes followed by fast exchange between the free and the coordinated phosphine. Reaction with $P(OPh)_3$ produced Rh(β-diketone)[$P(OPh)_3$]$_2$ or Rh(β-diketone)(CO)[$P(OPh)_3$] complexes, depending on the amount of $P(OPh)_3$ used.

The NMR results indicate considerable delocalization of the electron density in these compounds.

Introduction

Rh(I) complexes with β-diketones and triphenylphosphine or triphenylphosphite attracted our attention mainly because of their catalytic activity in the hydroformylation of olefins [1]. Since the understanding of the mechanism of activity of a catalyst requires an understanding of its structure, we have undertaken the physicochemical investigations of complexes of our interest. Herein we report the results of spectroscopic investigations of [Rh(β-diketone)$(CO)_2$] type complexes and of their derivatives: [Rh(β-diketone)(CO)(PPh_3)], [Rh(β-diketone)(CO)($P(OPh)_3$)] and [Rh(β-diketone)($P(OPh)_3)_2$]. Complexes with triphenylphosphite were synthesized for the first time; the others were reported in the literature. Dicarbonyl complexes were first obtained by Bonati and Wilkinson in 1964 [2]. In 1967 a modified method of their preparation was reported [3]. Synthesis of the phosphine complex [Rh(ACA)(CO)(PPh_3)] (ACA = acetylacetone) has been known since 1964. Recently, the crystallographic results for [Rh(ACA)(CO)(PPh_3)] [4], [Rh(TTA)(CO)(PPh_3)] [5] (TTA = thenoyltrifluoroacetone) and [Rh(ACA)$(CO)_2$] [6] were published.

Except for the X-ray investigations no spectroscopic data were reported for these complexes. We have described earlier the synthesis and the physicochemical data for the phosphite complexes [Rh(ACA)(CO)($P(OPh)_3$)] and [Rh(ACA)($P(OPh)_3)_2$] [7, 8]; we report here our results achieved for the phosphite complexes of that type with the other β-diketones.

Activity of the [Rh(β-diketone)$(CO)_2$]-type complexes in substitution reactions has been studied recently by Leipold *et al.* [9], who also noted an effect of β-diketone substituents on the rate of substitution of CO ligands by cyclooctadiene.

Exchange of phosphine is another process of interest to us. We have reported [10] the fast exchange of the free and the coordinated phosphine in the system containing [Rh(ACA)(CO)(PPh_3)] and PPh_3. Next, we extended our studies to the other phosphine complexes, to find out whether this reaction is characteristic for all complexes of that type.

Results and Discussion

IR Spectra

The band positions of ν_{CO} for complexes containing one or two CO groups are tabulated in Table I. Comparison of ν_{CO} band positions in complexes of one type having various chelate ligands allowed us to estimate the influence of β-diketone structure on Rh–C and C–O bonding strength. A regularity was observed: increase of electronegativity of the substituents in β-diketone caused the shift of ν_{CO} band to higher frequencies. This refers to weakening of the Rh–C and to strengthening of the C–O bonding. Such a tendency was strongest in dicarbonyl complexes. Analysis of the position of the ν_{CO} bands revealed one more regularity: in all phosphite complexes [Rh(β-diketone)(CO)($P(OPh)_3$)] the ν_{CO} band was located over 2000 cm^{-1}, while in the analogous phosphine complexes it was found at about

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TABLE I. Band Positions of ν_{CO} Vibrations (in cm^{-1}) in Infrared for Rh(I) Complexes.

β-diketone[a]	[Rh(β-diketone)(CO)$_2$]	[Rh β-diketone (CO)(PPh$_3$)]	[Rh(β-diketone)(CO)(P(OPh)$_3$)]
ACA	2000, 2070	1975	2006
BAC	1990, 2060	1960	2005
TFA	2020, 2080	1983	2013
BTA	2020, 2037; 2080, 2097	1973	2013
NTA	2005, 2030; 2077, 2084	1963	2013
TTA	2010, 2027, 2033; 2080, 2097	1977	2020

[a] ACA = acetylacetone; BAC = benzoylacetone; TFA = trifluoroacetyloacetone; BTA = benzoyltrifluoroacetone; NTA = naphtoyltrifluoroacetone; TTA = thenoyltrifluoroacetone.

TABLE II. Line Positions δ (ppm) of CH$_3$ Groups in the ^{1}H NMR Spectrum and of CF$_3$ Groups in the ^{19}F NMR Spectrum for Rh(I) Complexes.

β-diketone[a]	[Rh(β-diketone)(CO)$_2$]	[Rh(β-diketone)-(CO)(PPh$_3$)]		[Rh(β-diketone)-(CO)(P(OPh)$_3$)]		[Rh(β-diketone)-(P(OPh)$_3$)$_2$]
ACA	1.69	1.55	2.04	1.52	2.86	1.36
BAC	1.71	1.72	2.22	1.67	2.02	1.5
TFA	1.4	1.74	2.26	1.66	2.02	1.47
BTA	78.9	77.7	80.7	82.3	81.9	85.0
NTA	78.8	77.7	80.6	79.0	78.6	79.0
TTA	78.8	78.1	80.9	78.7	79.7	84.3

[a] See footnote of Table I.

1970 cm^{-1}. This is not surprising because of the donor–acceptor properties of PPh$_3$ and P(OPh)$_3$ ligands. (P(OPh)$_3$ is known to be a good π-acceptor and a poor σ-donor compared to PPh$_3$ [11, 14], and thus the electron density on rhodium ion is lower in the complexes with P(OPh)$_3$ than in those with PPh$_3$. Due to this the Rh–C bonding strength declines, the C–O bonding grows stronger and the ν_{CO} band is shifted upfield. The fact that only one CO group is substituted by PPh$_3$ and both CO groups are substituted by P(OPh)$_3$ may be explained in two ways: the weaker donor and better π-acceptor properties of P(OPh)$_3$ weakens the remaining Rh–C bond in the complex [Rh(β-diketone)(CO)(P(OPh)$_3$)], with the result that it is also substitutable with P(OPh)$_3$, or it may be the result of the smaller cone angle of P(OPh)$_3$ compared to that of PPh$_3$ [14].

^{1}H and ^{19}F NMR

The results obtained by ^{1}H and ^{19}F NMR spectroscopy are discussed together, because they provide information about the same fragment of a complex, *i.e.* about the β-diketonate ligand. Positions of lines related to the CH$_3$ or CF$_3$ groups in all complexes under study are presented in Table II. The spectra of dicarbonyl [Rh(β-diketone)(CO)$_2$] and diphosphite [Rh(β-diketone)(P(OPh)$_3$)$_2$] compounds exhibit single lines corresponding to CH$_3$ or CF$_3$ groups, as could have been expected because of the symmetry of complexes. Among the other complexes we first consider the compounds with acetylacetone – the only symmetrical β-diketone used by us. The ^{1}H NMR spectra of the complexes [Rh(ACA)(CO)(PPh$_3$)] and [Rh(ACA)(CO)(P(OPh)$_3$)] show two CH$_3$ lines of equal intensity. The distance between them is 0.5 ppm for the complex with PPh$_3$ and 0.34 ppm for the complex with P(OPh)$_3$. Obviously, the presence of two CH$_3$ lines was expected – the first corresponding to the CH$_3$ group *trans* to PPh$_3$ or P(OPh)$_3$ and the second line in a *trans* position to CO. Shorter distances between lines in the complex with P(OPh)$_3$ indicate that the properties of the P(OPh)$_3$ and CO ligands are more similar than those of PPh$_3$ and CO.

Surprisingly, however, for complexes with β-diketones having one CH$_3$ group, *i.e.* [Rh(BAC)(CO)(PPh$_3$)] and [Rh(BAC)(CO)(P(OPh)$_3$)] (BAC = benzoylacetone) as well as for [Rh(TFA)(CO)(PPh$_3$)] and [Rh(TFA)(CO)(P(OPh)$_3$)] (TFA = trifluoroacetylacetone) almost identical spectra were obtained, as for acetylacetonate complexes. The spectra show two CH$_3$ lines and the distance between them is the same as for [Rh(ACA)(CO)(PPh$_3$)] and [Rh(ACA)(CO)(P(OPh)$_3$)]. The ^{19}F NMR spectra of complexes with one CO group quite surprisingly also present two lines. This refers to compounds with BTA (BTA = benzoyltrifluoroacetone), NTA (NTA = naphthoyltrifluoroacetone) and TTA (TTA = tenoyl-

TABLE III. Line Positions (δ) ppm and J(Rh–P) Coupling Constants in ^{31}P NMR Spectra of Rh(I) Complexes.

β-Diketone[a]	[Rh(β-diketone)(CO)(PPh$_3$)]		[Rh(β-diketone)(CO)(P(OPh)$_3$)]		[Rh(β-diketone)(P(OPh)$_3$)$_2$]	
ACA	48.6	179.7	121.1	293.0	123.1	308.6
BAC	49.1	179.7	120.6	293.0	123.0	307.6
TFA	49.5	179.7	118.3	293.0	121.8	312.5
	47.8	179.7				
BTA	49.3	177.7	118.0	293.0	121.5	308.6
	47.7	177.7				
NTA	48.9	175.8	118.1	296.9	122.0	308.6
	47.5	179.7				
TTA	47.6	179.7	117.8	296.9	121.1	304.7
	47.1	175.8				

[a] See *footnote of Table I.*

trifluoroacetone). For complexes with PPh$_3$ the distances between these lines are 3 ppm, while for complexes with P(OPh)$_3$ we find 0.4 to 1.0 ppm. Since all examined ligands contain only one CH$_3$ or CF$_3$ group in a molecule, the observed spectrum indicates the presence of two isomers in solution.

The first possible isomer contains the CH$_3$ or CF$_3$ group *trans* and the second one *cis* to P. Comparable intensity of both lines points to a similar concentration of both forms. The equilibrium has no dynamic character, because the changes in temperature have little influence on the spectra.

Two isomers were not expected in solution, because according to Leipold *et al.* [5, 15–18] the [Rh(LL)(CO)(PPh$_3$)] type complexes (where: LL = β-diketone or chelate ligand) appear as one isomer only. The X-ray studies [5, 15–18] revealed that it is the isomer with PPh$_3$ in position *cis* to the more electronegative group of the chelate ligand. The presence of two forms of complexes in solutions under study was confirmed by ^{31}P NMR. For this reason the discrepancy between the Leipold results and ours will be discussed after presentation of the results of all our experiments.

^{31}*P NMR*

The ^{31}P NMR spectra are a rich source of information about the phosphorous ligands coordinated in compounds. The chemical shifts [19], and especially the J(Rh–P) coupling constants, are very sensitive to electron density variations on rhodium ions. In the case of a given group of isostructural compounds, *e.g.* [Rh(β-diketone)(CO)(PPh$_3$)], the influence of chelate ligand on the electron density change is predominant. Therefore the ^{31}P NMR spectra allow us to recognize the influence of β-diketones on the electronic structure of compounds. The data in Table III indicate that the change of β-diketone has very little effect on shift values and, in practice, none on the coupling constant values. Typical coupling constants are: J(Rh–P) = 179.7 Hz for [Rh(β-diketone)(CO)(PPh$_3$)] complexes; J(Rh–P) = 293.0 Hz for [Rh(β-diketone)(CO)(P(OPh)$_3$)]; J(Rh–P) = 308.6 Hz for [Rh(β-diketone)(P(OPh)$_3$)$_2$]. The observation that the coupling constant values for the phosphite complexes exceed those for the phosphine ones is consistent with the literature reports [19], *e.g.* two structurally similar complexes RhCl(PPh$_3$)$_3$ and RhCl(P(OPh)$_3$)$_3$ are characterized by the following ^{31}P NMR parameters: δ_1 = 48.9 ppm; J(Rh–P) = 192 Hz; δ_2 = 32.2 ppm J(Rh–P) = 146 Hz, J(PP) = 37.5 Hz for the complex with PPh$_3$ [20] and δ_1 = 119 ppm, J(Rh–P) = 292 Hz, δ_2 = 111 ppm J(Rh–P) = 224.5 Hz J(PP) = 52.5 Hz for the complexes with P(OPh)$_3$ [21].

The data in Table III indicate that the J(Rh–P) coupling constants for [Rh(β-diketone)(CO)(P(OPh)$_3$] and [Rh(β-diketone)(P(OPh)$_3$)$_2$] vary very little. This could be due to the comparable donor–acceptor properties of CO and P(OPh)$_3$ ligands, evidenced earlier by the ^{1}H and ^{19}F NMR data. For four phosphine complexes [Rh(β-diketone)(CO)(PPh$_3$)] with ligands having the CF$_3$ groups (β-diketone = TFA, BTA, NTA, TTA) the spectra exhibit two doublets of almost identical J(Rh–P) coupling constant values. Since these compounds contain only one PPh$_3$ molecule, the double spectrum must exclusively be the effect of the presence of two isomers. According to Leipold *et al.* [5, 15–18] in the [Rh(β-diketone)(CO)$_2$] type complexes the determined CO group is replaced by PPh$_3$. The X-ray studies for [Rh(TTA)(CO)(PPh$_3$)] revealed that PPh$_3$ was in a *trans* position *versus* the tenoyl group [5]. According to Leipold the reason for this is the different *trans* influence of the two oxygen atoms in the non-symmetrical β-diketone. The *trans* influence is responsible for the formation of one isomer only for [Rh(LL)(CO)(PPh$_3$)] type complexes [15–18].

To explain the discrepancies in our observations we recorded the series of ^{31}P NMR spectra of [Rh(TTA)(CO)(PPh$_3$)] complex synthesized by different methods. The first spectrum exhibiting two doublets of equal intensity was obtained for the non-crystallized complex. Next, fine crystals were obtained by recrystallization of the compound from acetone. The spectrum of the solution made by dissolving in C_6H_6 shows four lines; however, the intensity of the second doublet (at $\delta = 47.1$ ppm) is lowered by *ca.* 1/3. Repeated but slower crystallization produced the compound whose ^{31}P NMR spectrum shows the line intensity ratio of both doublets *ca.* 2:1. In our opinion this experiment indicates that crystallization increased the amount of one isomer, most likely the one whose crystallographic structure was determined. However, the substitution of any CO group by PPh_3 is still possible, but only one CO group in a molecule could be substituted. *Trans* influence of β-diketone oxygen atoms was too weak to cause the formation of only one isomer. This conclusion was confirmed by one more experiment: the ^{31}P NMR spectrum of equimolar mixture of $[Rh(TTA)(CO)_2]$ and PPh_3 in C_6H_5 shows two doublets of equal intensity. This means that equal amounts of both isomers arise at the moment of formation of a complex.

One more fact is noteworthy in the discussion of the *trans* influence of oxygen atoms of β-diketone. The ^{31}P NMR spectra of $[Rh(\beta\text{-diketone})(CO)(PPh_3)]$ complexes show the different spectra of both isomers only when the β-diketone has the CF_3 group. There is no 'double' spectrum for $[Rh(BAC)(CO)(PPh_3)]$ complex, although as it follows from the ^1H NMR spectrum, it should appear in the form of two isomers. Nevertheless the difference of *trans* influence of C_6H_5 and CH_3 substituents is not so great as in the case of C_6H_5 and CF_3. The ^{31}P NMR spectra of $[Rh(\beta\text{-diketone})(CO)(P(OPh)_3)]$ and $[Rh(\beta\text{-diketone})(P(OPh)_3)_2]$ complexes is present in all cases only as doublets, although the ^1H and ^{19}F NMR spectra indicate the presence of two isomers in the CO containing complexes. Hence, four lines should be seen. The appearance of four lines was also expected for complexes with two phosphites and with non-symmetrical β-diketone. The spectra recorded by us indicated only one ^{31}P resonance. This fact could be explained in two ways: either both oxygen atoms of the β-diketone have equal *trans* influence or the difference of both donor groups of β-diketone is very small with $P(OPh)_3$. The latter explanation seems to be more reasonable; if both β-diketone groups would be equivalent, no different spectra for both isomers would be observed for $[Rh(\beta\text{-diketone})(CO)(PPh_3)]$ complexes. The stronger Rh–P bonds in the phosphite complexes compared to the phosphine complexes (due to the better π-acceptance of $P(OPh)_3$ compared to PPh_3) tend to equalize the Rh–P bonding for the two isomers in the $[Rh(\beta\text{-diketone})(CO)(P(OPh)_3)]$ compounds. The greater electron density delocalization in complexes with $P(OPh)_3$ could exercise some effect on the catalytic activity of compounds. Our studies revealed [1] a greater activity of the phosphite complexes in hydroformylation reactions, compared to the phosphine complexes.

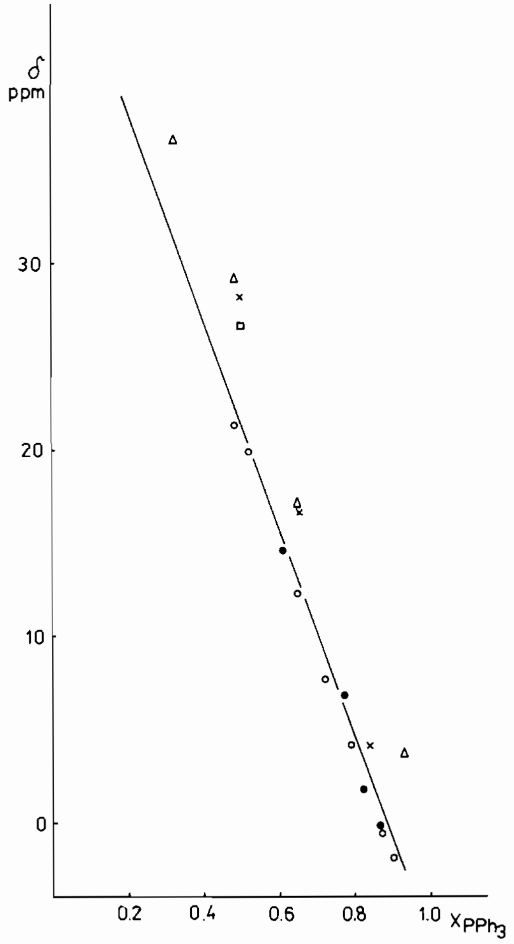

Fig. 1. Dependence of the (δ) chemical shifts in the ^{31}P NMR spectra in C_6D_6 on mol fractions of the added phosphine X_{PPh_3} for complexes: $[Rh(\beta\text{-diketone})(CO)(PPh_3)]$ where β-diketone: ○ ACA, ● BAC, × NTA, △ BTA, □ TTA. The full line obeys the equation: $49.3\ (1 - X_{PPh_3}) - 6.1\ X_{PPh_3} = \delta$.

Exchange of Phosphine in $[Rh(\beta\text{-diketone})(CO)(PPh_3)]$ Complexes

In our previous studies we have discovered [10] that the presence of free phosphine in a solution containing $[Rh(ACA)(CO)(PPh_3)]$ caused fast exchange between free and coordinated phosphine. Now we report our results concerning the other complexes. In all cases introduction of phosphine to the solution containing a $[Rh(\beta\text{-diketone})(CO)(PPh_3)]$ complex was followed by disappearance of the Rh–P coupling in the ^{31}P NMR spectrum. The spectrum exhibits one line; its position and width depend on the phosphine concentration. Dependence of line position on the phosphine mol

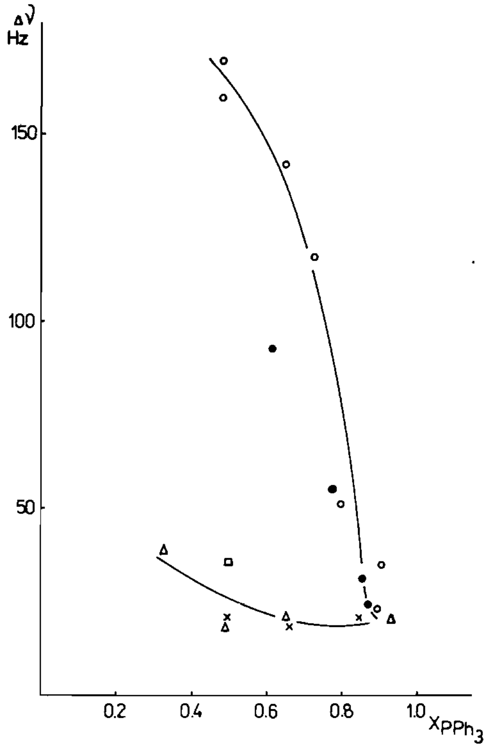

Fig. 2. Dependence of the halfwidth of the line (Δν) in the ^{31}P NMR spectra in C_6D_6 on mol fractions of the added phosphine X_{PPh_3} for complexes: [Rh(β-diketone)(CO)-(PPh_3)] where β-diketone: ○ ACA, ● BAC, X NTA, △ BTA, □ TTA.

fraction is shown in Fig. 1. The line was obtained assuming fast exchange with the equation: $\delta_1 \cdot x_1 + \delta_2 \cdot x_2 = \delta$, [22], where: δ_1, δ_2 are line positions in ^{31}P NMR spectrum for the complex and for the free phosphine and x_1, x_2 are mol fractions and δ is position of the average line. For all compounds under study the calculated and the measured position of lines was in good agreement.

Relation of the halfwidth of a line with mol fraction of the added phosphine is shown in Fig. 2. The narrowing of the line with increasing phosphine concentration was observed in all cases, so that increasing the phosphine concentration increases the exchange rate. The maximal exchange rate which could be recorded was observed at a tenfold phosphine excess, with a line width of about 20 Hz. It should be noted that for complexes with β-diketonates containing the CF_3 group the exchange rate was greater than for the other complexes; to obtain a maximum narrow line, the presence of only one phosphine molecule per complex molecule is sufficient. A similar situation was observed for CO substitution by cyclooctadiene in [Rh(β-diketone)$(CO)_2$] complexes [9]. The compounds with β-diketones containing CF_3 groups undergo substitution more easily. Exchange of phosphine in the complexes under study follows most likely an assocation S_N2 mechanism, as may be concluded from the dependence of the rate of the free phosphine concentration and the effect of CF_3 in the β-diketone.

The phosphine exchange rate increases with temperature. For the system: [Rh(ACA)(CO)-(PPh_3)] : [PPh_3] = 1:1 at 20 °C the ^{31}P NMR spectrum showed one line of halfwidth 160 Hz; after heating to 35 °C the halfwidth decreased to 74 Hz.

Phosphine exchange is the reaction characteristic for [Rh(β-diketone)(CO)(PPh_3)] complexes.

For the phosphite complexes the presence of the free ligand exercised no dynamic effects. For [Rh(β-diketone)(CO)($P(OPh)_3$)] complexes at the presence of $P(OPh)_3$ only the spectra characteristic for [Rh(β-diketone)$(P(OPh)_3)_2$] and the line derived from the free phosphite were observed.

Experimental

Synthesis

The [Rh(β-diketone)$(CO)_2$] type complexes were prepared according to literature methods [3]. [Rh(β-diketone)(CO)(PPh_3)] and [Rh(β-diketone)(CO)-($P(OPh)_3$)] were obtained in reaction of [Rh(β-diketone)$(CO)_2$] with the appropriate ligand in 1:1 ratio in benzene. After evaporation of a solvent, the precipitate was repeatedly washed with methanol and dried . [Rh(ACA)$(P(OPh)_3)_2$] was obtained according to the method described in [7]. The other [Rh(β-diketone)$(P(OPh)_3)_2$] complexes were obtained by evaporation of solutions containing [Rh(β-diketone)$(CO)_2$] and $P(OPh)_3$, in 1:2 ratio in benzene. The precipitates were repeatedly washed with methanol. Infrared spectra in KBr pellets were recorded on a Specord 75 IR spectrometer.

NMR Spectra

^{1}H NMR measurements were run on a Tesla 80 Hz instrument in C_6D_6 or in $CDCl_3$; TMS was used as reference.

^{19}F NMR measurements were recorded on a Jeol-JNM-ES 100 MHz spectrometer at 94.1 MHz, using $CFCl_3$ as an internal standard. All lines were located upfield of the standard. ^{31}P NMR measurements were obtained with a Jeol-JNM-ES 100 MHz spectrometer at 40.5 MHz; 85% H_3PO_4 was used as an internal standard. All spectra were proton-decoupled; downfield shifts are positive.

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