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LETTERS
TO THE EDITOR

Direct ^{13}C–^{31}P Coupling Constant of Coordinated Triphenylphosphine as a Characteristic of Electron-Withdrawing Power of the Metal Center

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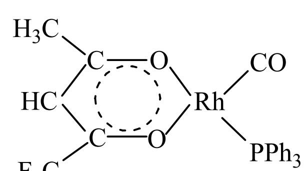
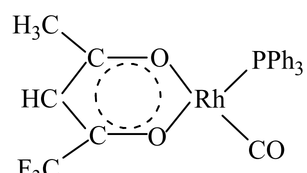
It is known that ^{13}C signals of phenyl groups attached to a phosphorus atom are split due to coupling with the ^{31}P nucleus. The direct ^{13}C–^{31}P coupling constant ($^1J_{CP}$) sharply increases in going from aromatic phosphines to the corresponding phosphine oxides. In keeping with our and published data [1–10], the $^1J_{CP}$ value of PPh_3 is negative and is –11 Hz, and the $^1J_{CP}$ value of $Ph_3P{=}O$ is positive (104 Hz). It is reasonable to rationalize increase of $^1J_{CP}$ by change of the valence state of the phosphorus atom. The phosphorus atom in the triphenylphosphine molecule possesses a lone electron pair (LEP), whereas the latter is involved in interaction with a strong electron acceptor (oxygen atom) in the phosphine oxide molecule.

It may be expected that $^1J_{CP}$ values for triphenylphosphine complexes with transition metals $L_xM{\leftarrow}PPh_3$, where the dative bond between the phosphine ligand and electron-withdrawing metal cation is also formed by the LEP on the phosphorus atom, should fall into the range defined by the $^1J_{CP}$ values for triphenylphosphine and triphenylphosphine oxide. Increase of $^1J_{CP}$ in the spectra of tertiary phosphines due to complexation with transition metals was noted in [10]. Analogous tendency was observed by us while studying the ^{13}C NMR spectra of structurally related triphenylphosphine complexes with rhodium carbonyls.

In the examined complexes, the triphenylphosphine ligand is coordinated to Rh(Bident)(CO) where Bident is a bidentate singly charged anionic ligand, β-diketonate [Diket, $R^1C(O)CHC(O)R^2$, $R^1 = R^2 = Me$ (acac), $R^1 = Me$, $R^2 = CF_3$ (trifluoroacetylacetone, TFA), $R^1 = R^2 = CF_3$ (hexafluoroacetylacetone, HFA) of β-ketoiminate [Ketim, $CF_3C(O)CHC(NH)CH_3$]. This family of complexes is grouped around the known rhodium(I) complex, Rh(acac)(CO)(PPh_3) (**I**), and it includes isomeric complexes Rh(TFA)(CO)PPh_3 (**IIa**, **IIb**), complexes Rh(HFA)(CO)PPh_3 (**III**), Rh(acac)(CO)PPh_3I_2 (**IV**), and *trans*-P,N isomer of Rh(Ketim)(CO)PPh_3 (**V**).



IIa



IIb

The complex Rh(acac)$(PPh_3)_2$ (**VI**) containing the second PPh_3 ligand instead of CO is also closely related to the above family. All these complexes, except for octahedral rhodium(III) complex **IV**, are planar. The ^{13}C NMR parameters (chemical shifts of the *ipso*-carbon nuclei and the corresponding $^1J_{CP}$ values) of compounds **I**–**VI** are given below.

Compound	**I**	**IIa**	**IIb**	**III**	**IV**	**V**	**VI**
$^1J_{CP}$, Hz	51	52	53	54	57	47	43
δ_C, ppm	132.6	131.8	132.0	131.1	133.1	132.6	136.0

These data allowed us to draw the following preliminary conclusions: (1) The $^1J_{CP}$ values in the spectra of complexes **I**–**VI** are centered near the middle of the range defined by the $^1J_{CP}$ values of Ph_3P and $Ph_3P{=}O$; (2) Replacement of the methyl groups in the β-diketonate ligand by electron-withdrawing trifluoromethyl groups in going from complex **I** to **IIa**, **IIb**, and **III** is accompanied by successive increase of the $^1J_{CP}$ value; (3) Increase of the degree of oxidation of the central rhodium atom and the corresponding increase of its coordination number (**I**→**IV**) leads to considerable growth of the $^1J_{CP}$ values; (4) The coupling constant $^1J_{CP}$ is sensitive to the nature of the *trans*-ligand: among isomeric complexes **IIa** and **IIb**, the higher $^1J_{CP}$ value corresponds to isomer **IIb** where the triphenylphosphine ligand occupies the *trans* position with respect to the carbonyl oxygen atom neighboring to the CF_3 group; (5) Replacement of one oxygen atom in the ligand by nitrogen (**IIa**→**V**), i.e., reduction of the electron-withdrawing power of the Bident ligand is accompanied by decrease of the $^1J_{CP}$ value; 6) Even stronger decrease of the $^1J_{CP}$ value is induced by replacement of the CO ligand by electron-donating PPh_3 ligand (**I**→**VI**).

On the whole, any structural variation accompanied by enhancement of the acceptor power of the rhodium atom toward lone electron pair on the phosphorus atom in PPh_3 leads to increase of $^1J_{CP}$ and vice versa, reduction of the electron-acceptor power of the metal center as a result of introduction of stronger electron-donating ligands into its coordination sphere decreases the $^1J_{CP}$ value. From this viewpoint, the value $^1J_{CP}$ = 36.1 Hz found for the complex $Cr(PPh_3)(CO)_5$ [11, 12] indicates that the $Cr(CO)_5$ fragment is a weaker electron acceptor than all Rh(Bident)(CO) fragments considered above.

Quantum-chemical calculations of complexes **I**, **III**, **V**, and **VI** and free ligands Ph_3P and $Ph_3P{=}O$ showed that their direct ^{13}C–^{31}P coupling constants are contributed mainly by the Fermi contact interaction. The calculated $^1J_{CP}$ values (Hz) for complexes **I** (49.9), **III** (54.6), **V** (47.6), and **VI** (42.0) and PPh_3 (–11.9) and $Ph_3P{=}O$ molecules (107.7) agree well with the experimental data. In addition, a distinct correlation exists between the calculated $^1J_{CP}$ values and charges on the PPh_3 fragment: the charge increases in parallel with $^1J_{CP}$: 0 for free PPh_3 molecule, 0.39, 0.45, 0.39, and 0.32 for complexes **I**, **III**, **V**, and **VI**, respectively, and 1.12 for triphenylphosphine oxide.

Compounds **I**–**III** and **V** were synthesized by reaction of triphenylphosphine with the corresponding rhodium complexes $Rh(Bident)(CO)_2$ [13, 14] in chloroform. The reaction of PPh_3 with $Rh(TFA)(CO)_2$ gave a mixture of two isomers **IIa** and **IIb** at a ratio of ~2 : 1. Complex **IV** was prepared by treatment of **I** in toluene solution with an equimolar amount of molecular iodine; the product was isolated as a mixture of isomers, and the spectral data given above characterize the major isomer (≥90%). Compound **VI** was synthesized by reaction of $Rh(acac)(C_2H_4)_2$ in petroleum ether with 2 equiv of PPh_3.

The ^{13}C–{^1H} NMR spectra of complexes **I**–**VI** were measured on a Bruker DPX-300 spectrometer at 75 MHz from solution in $CDCl_3$ or CD_2Cl_2. The C^i signals in the spectra of **I**–**V** were doublets due to coupling with the phosphrus atom ($^1J_{CP}$). In the spectrum of **VI** the C^i signal was a part of an *ABX* spin system (P^2P^1C), where the $|^2J_{PP}|$ value (~60 Hz) considerably exceeded the difference in the chemical shifts of the phosphorus nuclei (~2 Hz, ^{13}C isotope effect), as well as the $|^1J_{CP1}|$ value. Therefore, the most intense part of the C^i signal appeared as a triplet with the distance between the left and right components equal to $|^1J_{CP1}|$ (assuming that $^3J_{CP}$ = 2 0) [15]. In all cases, the absolute value of $^1J_{CP}$ was determined by analysis of the experimental spectra, and the sign of $^1J_{CP}$ was determined by our quantum-chemical calculations performed in terms of the density functional theory using B3LYP functional [16] and a composite basis set (SDD valence basis set with the corresponding core orbital potential [17] for rhodium and DZVP basis set [18] for the other atoms); charges on atoms and molecular fragments were estimated using natural population analysis (NPA) [19]. The calculations were carried out with the aid of GAUSSIAN-03 software package [20] at the High-Performance Computational Center (St. Petersburg State University).

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