

Note

# “Through-space” $^{31}\text{P}$ spin–spin couplings in ferrocenyl tetraphosphine coordination complexes: Improvement in the determination of the distance dependence of $J_{\text{PP}}$ constants

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This article is dedicated to Prof. P. Kalck for his 60th year.

## Abstract

From the analysis of several nickel and palladium halide complexes of a constrained ferrocenyl tetraphosphine, the existence in solution phase of unique  $^{31}\text{P}$ – $^{31}\text{P}$  “through-space” nuclear spin–spin coupling constants ( $J_{\text{PP}}$ ) had been previously evidenced. Due to the blocked conformation of the species in solution, and based on the NMR spectra obtained for the complexes and their corresponding solid state X-ray structures, these  $J_{\text{PP}}$  constants had been shown to clearly depend on the mutual spatial position of the corresponding phosphorus atoms. Herein, the quantitative correlation disclosed at that time ( $\text{P}\cdots\text{P}$  distance dependence of coupling constants) is remarkably confirmed, and mathematically refined owing to the study of a new palladium dibromide tetraphosphine complex, for which the synthesis and the solution NMR and solid state X-ray characterizations are reported.

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**Keywords:** Polyphosphine; NMR; Spin coupling; Through-space; Ferrocene; Phosphorus

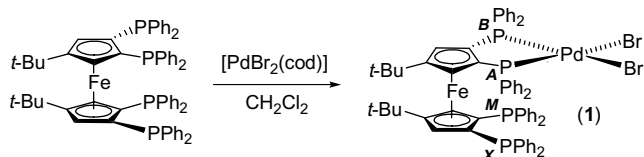
## 1. Introduction

The analysis of high-resolution NMR parameters is a critical issue for the elucidation of complex molecular structures [1]. In this prospect, a deeper understanding of the relationship between coupling constants and molecular structures could greatly broaden future applications of high-resolution spectroscopy [2]. Presently, the indirect nuclear spin–spin coupling  $J$  already provides critical data for the characterization of organic and biological molecules. The through-space transmission of spin–spin couplings has been first reported by Robert, Davies and Lutz [3], however, this electron-mediated coupling is still com-

monly regarded by the routine NMR users as mainly (if not only) originating from clearly covalently bonded magnetic nuclei. Nevertheless, experimental and theoretical reports highlighted the existence of  $J$  couplings nonbonded by nature (also called “through-space” couplings, TS) [4]. These non-bonded couplings constitute one of the exploration field of high-interest of modern NMR due to their intriguing nature, and also their significance in establishing molecular structure. Therefore, this topic of investigation yielded relevant results from both a theoretical and experimental perspective, as attested by the studies and reviews devoted to it, many of them transmitted through hydrogen bonding [5].

We have reported on  $^{31}\text{P}$ – $^{31}\text{P}$  nuclear spin–spin coupling constants of the ferrocenyl tetraphosphine 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-di-*tert*-butylferrocene, named

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Scheme 1. Palladium dibromide complex of the ferrocenyl tetraphosphine  $\text{Fc}(\text{P})_4^t\text{Bu}$ .

$\text{Fc}(\text{P})_4^t\text{Bu}$  (see Scheme 1), and on its nickel and palladium complexes in solution [6]. The eclectic array of puzzling NMR patterns obtained for these compounds had finally been established as being due to the existence of unanticipated  $J_{\text{PP}}$  “through-space” nuclear spin–spin coupling, never reported in the coordination chemistry literature up to then. We had provided a rationale to the coupling constants observed between the different phosphorus atoms, clearly demonstrated to be a result of nonbonded interactions [6]. In particular, based on a model developed by Mallory and co-workers [7], an expression of the nucleus distance-dependence of  $^{31}\text{P}$ – $^{31}\text{P}$  spin–spin couplings in coordination complexes has been given [6,8,9]. In the course of searches devoted to the electrochemistry of palladium halide tetraphosphine complexes, we synthesized a new palladium complex that had not been considered in our previous studies. We realized afterward the great interest of this compound for which synthesis and NMR/X-ray characterizations are reported. Consequently, we give herein a novel quantitative correlation of the distance dependence of  $J_{\text{PP}}$  couplings, which not only confirm our previously established theory and predictions, but provides as well a mathematically refined correlation-equation.

## 2. Results and discussion

Reaction of  $\text{Fc}(\text{P})_4^t\text{Bu}$  with the complex  $[\text{PdBr}_2(\text{cod})]$  ( $\text{cod} = 1,5$ -cyclooctadiene), under high dilution conditions in chlorinated solvent, selectively affords the 1,2-*P* bonded palladium mononuclear complex **1** expected (Scheme 1) [6,9].

The four non-equivalent phosphorus of **1** give in NMR four multiplets which might be described as a first order ABMX spin system: for accuracy reasons in determining  $J_{\text{PP}}$  constants the chemical shift of the multiplets are detailed:  $\delta_{\text{A}}$  (ddd) = 40.08, 40.07, 39.91, 39.90, 39.87, 39.86, 39.70, 39.69 ppm,  $J_{\text{AB}} = 20.6$  Hz,  $J_{\text{AM}} = 25.6$  Hz,  $J_{\text{AX}} = 1.9$  Hz;  $\delta_{\text{B}}$  (dd) = 37.49, 37.44, 37.32, 37.27 ppm,  $J_{\text{BA}} = 20.6$  Hz,  $J_{\text{BM}} = 5.8$  Hz,  $\delta_{\text{M}}$  (ddd) = –24.88, –24.93, –24.98, –25.02, –25.09, –25.14, –25.19, –25.23 ppm,  $J_{\text{MA}} = 25.6$  Hz,  $J_{\text{MB}} = 5.8$ ,  $J_{\text{MX}} = 11.5$  Hz;  $\delta_{\text{X}}$  (dd) = –27.26, –27.28, –27.36, –27.37 ppm,  $J_{\text{XA}} = 1.9$  Hz,  $J_{\text{XM}} = 11.5$  Hz. The simulated spectra computed by G-NMR program confirmed the values for coupling constants at  $\pm 0.1$  Hz (Fig. 1).<sup>1</sup>

The pattern of coupling constants of this kind of highly-unsymmetrical spin system was found to originate from strong  $J_{\text{PP}}$  “through-space” couplings [6]. Single crystals suitable for X-ray diffraction were obtained from crystallization in  $\text{CH}_2\text{Cl}_2$  (ORTEP view in Fig. 2).<sup>1,2</sup>

The  $^{31}\text{P}$  NMR and X-ray analysis of **1** is fully consistent with the TS theory we exposed, wherein one lone-pair orbital (from  $\text{P}_{\text{M}}$ ) with an appropriate orientation (namely  $\text{P}_4$  in Fig. 2) can interact with a bonding electron-pair shared between a phosphorus atom ( $\text{P}_{\text{A}}$  or  $\text{P}_{\text{B}}$ ) and another nucleus (Pd) [6,10]. Table 1 shows the correlation existing between the internuclear distances of heteroannular phosphorus atoms (determined from crystallographic data) and the coupling constants collected for **1** and its palladium chloride parent. It must be specified that this correlation is, from a strict point of view, only an approximation in the absence of a more developed tool that might show that these TS couplings depend both on the orientation of the lone-pair and on the orientation of the intermediate moiety [11]. However, the phosphorus nucleus being a statistical centre for the electron clouds involved, the resulting approximation is good-enough to evaluate a TS spin-coupling from the internuclear distance.

Since we had previously reported the solution NMR and single crystal X-ray characterization of the palladium compound bearing chlorine atoms instead of bromines [6,9], we were not expecting spectacular differences. However, a noticeable disparity in  $^{31}\text{P}$  NMR spectrum was revealed: the existence of a small but clear  $J_{\text{AX}}$  around 2 Hz for **1** that is correlated to the longest internuclear distance detected up to now in this family of compounds (5.40 Å). We previously thought that, due to effectiveness of electron-clouds overlapping, TS spin transmission would not last above 4.90 Å [6]. We had reported a first plot constructed by using some of the data collected in Table 1 (column 2) as well as similar correlation for nickel halides analogs, which gave a very good fit for an exponential curve expressed by Eq. (1) (dotted line in Fig. 3) [6]. The data points were plotted as  $J_{\text{PP}}$  vs  $d_{\text{P}\cdots\text{P}}$  in which  $J_{\text{PP}}$  is in units of hertz and  $d_{\text{P}\cdots\text{P}}$  in units of angstroms. The regression coefficient  $R^2 = 0.975$  was obtained for the fitted data all corresponding to experimentally determined values [12].

$$J_{\text{PP}} = (9691.9)e^{-1.6102d_{\text{P}\cdots\text{P}}} \quad (1)$$

The new data [ $\text{P}\cdots\text{P}$  distances/ $J_{\text{PP}}$  couplings] collected for **1** (Table 1, column 3) were added to the plot (Fig. 3) and we were delighted to see that the new plotted data, which span a large range of coupling constants (from 1.9 to 25.6 Hz) as well as distances (from 3.68 to 5.40 Å), were nicely consistent with the first reported correlation. Additionally, the renewed set of data gives a corrected correlation

<sup>1</sup> Full details are reported in Supporting Information.

<sup>2</sup> Crystal data such as tables of atomic positional parameters are available in supporting information.

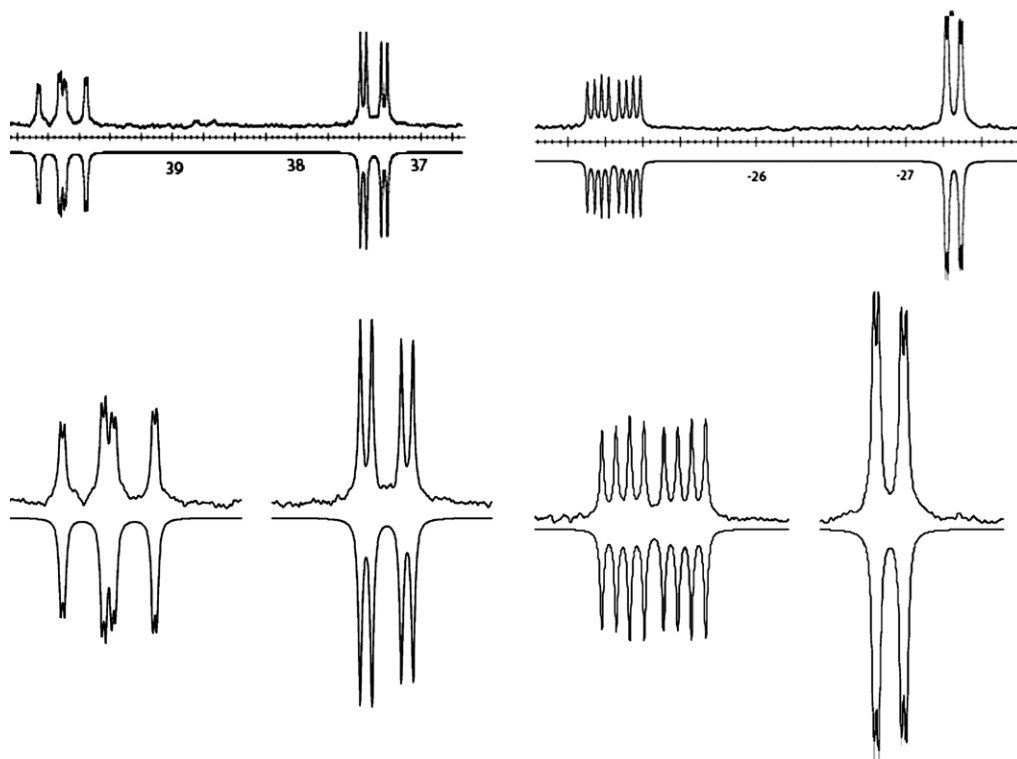


Fig. 1. (a)  $^{31}\text{P}$  NMR spectrum (top) and enhancement (bottom) with the corresponding G NMR simulations (mirror) for the four P atoms of  $[\text{PdBr}_2\{\text{Fc}(\text{P})_4'\text{Bu}\}]$  (1) in  $\text{CD}_2\text{Cl}_2$  ( $^{31}\text{P}$  at 121.4948 MHz on Bruker 300).

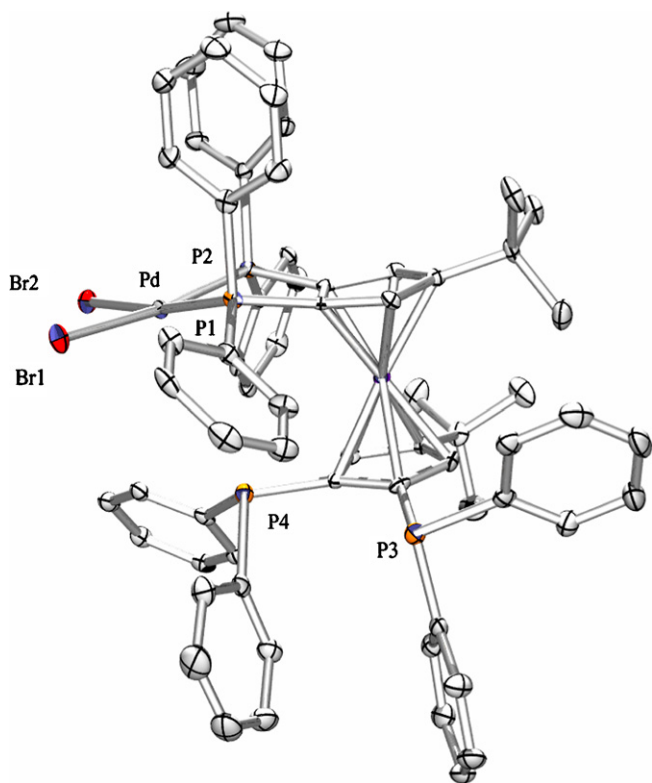


Fig. 2. Molecular structure of 1 (Pov-Ray illustration with ORTEP ellipsoids 50%).

Table 1

$^{31}\text{P}$  NMR  $J_{\text{PP}}$  coupling constants and X-ray crystallographic data (“through-space” distances) correlation table

$\text{P}\cdots\text{P}$ distances ( $\text{\AA}$ )/ $J_{\text{PP}}$ constants (Hz)	$[\text{PdCl}_2\{\text{Fc}(\text{P})_4'\text{Bu}\}]$	$[\text{PdBr}_2\{\text{Fc}(\text{P})_4'\text{Bu}\}]$
$d\text{P}_A\cdots\text{P}_M/J_{\text{AM}}$	3.842(1)/24.0	3.6765(12)/25.6
$d\text{P}_A\cdots\text{P}_X/J_{\text{AX}}$	4.698(2)/n.d.	5.3971(13)/1.9
$d\text{P}_B\cdots\text{P}_M/J_{\text{BM}}$	4.440(1)/6.4	4.4879(13)/5.8
$d\text{P}_B\cdots\text{P}_X/J_{\text{BX}}$	6.292(2)/n.d.	6.7628(13)/n.d.

Data for  $d\text{P}_A\cdots\text{P}_B$  and  $d\text{P}_M\cdots\text{P}_X$  are not suitable for TS correlation since through-bond  $^3J_{\text{PP}}$  contributions cannot be neglected [4]. n.d. = not detected. Compared to a first order interpretation previously reported [9], the simulations for the Pd dichloride complex afford coupling constants with only a slight deviation (0.1–3 Hz).

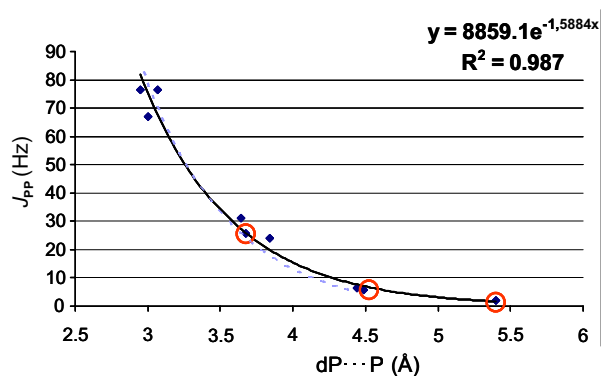


Fig. 3. Plot of  $J_{\text{PP}}$  vs  $d\text{P}\cdots\text{P}$  TS distances. New data from Table 1 are encircled. The plot is fitted by the exponential relationship defined by Eq. (2) (curve-fitting Excel 2003). The dotted line corresponds to earlier Eq. (1).

defined by Eq. (2) (main curve in Fig. 3). The corresponding regression coefficient  $R^2 = 0.987$  obtained for the fitted data was noticeably improved, and reaches the ones associated to analogous correlations incorporating computed data [12].

$$J_{PP} = (8859.1)e^{-1.5884d_{P...P}} \quad (2)$$

In the new formulation found, record [5.398 Å; 1.9 Hz] is fully consistent with Eq. (2) despite the unusual long distance. This could be a result of the extent of palladium 4d orbitals. Another hypothesis could be a combination of TS and through-bond transmission ( $J_{AX}$  resulting of  ${}^{\text{TS}}J_{AM} + {}^3J_{MX}$ ) neither mentioned before. This question is of high fundamental interest but requires further data and analysis.

In the mononuclear palladium complex **1** and its chloride analogue, two phosphorus electron pairs “interacting through-space” are involved in P–Pd bonding interactions. In this case, the “through-space” interaction involves a three-center system composed of P–M (M = Pd) and P. This presents an important difference with TS couplings in which two lone-pairs strictly are interacting (often encountered in purely organic fluorinated compounds but known for many NMR active nucleus holding lone-pairs: Se, P, N, etc.). Based on the model from Mallory a possible pathway for this particular coupling is discussed in the following. For simplicity, only the three localized orbitals involved in the “through-space” interaction are sketched in Fig. 4. The metal–ligand bond between P and Pd is regarded in this basic model as coming from the  $\sigma$ -overlap between a  $3sp^3$  and a  $d_z^2$  orbital. To account for the fact that nuclear spin information is transmitted between the phosphorus atoms, two filled molecular orbitals have been constructed which incorporate a contribution from the metal. The qualitative orbital ordering as well as the symmetry of the interacting orbitals allow this schematic view. Consequently, to observe “through-space” nuclear spin coupling, two lone-pair orbitals are not required. One lone-pair orbital with an appropriate orientation can interact with a bonding electron-pair shared between a phosphorus and a metal for instance and thus transmit “through-space” nuclear spin P...P information. The present results confirm this assertion previously disclosed [6,10].

### 3. Conclusion

The quantitative experimental formulation determined herein is very convenient, as it presents an intuitive correlation between “geometric parameters” (internuclear distances) and “through-space” nucleus spin–spin couplings; a more accurate correlation should probably be expressed in terms of overlap efficiency of lone-pair and metallic orbitals (taking into account shape and diffuse character of the electronic clouds). The study from Malkin and Malkina might be an interesting foundation for starting a more detailed visualization of these spin couplings transmission [11]. Further works we envision would concern the construction of reliable quantum mechanics calculation models for the “through-space” spin–spin coupling contribution [13], based for instance on the set of consistent experimental data and equations supplied herein.

### 4. Experimental

The tetraphosphine ligand 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-di-*tert*-butylferrocene called Fc(P)<sub>4</sub>'Bu is obtained as air-stable, moisture-resistant red crystals in a high yield one-step reaction of FeCl<sub>2</sub> with 2 equiv. of the anionic cyclopentadienyl (Cp) moiety [*t*-BuCp(PPh<sub>2</sub>)<sub>2</sub>]<sup>−</sup> [14]. This subsequent lithiated cyclopentadienyl fragment results from two successive phosphorylation/lithiation reactions operated on [*t*-BuCp]Li, which is easily obtained from reaction of methyl lithium with dimethylfulvene [15].

#### 4.1. Synthesis of [PdBr<sub>2</sub>{Fc(P)<sub>4</sub>'Bu}] (1)

To [Pd(cod)Br<sub>2</sub>] (0.35 mmol, cod = 1,4-cyclooctadiene) in CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) was added Fc(P)<sub>4</sub>'Bu (0.35 mmol). The solution was stirred for 4 h and evaporated to dryness. The red orange residue was washed by vigorous stirring overnight in 20 mL of hexane. The filtration of the mixture afforded pure complex **1** as a red powder in 75% yield.

#### 4.2. Crystal data for **1**

C<sub>66</sub>H<sub>62</sub>Br<sub>2</sub>FeP<sub>4</sub>Pd, 3CHCl<sub>3</sub>, fw 1659.21, monoclinic, space group, *P*21/*n* (no. 14), *a* = 12.158(5), *b* = 40.221(5),

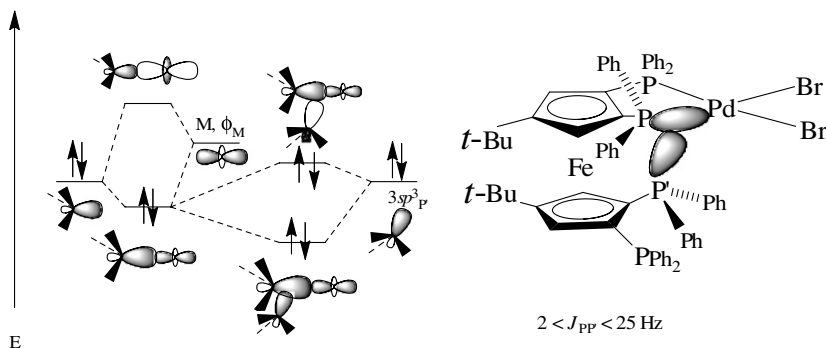


Fig. 4. Plot of orbital overlap at the origin of TS coupling.

$c = 14.522(5) \text{ \AA}$ ,  $\beta = 93.363(5)^\circ$ ,  $V = 7089(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.555 \text{ g/cm}^{-3}$ ,  $\mu (\text{Mo K}\alpha) = 2.055 \text{ mm}^{-1}$ ,  $T = 105(2) \text{ K}$ , 16021 unique reflections ( $R_{\text{int}} = 0.0476$ ). The structure was refined with 781 parameters to  $R_1 = 0.044$  (for 10805 reflections with  $I > 2\sigma(I)$ ),  $wR_2 = 0.102$  (for all data), goodness-of-fit = 1.039.

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 670371 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.035](https://doi.org/10.1016/j.jorganchem.2007.11.035).

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