A 2,2',6,6'-Tetraphosphinobiphenyl[1]

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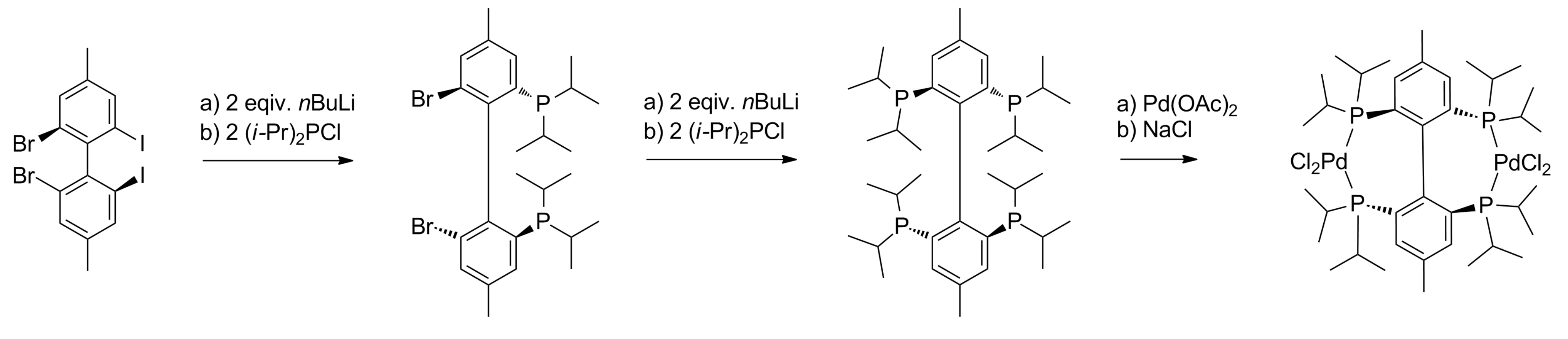
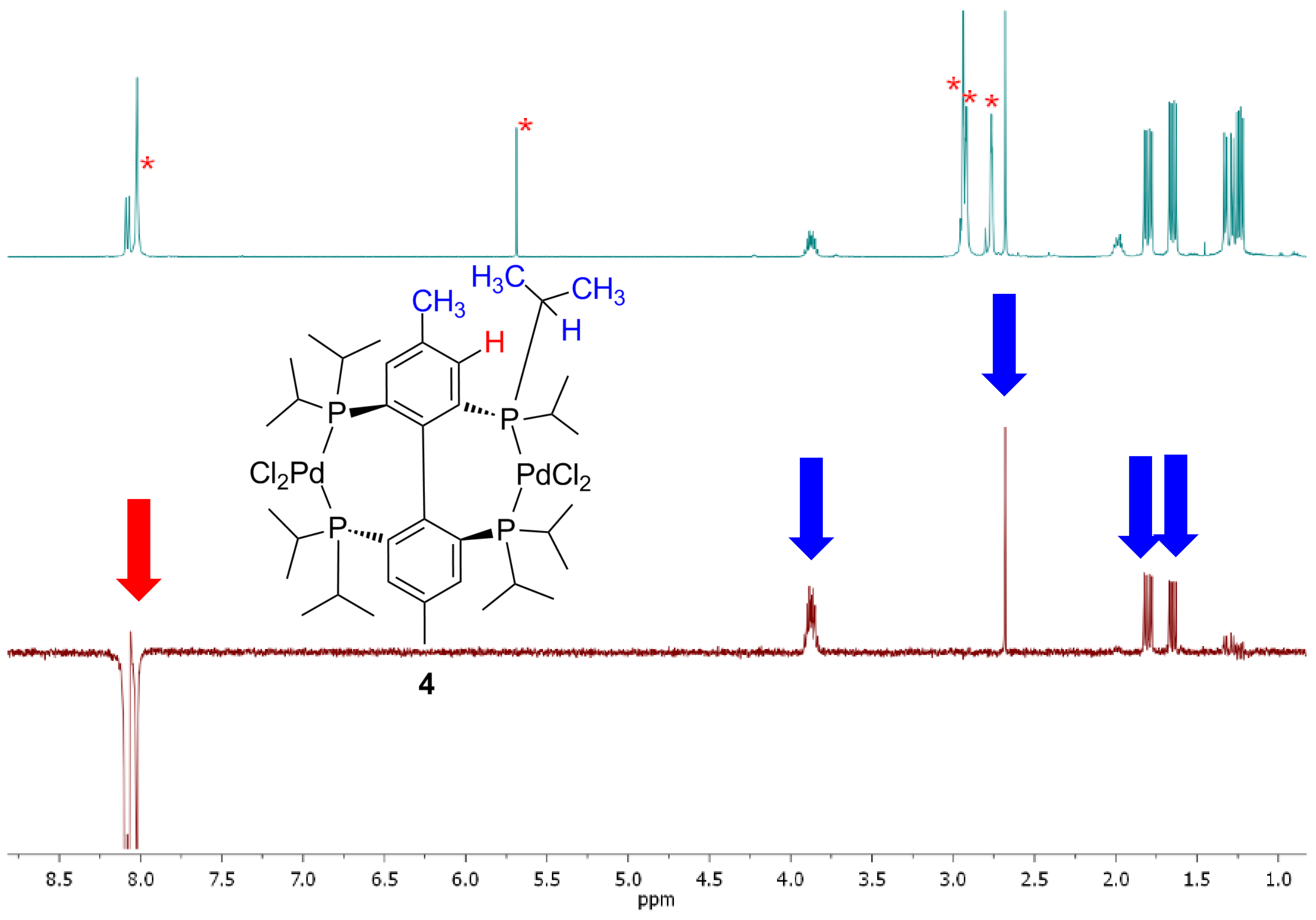
Introduction

Bidendate chelating ligands are key building blocks in modern transition metal catalysts. For enantioselective catalysis especially 2,2'-diphosphinobiphenyls have attracted much interest. The most prominent derivative is 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) first synthesized by Noyori and coworkers.[2] Noyori was not only encouraged to the synthesis of BINAP by the fascinating applications in asymmetric chemistry but was also inspired by "its molecular beauty" due to the high symmetry.[3] Nowadays a high number of derivatives has been synthesized and numerous publications appear every year applying 2,2'-diphosphinobiphenyl derivatives as ligands for catalytic active transition metal complexes. Here, we would like to report on the first synthesis of a highly symmetric 2,2',6,6'-tetraphosphinobiphenyl **3** and its dinuclear palladium(II) complex **4**.

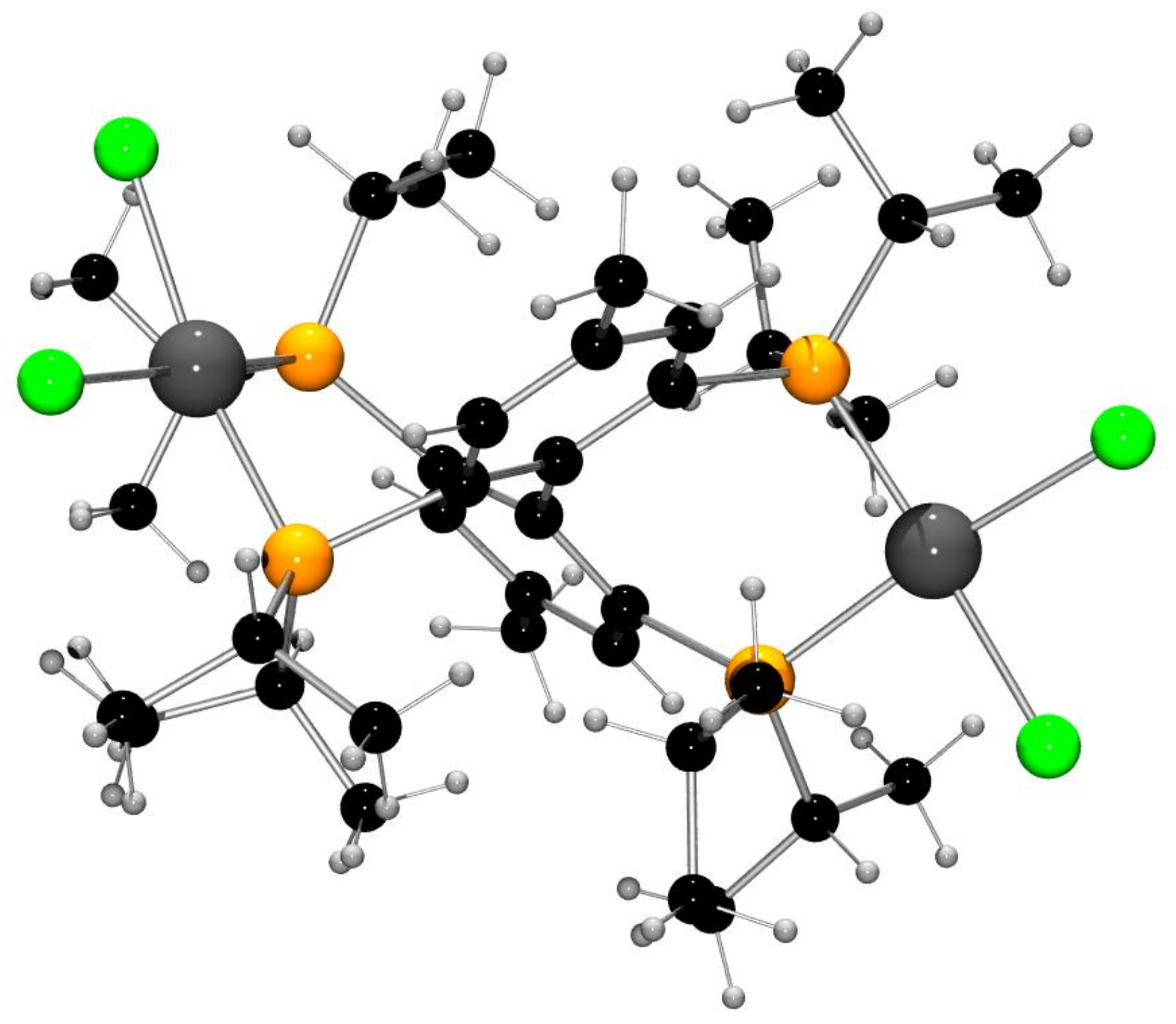


1 **2** **3** **4**

Synthesis of a 2,2',6,6'-tetraphosphinobiphenyl
Employing well known synthesis strategies[4], we gained access to the isopropyl decorated tetraphosphane **3** by a "one-pot-two-step" synthesis starting from the easily available 2,2'-dibromo-6,6'-diiodo-4,4'-dimethylbiphenyl **1**[5]. Upon treatment of **1** with two equivalents of *n*-BuLi and subsequent reaction with excess of chlorodiisopropylphosphane compound **2** is formed. Diphosphane **2** gives upon reaction with another two equivalents of *n*-BuLi and subsequently with chlorodiisopropylphosphane crude product **3**. Column chromatography and crystallization from ethanol yields pure **3**.
The ^{1}H NMR spectrum of **3** shows one set of signals for the eight equivalent isopropyl groups, one signal for the four equivalent aromatic protons as well as one resonance which can be assigned to the two equivalent methyl groups in the 4,4'-positions of the biphenyl moiety. The number of signals is consistent with the expected D_{2h} symmetry of **3** with three C_2-axes ($C_2(z)$-axes in line with the central C-C bond of the biphenyl moiety and the two symmetry equivalent axes $C_2(x)$ and $C_2(y)$ perpendicular to the central C-C bond) as well as an S_4-axis and two mirror planes.
Molecule **3** was reacted with palladium acetate followed by addition of sodium chloride solution to yield the desired dinuclear palladium complex **4**.

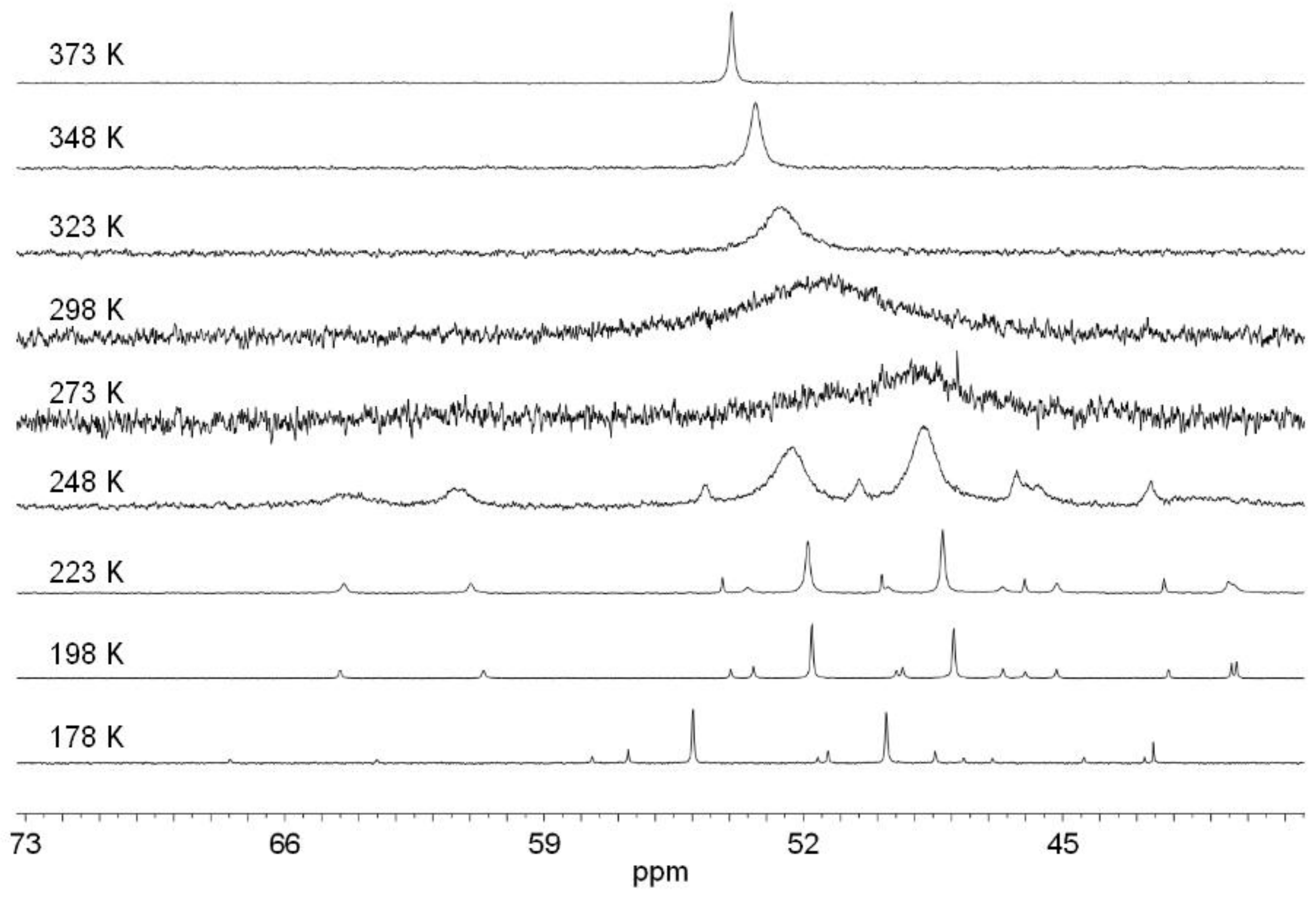


↑ Standard proton NMR spectrum of complex **4** (top) in d$_7$-dmf and ^{1}H selective NOE spectrum (bottom) with irradiation at the aromatic proton at $\delta = 8.25$, applying a mixing time of 0.5 sec and 64 transients recorded in d$_7$-dmf at 373K. Peaks marked with * are from water, residual solvent protons and CH_2Cl_2.

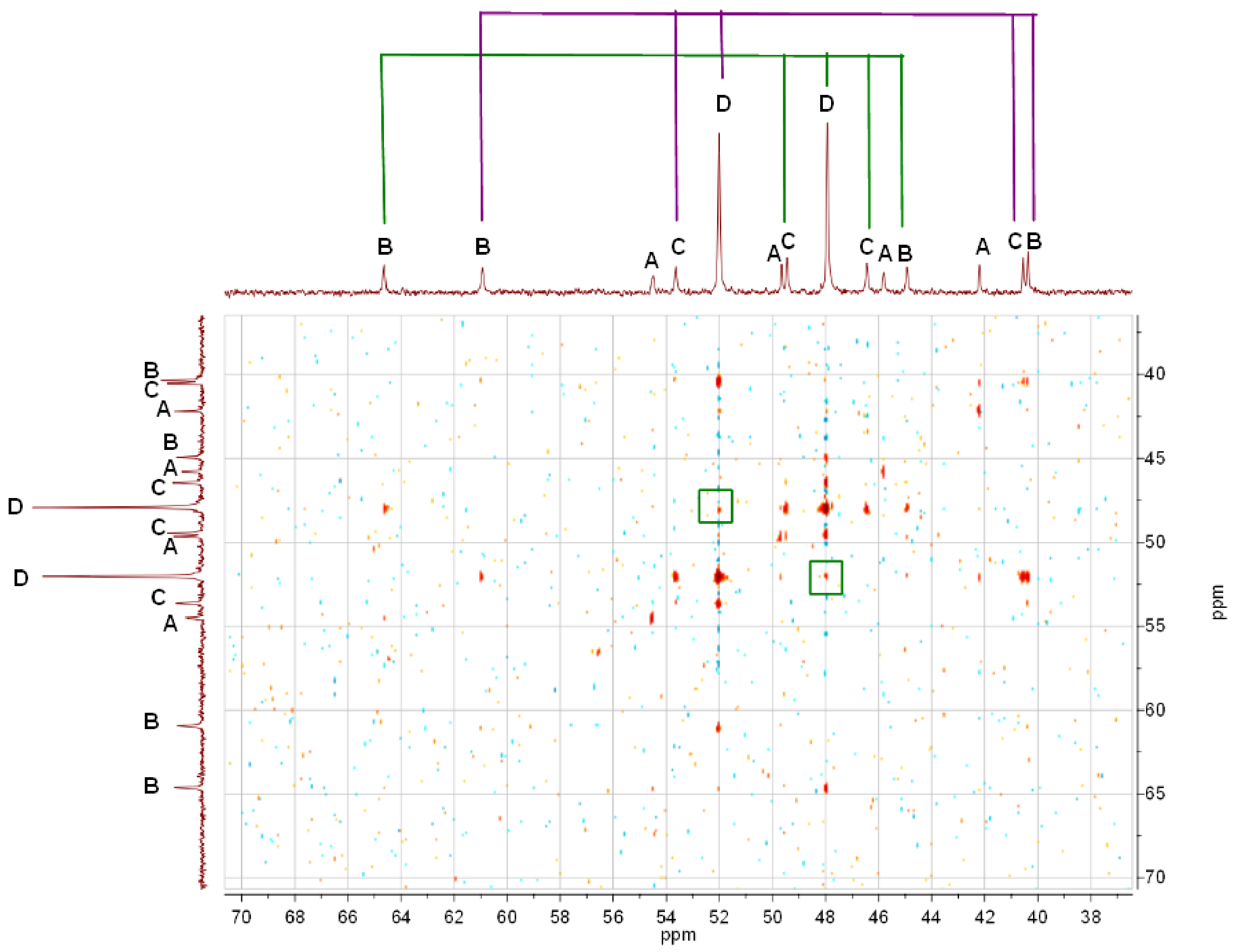


← Molecular structure of complex **4** in solid state, the second molecule and solvent molecules have been omitted for clarity. Bond lengths (Å): Pd1-Pd2 7.7430(4), Cl1-Pd1 2.3738(9), Cl2-Pd1 2.3628(9), Cl3-Pd2 2.3640(9), Cl4-Pd2 2.3327(12), P1-Pd1 2.2744(9), P2-Pd1 2.2782(9), P3-Pd2 2.2993(11), P4-Pd2 2.2492(9), and bond angle (˚): P1-Pd1-P2 91.46(3), P1-Pd1-Cl2 170.51(4), P2-Pd1-Cl2 95.37(3), P1-Pd1-Cl1 86.78(3), P2-Pd1-Cl1 176.01(4), Cl2-Pd1-Cl1 85.98(3), P4-Pd2-P3 92.80(4).

VT ^{31}P{^{1}H}-NMR spectroscopy



VT ^{31}P{^{1}H} NMR spectra of complex **4** in d$_7$-dmf solution at 178, 198, 223, 248, 273, 298, 323, 348, and 373 K, respectively (from bottom to top); the spectra have been scaled in order to make the broad signals visible, the spectrum at 178 K has been recorded in CD_2Cl_2/d$_7$-dmf mixture.



^{31}P{^{1}H} EXSY spectrum of complex **4** at 208K in d$_7$-DMF/CH_2Cl_2 mixture (ratio 1:2), the cross peaks for the P-P exchange within conformer **D** is marked with green boxes, note that this cross peaks would have higher intensity due to the dominant conformer **D** if the P-P exchange would be comparably fast within **D**. The colored lines on the top should indicate the correlation between the exchanging signals. This spectrum has been recorded with 2048 transients in F2 and 128 transients in F1 and a mixing time of 0.6 sec. Conformer **A** does not show exchange signals in this spectrum.

Conclusion

In summary, we have for the first time synthesized a highly symmetric 2,2',6,6'-tetraphosphinobiphenyl **3** and a related dinuclear palladium complex **4**. The complex shows complicated temperature dependent NMR spectra which is due to intramolecular interaction of the isopropyl groups (gear effect). Only a minor number (**A**-**D**) of the possible conformers of complex **4** are observed at low temperatures with more than 50 % of the molecules adopting the C_2 symmetric conformation **D**.

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References

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