Inorg. Chem. **2008**, *47*, 1607−1615

Inorganic Chemistry
Article

Coordination Chemistry of Tetra- and Tridentate Ferrocenyl Polyphosphines: An Unprecedented [1,1′-Heteroannular and 2,3-Homoannular]-Phosphorus-Bonding Framework in a Metallocene Dinuclear Coordination Complex

D. A. Thomas,[†] V. V. Ivanov,[‡] I. R. Butler,[*,†] P. N. Horton,[#] P. Meunier,[‡] and J.-C. Hierso[*,‡]

Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, Wales, Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BG, U.K., and ICMUB (Institut de Chimie Moléculaire de l'Université de Bourgogne), UMR CNRS 5260, Université de Bourgogne, 9 avenue Alain Savary, 21078 Dijon, France

Received November 9, 2007

Palladium(II) and nickel(II) halide complexes of the ferrocenyl polyphosphines 1,1′,2,3-tetrakis(diphenylphosphino)ferrocene (**1**), and 1,1′,2-tris(diphenylphosphino)-4-*tert*-butylferrocene (**5**) were prepared and characterized by multinuclear NMR. The metallo-ligand **1**, the palladium [Pd_2Cl_4(**1**)] (**3b**) and nickel [$NiCl_2$(**5**)] (**6**) coordination complexes were additionally characterized by X-ray diffraction crystallography. The behavior of **1** toward coordination to nickel and palladium was surprisingly different because the coordination of a second metal center after the initial 1,2-phosphorus-bonding of nickel was markedly difficult. The preference of nickel for 1,2-P coordination on 1,1′-bonding was confirmed by the exclusive formation of **6** from **5**. The changes noted between the solid state structure of the ligand **1** and the structure obtained for the dinuclear palladium complex **3b** reveal the rotational flexibility of this tetraphosphine. This flexibility is at the origin of the unique framework for a metallocenic dinuclear metal complex in which both coexist a 1,1′-heteroannular chelating P-bonding and a 2,3-homoannular chelating P-bonding with two palladium centers. Some reported specimens of ferrocenyl polyphosphines of constrained geometry have previously revealed that phosphorus lone pair overlap can lead to very intense "through-space" $^{31}P^{31}P$ nuclear spin−spin coupling constants (J_{PP}) (*J. Am. Chem. Soc.* **2004**, *126* (35), 11077–11087] in solution phase. In these cases, an internuclear distance between heteroannular phosphorus atoms below 4.9 Å, with an adequate orientation of the lone-pairs in the solid state and in solution, was a necessary parameter. The flexibility of the new polyphosphines **1** and **5** does not allow that spatial proximity (internuclear distances between heteroannular phosphorus above 5.2 Å in the solid state); accordingly the expected through-space nuclear spin−spin coupling constants were not detected in any of their coordination complexes nor in **1**.

Introduction

Polyphosphine compounds have been fascinating and useful species since their initial development in the early 1960s. In the recent years, the high-effectiveness of novel organic and organometallic multidentate phosphine ligands[1,2] in metal-catalyzed fine chemicals synthesis has been intensively investigated.[3] For instance, carbon−carbon couplings that result from reaction of organo bromides or chlorides with various organometallic reagents has excellent synthetic scope when catalytic systems combining palladium and a polyphosphine auxiliary are employed in reactions such as Suzuki−Miyaura arylations[3a,e] or Sonogashira−Heck alkynylations.[3b,f] Among multidentate ligands, ferrocenyl polyphosphines have been identified as versatile species

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[*] To whom correspondence should be addressed. E-mail: hiersojc@u-bourgogne.fr (J.-C.H.); i.r.butler@bangor.ac.uk (I.R.B.). Phone: +33 3 80 39 61 06(J.-C.H). Fax: +33 3 80 39 36 82 (J.-C.H.).

[†] Bangor University.

[‡] Université de Bourgogne.

[#] Southampton University.

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10.1021/ic7022105 CCC: $40.75

amenable to many structural modifications[3k] and therefore to the tuning of both chemical features and coordination properties. Their intrinsic characteristics such as the stability toward oxygen and moisture permit one to employ them under nonglove box laboratory conditions and to stock them under air at ambient temperature for months without troubles from light or moisture conditions. These features prompted us to further develop the synthetic routes toward a more diverse class of ferrocenyl polyphosphines of higher "rank" than classical ferrocenyl mono or diphosphines.[4] The studies conducted by several other groups for the synthesis of specifically chiral polysubstituted ferrocenes represent also very important and complementary contributions in this area.[5]

Some representatives species of ferrocenyl polyphosphines of a constrained geometry have allowed the study of the intriguing and yet poorly known phenomenon of nonbonded indirect nuclear spin−spin couplings detected by NMR ("through-space" nuclear spin-coupling, TS). In these compounds, abnormally strong J_{PP} and J_{CP} spin–spin coupling constants have been observed, and attributed to the spatial proximity of the NMR-active nucleus.[1,3k,4a,b] Clear qualitative and a semiquantitative experimental correlations have been obtained, which links the geometric parameters of the constrained structures and the intensity of the corresponding P···P spin coupling constants. The lone-pair overlap theory, developed for $^{19}F^{19}F$ and $^{15}N^{19}F$ through-space couplings in organic compounds,[6] has appeared to be a reliable foundation to account for our results.[1,3k] This model was extended to $^{31}P^{31}P$ spin–spin couplings, showing that only one lone pair of electrons that interacts with another bonding electron pair can transfer the $^{31}P^{31}P$ nuclear spin information through space between two phosphorus nuclei in a coordination complex. The exponential dependence of the *J* coupling intensity on internuclear distances, initially predicted by modeling and theoretical means,[6h] has been experimentally established through the example of several palladium and nickel tetraphosphine mononuclear complexes. As a part of our continuous effort to investigate the TS coupling phenomenon, and to develop novel multidentate ferrocenyl-based metalloligands, the present paper provides details on the synthesis and characterization of the original dissymmetric tetraphosphine 1,1′,2,3-tetrakis(diphenylphosphino)ferrocene **1**. The coordination chemistry of **1** toward palladium and nickel is presented. In particular, the behavior of **1** toward coordination to nickel or palladium was found surprisingly different. A critical comparison of NMR and X-ray structure between the new-formed species and already known tetraphosphine and triphosphine derivatives was conducted to pursue our efforts at revealing and toward understanding of through-space $^{31}P^{31}P$ nuclear spin couplings and their internuclear distance dependence. The preference of nickel compounds for 1,2-phosphorus bonding coordination was verified with the triphosphine parent ligand 1,1′,2-tris(diphenylphosphino)-4-*tert*-butylferrocene **5**, and its nickel chloride coordination complex for which an X-ray structure was solved.

The changes noted between the solid-state structure of the ligand **1** and the structure obtained for its dinuclear palladium complex **3b** revealed the rotational flexibility of this novel tetraphosphine. This flexibility is at the origin of an unique framework for a dinuclear complex coordinated by a metallocene, in which both coexist a 1,1′-heteroannular P-bonding and a 2,3-homoannular P-bonding.

Experimental Section

The reactions were carried out in oven-dried (115 °C) glassware under an argon atmosphere using Schlenk and vacuum-line techniques. Palladium and nickel precursors, ferrocene, and $FeCl_2$ from commercial source were used ($FeCl_2$ anhydrous beads, 99.9%, H_2O < 100 ppm). The solvents were distilled over appropriate drying and deoxygenating agents prior to use. ^1H (500.13 MHz), ^{31}P (202.44 MHz), and ^{13}C NMR (125.77 MHz) were performed in our laboratories (on Bruker DRX 500, or on Bruker 300) in $CDCl_3$ at 298 K unless otherwise is stated. Mass and elemental analyses were performed by the analytical services of ICMUB (Dijon) on a Kratos Concept IS instrument and on Eager 200, respectively.

1,1′,2,3-Tetrakis(diphenylphosphino)ferrocene (1). LDA (1 mol equiv to 1,1′-dibromoferrocene) was prepared in situ from *n*-butyllithium and di-isopropylamine at −80 °C in THF. 1,1′-

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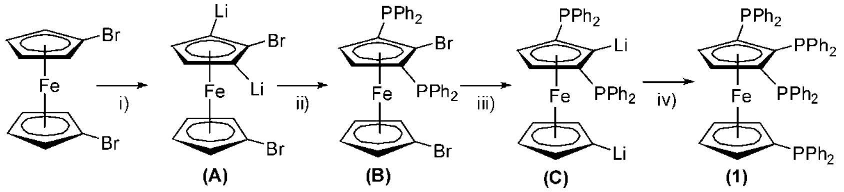
Scheme 1. Four-Step Synthesis of the Tetraphosphine **1**



Dibromoferrocene (0.5 mol equiv. to LDA), dissolved in the minimum quantity of THF required for its complete dissolution, was then added. The reaction mixture was stirred for 2 h at a temperature between −50 and −80 °C, with external cooling by a dry ice/acetone bath. $ClPPh_2$ (1 mol equiv to 1,1′-dibromoferrocene) was added to get product **B** (Scheme 1), and the reaction mixture was allowed to warm to room temperature over 2 h. Water was added to the reaction mixture (in some cases quantities of diethyl ether were also added to facilitate phase separation), and the organic phase was separated; the aqueous phase was further extracted with diethyl ether before the combined organic phases were dried over anhydrous magnesium sulfate. Following filtration, silica gel was added, and the solvent was removed to leave the products adhered to silica gel. The silica gel fraction was then added as a top layer to column chromatographic support, and the products were isolated. The first bright yellow orange fraction eluted with a 3% solution of diethyl ether in petroleum ether was a low-yield mixture of unreacted dibromoferrocene and traces of monobromoferrocene. The reactions products [1,1′-dibromo-2,5-bis(diphenylphosphino)]ferrocene **B** (55%) and [1,1′-dibromo-2,2′-bis(diphenylphosphino)]-ferrocene (45%) were subsequently eluted by incremental addition of further quantities of diethyl ether. The isolation procedure can be simplified since we have observed that mixtures of the previous compounds, which coelute, crystallize independently upon ether evaporation, with compound **B**, forming large well-formed brown-orange crystals easily separable from the pale yellow powder formed by the over ferrocene derivatives. Compound **B**: $C_{34}H_{26}Br_2FeP_2$; *m*/*z* 712 (parent ion); calcd C 57.34, H 3.68; found C 57.43, H 3.61; ^{1}H NMR δ 3.74 (s, 2H, Cp), 4.12 (m, 2H, Cp), 4.29 (pt, 2H, Cp), 7.15–7.41 (series of m, 20H Ph); ^{31}P{^{1}H} NMR δ −22.4. A crystal structure of the product **B** is reported in ref 4f.

1,1′,2,3-Tetrakis(diphenylphosphino)ferrocene **1** was obtained in a high 90% yield from lithiation of **B** (1 mol equiv) with *n*-butyllithium (2.2 mol equiv) at −80 °C in diethyl ether (1 h), followed by quenching with chlorodiphenylphosphine (2.2 mol equiv.); the reaction mixture was allowed to warm to room temperature over 2 h. Water was added to the crude product, and the organic phase separated was subjected to column chromatography for purification. $C_{58}H_{46}FeP_4$; *m*/*z* 922 (parent ion); calcd C 75.50, H 5.02; found C 75.60, H 4.88; ^{1}H NMR δ 3.50 (pq, 2H, $J \approx 1.8$ Hz), 3.90 (s, 2H), 4.38 (pt, 2H, $J \approx 1.8$ Hz), 6.80–7.30 (series of m, 40H); ^{31}P{^{1}H} NMR δ −24.1 (d, $J_{PP} = 59.7$ Hz), −18.7 (s), −15.0 (t, $J_{PP} = 59.7$ Hz); ^{13}C{^{1}H} NMR δ 75.4, 75.8, 75.9, 77.6 (s, 1 each, *C*−Fc), 78.7 (d, *C*−Fc), 87.0, 87.1, 87.3, 88.5, 88.7 (s, br, 1 each *C*−Fc), 127.5, 127.6, 127.8 (d, $J = 16$ Hz, *C*−Ph), 128.0 (m, *C*−Ph), 128.2 (s, *C*−Ph), 133.1 (dd, *C*−Ph), 134.7, 134.9, 137.0, 138.7, 139.2 (d, *C*−Ph). Crystallographic data are available as Supporting Information.

[PdCl$_2$(1)] (3a). The complex was immediately formed as an intermediate species, together with a minor amount of **3b**, upon addition at room temperature (RT) of [PdCl$_2$(cod)] or [PdCl$_2$(PhCN)$_2$] (2 mol equiv) in a minimum of chloroform to **1** (1 mol equiv): ^{1}H NMR δ 2.05 (s, 1H), 2.42 (s, 1H), 2.94 (s, 1H), 4.08 (s, 1H), 4.50 (s, 1H), 4.75 (s, 1H), 6.75–8.85 (series of m, 40H); ^{31}P{^{1}H} NMR δ −29.2 (s), −18.6 (s), 40.3 (d, $J_{PP} = 10.9$ Hz), 52.2 (d, $J_{PP} = 10.9$ Hz).

[Pd$_2$Cl$_4$(1)] (3b). The complex was isolated in quantitative yield and pure form from the addition at RT of [PdCl$_2$(cod)] or [PdCl$_2$(PhCN)$_2$] (2 mol equiv) to **1** (1 mol equiv) in a minimum of chloroform after stirring for 3 h and evaporation of solvent and volatiles. Slow evaporation of a chloroform solution allowed to obtained single crystals suitable for X-ray diffraction studies: $C_{58}H_{46}Cl_4FeP_4Pd_4$; *m*/*z* 1277 (parent ion); calcd C 54.54, H 3.63; found C 54.60, H 3.52; ^{1}H NMR δ 3.08 (s, 2H), 3.28 (s, 2H), 3.60 (s, 2H), 6.75–8.10 (series of m, 40H); ^{31}P{^{1}H} NMR δ 23.6 (d, $J_{PP} = 22.5$ Hz), 34.3 (d, $J_{PP} = 9.0$ Hz), 44.6 (d, $J_{PP} = 22.5$ Hz), 62.3 (d, $J_{PP} = 9.0$ Hz). Because of solubility troubles, a proper ^{13}C NMR assignment was difficult to obtain.

[NiCl$_2$(1)] (4a). The complex was quantitatively obtained by reaction of **1** with 1 mol equiv of $NiCl_2$DME in chlorinated solvent. Addition of a 2−10 excess of nickel halide and stirring for five days did not produce any dinuclear nickel complex; changes of solvent (such as DMSO) were not more helpful. After filtration and solvent/volatile evaporation, the complex is obtained as a red-orange powder: $C_{58}H_{46}Cl_2FeP_4Ni$; *m*/*z* 1050 (parent ion); calcd C 66.20, H 4.41; found C 66.08, H 4.48; ^{1}H NMR δ 2.00 (s, 1H), 2.31 (s, 1H), 3.01(s, 1H), 3.85 (s, 1H), 4.45 (s, 1H), 4.65 (s, 1H), 6.80–9.30 (series of m, 40H); ^{31}P{^{1}H} NMR: δ −28.6 (s), −18.8 (s), 38.3 (d, $J_{PP} = 69.8$ Hz), 49.4 (d, $J_{PP} = 69.8$ Hz).

1,1′,2-Tris(diphenylphosphino)-4-*tert*-butylferrocene (5). The ligand was synthesized in THF following a reported procedure:[4b] to a stirred suspension of $FeCl_2$ (0.53 g, 4.2 mmol) was added at −40 °C a THF solution of *t*BuCp(PPh$_2$)$_2$Li (2.18 g, 4.4 mmol) dropwise. After the mixture was stirred for 2 h, it was treated at −40 °C with a solution of Cp(PPh$_2$)Li (1.00 g, 3.9 mmol). The THF was evaporated under vacuum, and the residue was refluxed in toluene for 3 h. After filtration, the crude product was subjected to column chromatography (SiO$_2$, toluene hexane 4:1) to provide 2.60 g of **5** (yield 84%): $C_{50}H_{45}FeP_3$ (794.7); calcd C 75.57, H 5.71; found 75.59, H 5.68; *m*/*z* 794; ^{1}H NMR δ 1.03 (s, 9H, *t*-Bu), 4.07 (dd, $J_{PH} = 3.3$ Hz, $^{3}J_{HH} = 1.8$ Hz, 2H, Cp), 4.17 (dd, $^{3}J_{HH} \approx J_{PH} = 1.8$ Hz, 2H, Cp), 4.20 (dd, 2 $J_{PH} \approx 1.5$ Hz, 2H, 3,5-Cp), 6.91–7.12 (m, 10H, Ph, 1,2-PPh$_2$), 7.13–7.26 (m, 10H, Ph, 1′-PPh$_2$), 7.33 (m, 6H, *m*,*p*-Ph 1,2-PPh$_2$), 7.64 (m, 4H, *o*-Ph 1,2-PPh$_2$); ^{31}P{^{1}H}(CDCl$_3$) δ −22.7 (d, $^{TS}J = 2.8$ Hz, 1,2-PPh$_2$), −19.3 (t, $^{TS}J = 2.8$ Hz, 1′-PPh$_2$); ^{31}P{^{1}H}(C$_6$D$_6$) δ −21.9 (d, $J = 5.0$ Hz, 1,2-PPh$_2$), −20.0 (t, $J = 5.0$ Hz, 1′-PPh$_2$); ^{13}C{^{1}H} δ 30.5 (s, *C*(CH$_3$)$_3$), 31.3 (d, $J_{PC} = 1.5$ Hz, C(*C*H$_3$)$_3$), 71.4 (m, 3,5-Fc), 72.0 (m, 2 *C*-Cp), 74.4 (d, $J_{PC} = 11.0$ Hz, 2 *C*-Cp), 80.2 (d, $J_{PC} = 12.5$ Hz, 1′-Fc), 81.9 (m, 1,2-Fc), 106.8 (s, 4-Fc), 127.4 (t, $2J_{PC} \approx 3.5$ Hz, *m*-Ph), 127.5 (s, *p*-Ph), 128.0 (d, $J_{PC} = 7.2$ Hz, *m*-Ph), 128.1 (t, $2J_{PC} \approx 8.8$ Hz, *m*-Ph), 128.3 (s, *p*-Ph), 128.8 (s, *p*-Ph), 132.9 (t, $2J_{PC} \approx 10.3$ Hz, *o*-Ph), 133.8 (d, $J_{PC} = 21.0$ Hz, *o*-Ph), 135.1 (dt, $2J_{PC} \approx 10.9$ Hz, $J_{P'C} = 1.5$ Hz, *o*-Ph), 137.6 (t, $2J_{PC} \approx 2.9$ Hz, *ipso*-Ph), 138.8 (t, $2J_{PC} \approx 4.7$ Hz, *ipso*-Ph), 139.5 (d, $J_{PC} = 14.8$ Hz, *ipso*-Ph).

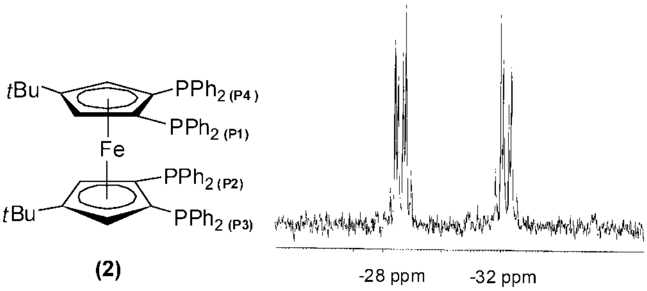
[$NiCl_2$(5)] (6). A mixture of 1,1′,2-tris(diphenylphosphino)-4-*tert*-butylferrocene (857 mg, 1.08 mmol) and $NiCl_2$DME (237 mg, 1.08 mmol) was refluxed in acetonitrile for 3 h. The solvent was evaporated, and the residue was refluxed in toluene for 10 min. After it cooled, the solid material was filtered off, giving a yield of 729 mg (73%): $C_{50}H_{45}Cl_2P_3FeNi$ (924.27); calcd. C 64.98, H 4.91; found C 64.83, H, 5.11; ^{1}H NMR δ 1.31 (s, 9H, *t*Bu), 3.29 (m, 2H, Fc), 3.63 (m, 2H, Fc), 4.35 (s, 2H, 3,5-Fc), 7.03–7.54 (m, 26H, *m*, *p*-Ph), 8.22 (m, 4H, *o*-Ph); ^{31}P{^{1}H} NMR: δ −20.1 (br, 1′-PPh_2), 36.2 (br, 1,2-PPh_2); ^{13}C{^{1}H} NMR: δ 32.1 ($C(CH_3)_3$), 32.7 ($C(CH_3)_3$), 68.5 (s, 2 *C*−Cp), 72.5 (s, 3,5-Fc), 75.4 (s, 2 *C*−Cp), 83.9 (s, 1′(or 1,2)-Fc), 86.9 (s, 1,2(or 1′)-Fc), 118.8 (s, 4-Cp), 128.6, 128.7, 128.8, 129.3, 131.1, 131.8, 133.2 (s, *C*H−Ph), 134.0 (br, *C*H−Ph), 135.3 (s, *C*H−Ph), 138.3 (s, *ipso*-Ph).

[$PdCl_2$(5)], (7). A mixture of 1,1′,2-tris(diphenylphosphino)-4-*tert*-butylferrocene (200 mg, 0.25 mmol) and $PdCl_2$ (47 mg, 0.27 mmol) was refluxed under stirring in THF overnight. The solvent was evaporated in vacuum, and the residue was dissolved in CH_2Cl_2. After addition of ether (20 mL), the reaction mixture was filtered and evaporated, and the residue was crystallized from a CH_2Cl_2−hexane mixture to yield 230 mg of **7** (95%): $C_{50}H_{45}Cl_2P_3FePd$ (972); calcd C 61.78, H 4.67; found C 61.62, H 4.56; ^{1}H NMR δ 1.35 (s, 9H, *t*-Bu), 3.35 (dd, J_{HH} = 1.8 Hz, J_{PP} = 3.3 Hz, 2H, Fc), 3.59 (dd, $J_{HH} \approx J_{PP} \approx$ 1.8 Hz, 2H, Fc), 4.47 (dd, $J_{HH} \approx J_{P-P} \approx$ 1.2 Hz, 2H, 3,5-Fc), 7.0–7.6 (m, 26H, the rest of Ph protons), 8.12 (m, 4H, *o*-Ph); ^{31}P{^{1}H} NMR δ −20.8 (s, 1′-PPh_2), 45.3 (s, 1,2-PPh_2); ^{13}C{^{1}H} NMR δ 32.1 (m, $C(CH_3)_3$), 32.8 (s, $C(CH_3)_3$), 69.2 (m, 3,5-Fc), 72.5 (d, J_{PC} = 2.3 Hz, 2 *C*−Cp), 75.6 (d, J_{PC} = 9.1 Hz, 2 *C*−Cp), 84.4 (d, J_{PC} = 13.6 Hz, 1′-Fc), 86.1 (m, 1,2-Fc), 119.7 (m, 4-Fc), 128.7–129.1 (m, *C*H-Ph), 129.4 (s, *C*H-Ph), 130.8 (dd, J_{PC} = 65.7 Hz, J_{PC} = 2.3 Hz, *ipso*-Ph), 131.5 (s, CH-Ph), 132.2 (dd, J_{PC} = 57.4 Hz, J_{PC} = 2.3 Hz, *ipso*-Ph), 132.3 (s, *C*H-Ph), 132.8 (m, *o*-Ph), 134.0 (d, J_{PC} = 21.1 Hz, *o*-Ph), 135.5 (m, *o*-Ph), 138.2 (d, J_{PC} = 13.6 Hz, *ipso*-Ph).

Crystallographic Data. For **1** and **3b** data were collected at the University of Southampton on a Nonius Kappa CDD diffractometer with Mo Kα radiation (λ = 0.71073Å, details are available as Supporting Information). The data for compound **6** (single crystals [**6**•2($CHCl_3$)] were obtained from $CHCl_3$) were collected at 160 K on a IPDS STOE diffractometer using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), and equipped with an Oxford Cryosystems Cryostream Cooler Device at the LCC-CNRS Toulouse. The final unit cell parameters were obtained by means of a least-squares refinement; structures were solved by direct methods using SHELX97 and were refined by means of least-squares procedures on F^2.

Results and Discussion

Tetraphosphine Synthesis and Characterization. An examination of the literature reveals that a number of efficient methods are available for the selective formation of 1,2-substituted ferrocenes via ortho-directing groups (chiral or nonchiral), for example, nonexhaustively, amine,[7] acetal,[8] oxazoline,[9] amide,[10] sulfoxide,[11] and phosphine oxide[12] groups. On the basis of an analogous ortho-metalation process, the tetraphosphine **1** can be obtained in four synthetic steps starting from the easily available 1,1′-dibromoferrocene (Scheme 1). The first synthesis step leading to compound **A** is the more delicate because an accurate adjustment of the amount of lithium diisopropylamide reagent (LDA) is necessary to limit the formation of side products as monolithiated and 2,2′-dilithiathed dibromoferrocenes.[4f] Quenching of the mixture with chlorodiphenylphosphine results in the major formation of compound **B**, which can then undergo after purification a selective substitution of bromides by lithium atoms using *n*BuLi, in a third step. Phosphorylation of the resulting compound **C**, using chlorodiphenylphosphine, quantitatively leads to the dissymmetric tetraphosphine **1**.



(2)

Figure 1. Tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene **2** exhibits an AA′BB′ ^{31}P NMR spectrum in $CDCl_3$.

The characterization of **1** both in solution and in the solid state is of great interest for comparison with the unusual spectroscopic and structural properties of the closely related tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene (**2** in Figure 1) that has been previously reported.[1] The blocked cisoid conformation of **2**, resulting from the presence of encumbering *t*Bu substituents on cyclopentadienyl (Cp) rings, enforces a close proximity of the four phosphorus atoms and lead to the existence of spin–spin nuclear coupling constants via non-bonded interaction (through-space spin coupling). The resulting AA′BB′ spin system (Figure 1, right) comprises a very intense J_{P1P2} coupling of 59.8 Hz between the two pseudoeclipsed heteroannular phosphorus P1 and P2, clearly identified as a through-space coupling arising from close vicinity of the nucleus (with lone-pair electronic cloud overlap) even in solution (the distance in the solid state P•••P = 3.728(2) Å).

In the ^{31}P NMR spectrum obtained for **1**, the signals corresponding to the phosphorus, (P1, P3) and P2, on the same cyclopentadienyl ring (Cp), are found as a doublet and a triplet at −24.1 and −15.0 ppm, respectively (Figure 2). A $^3J_{PP}$ coupling constant of ~60 Hz is observed between P2 and the isochronous nucleus (P1, P3). In contrast to the spectroscopic features reported for **2** concerning its heteroannular phosphorus atoms, the phosphorus P4 on the second Cp ring did not exhibit any nuclear spin coupling with the three other phosphorus (singlet at −18.7 ppm, see Figure 2). On the basis of the lone-pair phosphorus

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(7) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4405.

(8) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, 5835.

(9) Sammakia, T.; Latham, H. A.; Schaad, D. R. *J. Org. Chem.* **1995**, *60*, 10.

(10) Tsukazaki, M.; Tinkl, M.; Roglans, A.; Chapell, B. J.; Taylor, N. J.; Snieckus, V. *J. Am. Chem. Soc.* **1996**, *118*, 685.

(11) Hua, D. H.; Lagneau, N. M.; Chen, Y.; Robben, P. M.; Clapham, G.; Robinson, P. D. *J. Org. Chem.* **1996**, *61*, 4508.

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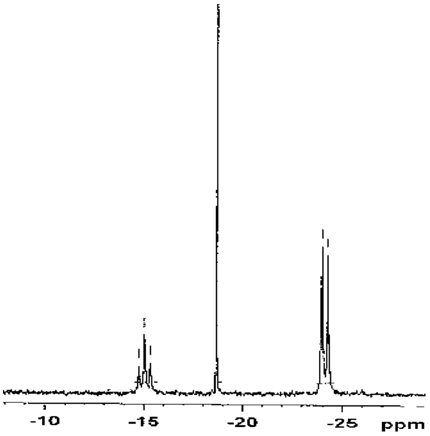

Figure 2. ^{31}P NMR spectrum of the tetraphosphine 1,1′,2,3-tetrakis(diphenylphosphino)ferrocene **1** in $CDCl_3$.

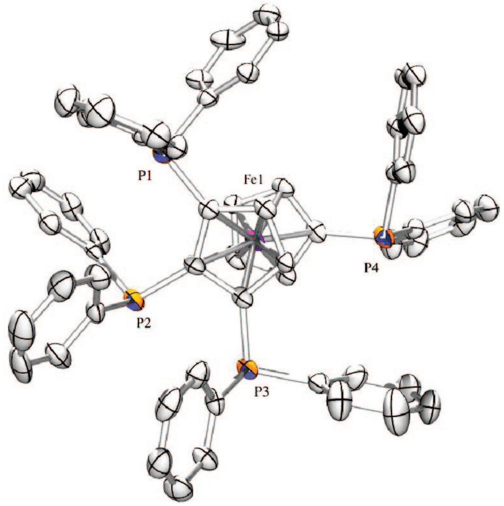

Figure 3. Plot of metallo-ligand **1** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Fe−CNT(1) = 1.637, Fe−CNT(2) = 1.653. Selected internuclear distances (Å): $P_1\cdots P_2$ = 3.805, $P_2\cdots P_3$ = 3.336, $P_1\cdots P_4$ = 6.335, $P_3\cdots P_4$ = 5.180.

interaction model we developed for tetraphosphine ferrocenyl derivatives,[1] we anticipated that the structure of the polyphosphine **1** would not enforce a position of close vicinity for P4 to any of the other phosphorus atoms. Our hypothesis was a posteriori supported by the solid-state molecular structure displayed in Figure 3 (crystallographic data are given in Table 1), in which P4 is facing in a direction opposite to that of P1, P2, and P3. In the absence of structural constraint for the rotation of the Cp rings, in this conformation, a through-space coupling transmitted via lone-pair electron overlapping interaction is barely conceivable (while a through-bond $^4J_{PP}$ coupling would be negligible). Table 2 presents the internuclear through-space distances found by X-ray diffraction between the four phosphorus atoms of ligand **1**, together with the corresponding data for ligand **2**. The internuclear distances between heteroannular phosphorus atoms P1···P4, P2···P4, and P3···P4 (Figure 3), for which no spin coupling was detected, range between 5.180 and 6.747 Å. This is consistent with previously reported studies in which ferrocenyl tetraphosphine derivatives were found to have no detectable $J_{PP'}$ that can be observed with P···P′ distances above 4.90 Å (this value is nevertheless far superior to the physical data known as the sum of van der Waals radii for phosphorus,[13] 3.6 Å).[1] Furthermore, we still consistently note that for P···P internuclear distances below 4.00 Å strong coupling constants (above 20 Hz) are observed.

It is noteworthy that in the conformation found in the solid state the P···P internuclear distances between (P1, P2) and (P2, P3) are substantially different (about 0.5 Å); the shortest distances is found between the phosphorus atoms (P2,P3) for which the lone-pairs are pointing toward each other.

Similarly, the position of P4 is much closer to P3 (P3···P4 = 5.180 Å) than to P1 (P1···P4 = 6.335 Å), inducing a general dissymmetry of the tetraphosphine in the preferred conformation found in the solid state.

Coordination of Tri and Tetraphosphines toward Group 10 Transition Metals. A correlation between the internuclear phosphorus atoms distances through-space and the intensity of ^{31}P nuclear spin couplings could be established within the framework of nickel and palladium coordination complexes of **2** (Figure 1).[1] We were, thus, much interested in the synthesis of some palladium and nickel coordination complexes incorporating the new ligand **1**. One of the goals was to estimate whether such a correlation could also exist for these derivatives. On the basis of the conformation obtained for **1** in the solid state (Figure 3), it was also interesting to find which kind of coordination species would be favored. Upon reaction of **1** with 2 equiv of palladium chloride precursors ($PdCl_2cod$ or $PdCl_2(RCN)_2$, cod = 1,5-cyclooctadiene, R = Me, Ph, Scheme 2) it was observed that within the ten first minutes a rapid coordination occurred, initially at the trisubstituted ring leading in majority to the formation of the palladium mononuclear complex **3a**.

For **3a**, the signals corresponding to the three phosphorus P1, P2, and P3 on the same Cp ring are easily distinguishable: two doublets at 40.3 and 52.2 ppm are attributed to P1 and P2 ($^2J_{P1P2}$ = 11 Hz), respectively. The signal corresponding to P3 appears as a singlet at −29.2 ppm, no longer showing any spin coupling to the phosphorus P2. This might be an indication of a possible contribution of the lone-pairs on the intensity of $^3J_{P1P2}$ coupling in the ligand **1** (Table 1, $^3J_{P2P3}$ = 59.7 H_Z).[14] The chemical shift corresponding to phosphorus P4, on the other Cp ring, is not affected by the coordination to palladium and a singlet at −18.7 ppm was still detectable. Because of the absence of nuclear spin-coupling between the bonded and the free phosphorus atoms, we definitely admit the absence of TS *J* couplings in **3a**.

The coordination of a second palladium is a slower process, which results in a complete conversion of the mixture of **1** and **3a** into the dinuclear palladium complex **3b** after three hours. The ^{31}P NMR spectrum observed for **3b** (Figure 4) gave the first evidence of the conformational changes in the ferrocenyl backbone: a rotation of the ring being required to allow the heteroannular coordination of a

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(13) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1945..

(14) With no certainty, *J* coupling might be, for example, increased by a TS contribution resulting from a lateral overlapping of phosphorus lone pairs in **1**, which is absent in **3a**.

Table 1. Crystal, Collection, and Refinement Parameters for **1** and **3b**

	1	**3b**
empirical formula	$C_{58}H_{46}FeP_4$	$C_{58}H_{46}Cl_4FeP_4Pd_2$
fweight	922.68	1277.28
temp	120(2) K	120(2) K
wavelength	0.71073 Å	0.71073 Å
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
unit cell dimensions	$a = 12.2404(10)$ Å, $\alpha = 90°$	$a = 21.099(17)$ Å, $\alpha = 90°$
	$b = 21.4422(11)$ Å, $\beta = 90.914(3)°$	$b = 19.036(19)$ Å, $\beta = 112.19(4)°$
	$c = 17.6539(14)$ Å, $\gamma = 90°$	$c = 17.797(6)$ Å, $\gamma = 90°$
vol	4632.9(6) Å^3	6619(9) Å^3
Z	4	4
density (calcd)	1.323 Mg/m^3	1.282 Mg/m^3
abs coeff	0.503 mm $^{-1}$	1.043 mm $^{-1}$
F(000)	1920	2560
cryst shape, color	shard, orange	rod, orange
cryst size	$0.24 \times 0.22 \times 0.14$ mm^3	$0.28 \times 0.04 \times 0.03$ mm^3
θ range for data collection	3.30–27.48°	2.91–27.48°
index range	$-14 \leq h \leq 15$	$-24 \leq h \leq 252$
	$-26 \leq k \leq 27$	$-22 \leq k \leq 2$
	$-19 \leq l \leq 22$	$-21 \leq l \leq 20$
reflns collected	44 519	48 345
independent reflns	10 084 [$R_{int} = 0.1261$]	11 234 [$R_{int} = 0.1810$]
completeness to $\theta = 27.48°$	95.0%	95.0%
abs correction	semiempirical from equivalents	semiempirical from equivalents
max. and min. transm	0.9329 and 0.8888	0.9694 and 0.7589
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	10 084/0/568	11 234 /623/622
GOF on F^2	1.054	1.028
Final R indices [$F^2 > 2\sigma(F^2)$]	R1 = 0.0826, wR2 = 0.1807	R1 = 0.1343, wR2 = 0.3333
R indices (all data)	R1 = 0.1939, wR2 = 0.2193	R1 = 0.2609, wR2 = 0.3821
largest diff. peak and hole	1.248 and −0.558 e Å^{-3}	0.959 and −1.133 e Å^{-3}

Table 2. Through-Space Distances between Phosphorus Nuclei (from X-ray Data) and the Corresponding ^{31}P NMR J_{PP} Coupling Constants

P···P distances[a] (Å)/coupling constant (Hz)	**2**[b]	**1**	**3b**
$d(P_1\cdots P_2)/J_{PP}$	3.728/59.8	3.805/59.7	3.119/9
$d(P_1\cdots P_3)/J_{PP}$	4.861/ND	5.788/ND	5.854/ND
$d(P_4\cdots P_2)/J_{PP}$	4.861/ND	6.747/ND	6.236/ND
$d(P_4\cdots P_3)/J_{PP}$	6.633/ND	5.180/ND	3.570/22
$d(P_1\cdots P_4)/J_{PP}$	3.364/74.5	6.335/ND	6.862/ND
$d(P_2\cdots P_3)/J_{PP}$	3.364/74.5	3.336/59.7	4.226/ND

[a] The numbers attributed to phosphorus nucleus correspond to those displayed in Figures 1 and 3 and in Scheme 2. [b] Data from ref 1. ND = no coupling detected.

$PdCl_2$ moiety via P3 and P4 (the closer atoms in an heteroannular pair). A confirmation of this unprecedented palladium dinuclear framework was given by the X-ray diffraction structure solved (Figure 5, Table 2). In the NMR spectrum of **3b**, four different signals are observed as two pairs of related doublets. The significantly different J_{PP} coupling constants, 9 and 22 Hz, allowed us to assign the signals by comparison with **3a**; the more shielded phosphorus nucleus are assumed to occupy external positions.[3a] Therefore, two doublets corresponding to P1 and P2 are found at 34.3 and 62.3 ppm, respectively ($J_{PP} = 9$ Hz, close to the *J* constant found in **3a**), and two doublets corresponding to P3 and P4 are found at 44.6 and 23.6 ppm, respectively ($J_{PP} = 22$ Hz).

In the molecular structure of **3b**, the palladium centers both lie in a square planar environment. However, whereas coordination complexes of metallocenes incorporating *either* 1,2-homoannular *or* 1,1′-heteroannular chelating frameworks are very common, the complex **3b** is a unique example of metallocene derivative incorporating both these coordination modes. The measured bite angles P−Pd−P (nonstandardized)[15] are within the range of typical values of the different modes of coordination (~96−102° for 1,1′-P bonded and around 84−88° for 1,2-P bonded ferrocene complexes) with a value of 102.4° for P3−Pd−P4 and 88.9° for P1−Pd−P2. These structural data are important with regard to complexes reactivity, and especially in catalysis.[16] The other distances and angles (Figure 5) are consistent with reported values for compounds of this family.[3a]

On the basis of these results, the coordination chemistry of **1** with nickel was of particular interest because it is known that the coordination framework with ferrocenyl diphosphines could be either tetrahedral (in 1,1′-P substituted derivatives such as with the ubiquitous 1,1′-bis(diphenylphosphino)ferrocene dppf)[17] or square planar (in 1,2-P substituted derivatives); the ligand **1** appeared as very useful to investigate the coordination preference of nickel. Upon reaction of **1** with 1 or 2 equiv of nickel halide precursors ($NiCl_2DME$ or $NiBr_2DME$, DME = 1,2-dimethoxyethane) it was observed, as in the case of palladium, the rapid coordination of a nickel dichloride fragment to two adjacent phosphorus atoms of the trisubstituted ring (Scheme 3).

In this case, however, in contrast to palladium, there was no indication of further coordination of the remaining heteroannular phosphine atoms toward a dinuclear species. The ^{31}P NMR characterization of **4a** in $CDCl_3$ (Figure 6)

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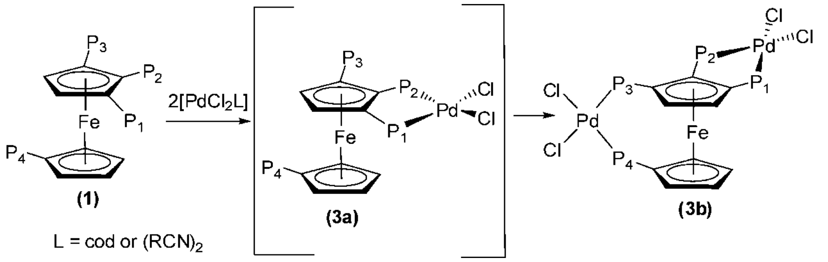
(15) For bite angle definitions, see: Dierkes, P.; van Leeuwen, P. W. N. M *J. Chem. Soc., Dalton Trans.* **1999**, 1519 and references therein.

(16) Fihri, A.; Meunier, P.; Hierso, J.-C. *Coord. Chem. Rev.* **2007**, *251*, 2017.

(17) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972.

Scheme 2. Formation of the Palladium Complexes **3a** and **3b** (the Phenyl Groups on Phosphorus Are Omitted for Clarity)



shows two doublets for the bonded phosphorus centered at 49.4 and 38.3 ($^2J_{PP}$ = 70 Hz). The signal corresponding to the last phosphorus of the trisubstituted ring was found as a singlet at −28.6 ppm, and as was the case of the mononuclear palladium complex **3a**, the chemical shift corresponding to P4 was not affected by the coordination to metal and a singlet was detected at −18.7 ppm.

With the view to get a dinuclear nickel complex analogous to **3b**, several experiments were conducted both in chlorinated solvents and in DMSO. The formation of such complex would either shift to lower fields the signals found around −20 to −30 ppm in **4a** or make it disappear (tetrahedral paramagnetic species). Curiously, it was not possible to induce or even detect any further coordination when a large excess of $NiBr_2(DME)$ or $NiCl_2(DME)$ was added to **4a**. The addition of $Pd(PhCN)_2Cl_2$ to **4a**, to form a hetero dinuclear complex, was also unsuccessful. For these reasons, in Scheme 3 (compared to Scheme 2), we suggested a first coordination of nickel between P2 and P3 (in solid state *d*(P2···P3) = 3.336 Å), which might make a subsequent coordination of a metal center between P1 and P4 (*d*(P1···P4) = 6.335 Å)[18] more difficult. Small differences were noted on samples run with excess nickel several days in DMSO, as shown in Figure 7, broadening of the signals appeared for the bonded phosphorus, possibly paramagnetic in origin. This is attributed to the effect of bonded DMSO molecules because DMSO-solvated nickel(II) complexes are known,[19] as well as paramagnetic five-coordinated nickel (II) halide phosphine complexes.[20]

This preference of nickel complexes for a 1,2-P coordination (in a square planar environment) on a 1,1′-P coordination (tetrahedral geometry) was confirmed by the study of the

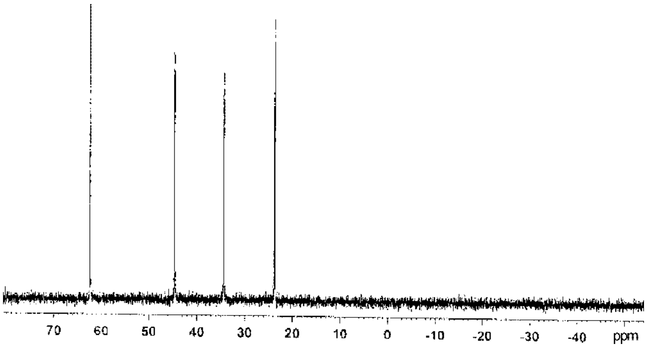


Figure 4. ^{31}P NMR spectrum of the dinuclear palladium complex **3b**.

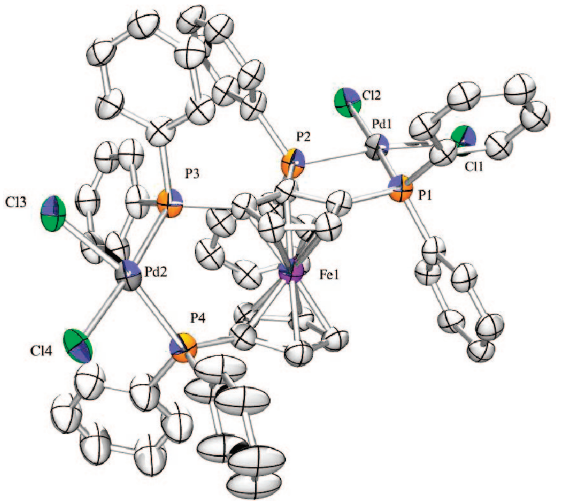
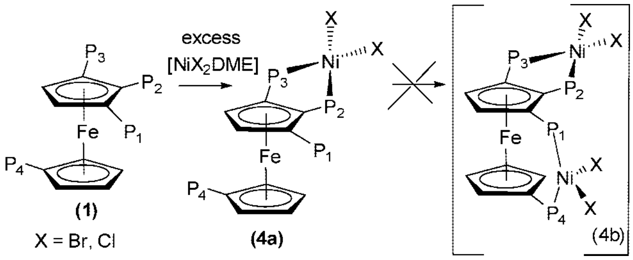


Figure 5. Plot of dinuclear palladium complex **3b** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe−CNT(1) = 1.627, Fe−CNT(2) = 1.654. P1−Pd1 = 2.207(4), P2−Pd1 = 2.247(5), P3−Pd2 = 2.304(5), P4−Pd2 = 2.278(6), Cl1−Pd1 = 2.355(5), Cl2−Pd1 = 2.383(4), Cl3−Pd2 = 2.336(5), Cl4−Pd2 = 2.343(5); P1−Pd1−P2 = 88.88(18), Cl1−Pd1−Cl2 = 93.12(17), P3−Pd2−P4 = 102.38(19), Cl3−Pd2−Cl4 = 87.64(19), Cl2−Pd1−P1 = 175.47(18), Cl2−Pd1−P2 = 87.72(17), Cl1−Pd1−P2 = 172.31(19), Cl1−Pd1−P1 = 90.65(17), Cl4−Pd2−P3 = 174.3(2), Cl4−Pd2−P4 = 83.3(2), Cl3−Pd2−P4 = 166.62(19), Cl3−Pd2−P3 = 86.94(19).

Scheme 3. Formation of the Mononuclear Nickel Complexes **4a**[a]



[a] The postulated dinuclear **4b** could not be formed despite the use of large excess of nickel halide precursors and long-time reactions.

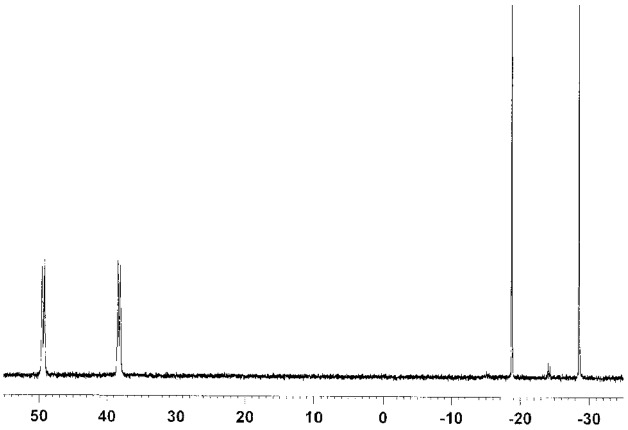


Figure 6. ^{31}P NMR spectrum of the mononuclear nickel complex in $CDCl_3$, **4a**.

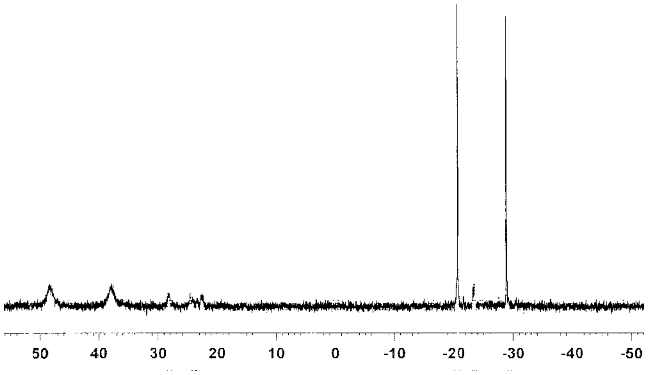
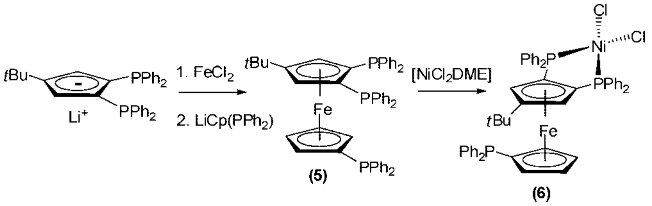


Figure 7. ^{31}P NMR spectrum of the complex obtained in DMSO [**4a**(DMSO)$_x$].

Scheme 4. Synthesis of the Ligand **5** and Its Corresponding Nickel Dichloride Complex **6**



coordination chemistry of a parent triphosphine ligand **5**. This triphosphine was also expected to allow a certain rotational flexibility and thus to potentially lead to 1,1′- or 1,2-P different coordination modes. The synthetic pathway for the synthesis of **5**, which is inherently different from synthesis for **1**, is displayed in Scheme 4.[4b]

The coordination chemistry of **5** toward nickel halides ($NiCl_2DME$ and $NiBr_2DME$) preferentially lead to the formation of the chelate complex **6**. The flexibility of the ferrocene backbone was somewhat confirmed by the ^{31}P NMR spectrum obtained at ambient temperature for **6**, which displays two broad peaks at −20.1 and 36.2 ppm in $CDCl_3$ with a relative integration of 1:2 respectively (Figure 8); in the low-temperature NMR spectrum, the signal broadness decreases as the complex lability is slowed, leading to two fine singlets with no phosphorus spin−spin coupling.

Single crystals of **6** solvated with chloroform were obtained, from which an X-ray diffraction study was carried out that consistently, with ^{31}P NMR, establishes the 1,2-P bonding preference of the nickel atom (Figure 9). The nickel center lies in a fairly regular square planar environment for which P1−Ni1−P2 = 90.2°, Cl1−Ni1−Cl2 = 93.7°, Cl2−Ni1−P2 = 87.5°, and Cl1−Ni1−P1 = 88.6°; the Ni−X (X = Cl, P) bonds range from 2.15 to 2.19 Å. The analogous palladium chloride complex **7** was also obtained; it displays

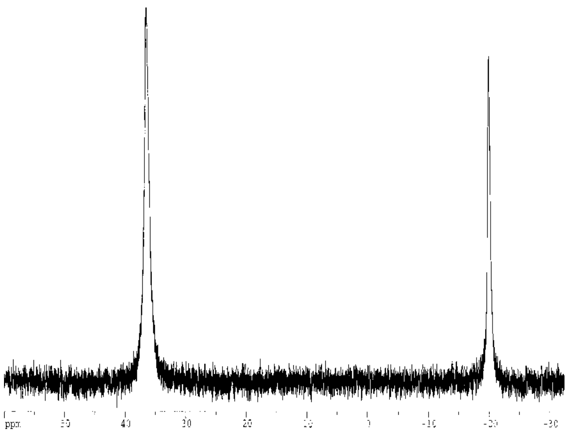


Figure 8. ^{31}P NMR spectrum of the complex **6** in $CDCl_3$ at RT.

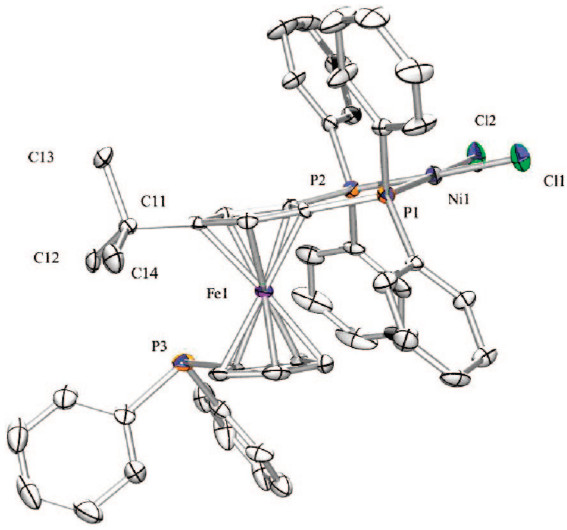


Figure 9. Plot of nickel complex **6**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe−CNT(1) = 1.668, Fe−CNT(2) = 1.659, P1−Ni1 = 2.1483(15), P2−Ni1 = 2.1554(12), Cl1−Ni1 = 2.1967(12), Cl2−Ni1 = 2.1949(15), P1−Ni1−P2 = 90.20(5), Cl1−Ni1−Cl2 = 93.72(4), Cl2−Ni1−P1 = 177.73(5), Cl2−Ni1−P2 = 87.53(4), Cl1−Ni1−P2 = 177.86(5), Cl1−Ni1−P1 = 88.55(5).

Table 3. Crystal, Collection, and Refinement Parameters for [**6**·2($CHCl_3$)]

	[**6**·2($CHCl_3$)]
empirical formula	$C_{52}H_{47}Cl_8P_3FeNi$
fw	1162.97
temp	160(2) K
wavelength	0.71073 Å
cryst syst	Monoclinic
space group	$P2_1/c$
unit cell dimensions	a = 10.00317(8) Å, α = 90° b = 23.3697(2) Å, β = 98.943(7)° c = 22.4018(6) Å, γ = 90°
vol	5173.9(3) Å^3
Z	4
density (calcd)	1.493 Mg/m^3
abs coeff	1.186 mm^{-1}
F(000)	2376
θ range for data collection	2.96–30.52°
index range	$-13 \leq h \leq 13$ $-31 \leq k \leq 32$ $-20 \leq l \leq 31$
reflns collected	45 905
independent reflns	14 596 [R_{int} = 0.0987]
completeness to 2θ = 61.04°	92.5%
refinement method	full-matrix least-squares on F^2
data/restraints/params	14 596/14/616
GOF on F^2	0.806
Final R indices [$F^2 > 2\sigma(F^2)$]	R1 = 0.0561, wR2 = 0.0590
R indices (all data)	R1 = 0.1696, wR2 = 0.0772
largest diff. peak and hole	0.499 and −0.558 e Å^{-3}

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(18) The difference of coordination behavior of the ligand depending on the metal might be then partly attributed to the relative atomic size of nickel and palladium in the decisive first 1,2-P chelation. Obviously, this hypothesis assumes that only small changes exist between solid-state structural features and solution behavior that should be further substantiated.

in ^{31}P NMR two singlets at −20.8 and 45.3 ppm with a relative integration of 1:2 respectively. In this case, 1,2-P-bonding was exclusively observed.

Summary and Conclusion

Ferrocenyl diphosphines are very well-known and useful compounds; conversely, only a few tri and tetraphosphines based on a ferrocene backbone have been developed to date. The present study details the two different synthetic routes employed to form the original 1,1′,2,3-tetrakis(diphenylphosphino)ferrocene (**1**) and 1,1′,2-tris(diphenylphosphino)-4-*tert*-butylferrocene (**5**) metallo-ligands. These species originally produced to observe possible intense ^{31}P^{31}P spin–spin couplings through-space originating from phosphorus atoms proximity in solution were shown to be too flexible (i.e., not constrained) for that purpose. The coordination behavior of the tetraphosphine **1** toward palladium and nickel was found markedly different since both dinuclear and mononuclear palladium complexes were obtained with palladium ([Pd_2Cl_4(**1**)], **3b** and **3a**), while only mononuclear nickel compounds were produced from nickel ([$NiCl_2$(**5**)], **6**). A reasonable explanation for that is based on a different regioselectivity of the first metal coordination, favoring or hampering the subsequent second metal coordination. The conformational features of tetraphosphine **1** gave rise to an unprecedented coordination framework in a metallocene coordination complex (**3b**), in which both coexist 1,1′ and 1,2 chelating P-bondings. The preference of nickel complexes for a 1,2-P coordination (in a square planar environment) on a 1,1′-P coordination was confirmed by the study of the coordination chemistry of the triphosphine ligand **5**. This study finally confirmed that in these ferrocenyl polyphosphine derivatives the correlation of solid state structures and solution multinuclear NMR is very profitable for the understanding of both their spectroscopic and coordination properties.

Acknowledgment. We thank B. Donnadieu for X-ray diffraction studies of nickel complex **6** and S. Royer and G. Delmas for technical support. We thank The “Conseil regional de Bourgogne” and CNRS for a postdoctoral grant to V.V.I. The cooperation program “Alliance” is also thanked for financial support of a France−U.K. collaboration between the Université de Bourgogne (Dijon) and the University of Wales (Bangor).

Supporting Information Available: Crystal details and data for **1**, **3b**, and **6**, conformation views of **1**, and typical ^{13}C, ^{1}H, and ^{31}P NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7022105

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