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Article

Reactivity of (Ferrocenylmethyl)phosphine toward Palladium and Platinum Chlorides. X-ray Structure of [Pd(PH_2CH_2Fc)Cl(μ-$PHCH_2Fc$)]$_4$ (Fc = Ferrocenyl), a Unique Complex Containing a Pd_4P_4 Cycle

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The reaction of 2 equiv of the air-stable primary phosphine (ferrocenylmethyl)phosphine (PH_2CH_2Fc, **1**) with [Pd(cod)Cl_2] (Fc = ferrocenyl; cod = 1,5-cyclooctadiene) at 298 K gave the phosphanido-bridged Pd(II) tetramer [Pd(PH_2CH_2Fc)Cl(μ-$PHCH_2Fc$)]$_4$ (**2**), which shows an unprecedented arrangement of four Pd atoms embedded in an eight-membered Pd_4P_4 ring. An X-ray diffraction study showed that **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 17.607(7)$ Å, $b = 17.944(7)$ Å, $c = 18.792(7)$ Å, $\alpha = 107.120(12)°$, $\beta = 96.344(13)°$, $\gamma = 117.087(15)°$. Each molecule contains four palladium atoms in a distorted square-planar coordination formed by one chlorine and three phosphorus atoms. Two of the latter belong to bridging primary phosphanides and the remaining one is contributed by a terminal PH_2CH_2Fc ligand. The coordination environments of neighboring metal centers adopt an almost perpendicular mutual orientation. The reaction of 2 equiv of **1** with [Pt(cod)Cl_2] at 323 K yielded the analogous Pt(II) tetramer of formula [Pt(PH_2CH_2Fc)Cl(μ-$PHCH_2Fc$)]$_4$ (**3**), which was fully characterized by multinuclear and dynamic NMR, IR, and elemental analyses. Single-crystal X-ray diffraction on **3** confirmed the tetranuclear arrangement in the solid state, but orientational disorder of the molecule precludes a more detailed discussion of the structure. Low-temperature NMR experiments in CD_2Cl_2 showed the presence of two slowly interconnecting conformers. Reaction of **1** and [M(cod)Cl_2] (M = Pd or Pt) at lower temperatures (273 K for Pd, 295 K for Pt) in dichloromethane allowed the detection in solution of the mononuclear species *cis*-[M(PH_2CH_2Fc)$_2Cl_2$] (M = Pd, **4**; M = Pt, **5**) which, upon heating, transformed into the tetramers **2** and **3**, respectively. Solid samples of **4** and **5** could be isolated after workup at low temperature and were characterized by conventional spectroscopic methods.

Introduction

Primary phosphines, PH_2R, are an important class of compounds[1] which, although discovered over a century ago, have been rarely employed as ligands for the synthesis of metal complexes,[2] mostly because of their high air-sensitivity, pyrophoricity (especially for alkyl phosphines), and toxicity. Nevertheless, the reactive character of the primary phosphines and the easy cleavage of the P−H bond[1] upon metal coordination make them interesting for the preparation of transition metal complexes.

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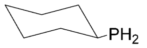
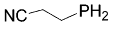
Pioneering studies on palladium and platinum complexes of primary phosphines were carried out using cyclohexyl- (**I**), 2-cyanoethyl- (**II**), and phenylphosphine (**III**)[3] or trimethylenediphosphine (**IV**).[4] In all cases, the reaction of 2 equiv of the organophosphorus ligand with metal chlorides gave the corresponding *cis*-$[L_2MCl_2]$ complexes, which underwent easy dehydrochlorination to give μ-phosphanido-bridged dimers, such as $[Pd(PH_2Cy)(\mu\text{-}PHCy)Cl]_2$,[5] or μ-phosphinidene dinuclear complexes, such as $[\{Pd(PH_2Ph)_2Cl\}_2(\mu\text{-}PPh)]$.[6] In recent years, the reactivity of sterically demanding primary phosphines such as 1-adamantylphosphine (**V**) or mesitylphosphine (**VI**) toward transition metal centers has attracted more interest due to the increased stability associated with the presence of bulky substituents. These reactions result in the formation of either mononuclear complexes of formula *cis*-$[ML_2Cl_2]$ (L = 1-adamantylphosphine[7] or mesitylphosphine;[8] M = Pd, Pt) or homoleptic metal complexes of Ni(0), Pd(II), Cu(I), and Ag(I) of general formula $[ML_4]^{n+}$ (L = mesitylphosphine, M = Ni, n = 0; M = Pd, n = 2; M = Cu, n = 1; M = Ag, n = 1).[9] With the exceedingly bulky PH_2Mes^* ligand [Mes^* = 2,4,6-$(t\text{-}Bu)_3C_6H_2$] the primary phosphine complexes $[ML_2Cl_2]$ (M = Pd, Pt) were isolated in the trans geometry. In contrast to *cis*-$[Pt(PH_2Mes)_2Cl_2]$, which underwent easy dehydrochlorination, these latter complexes are thermally stable in solution.[8]


(**I**)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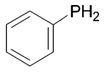
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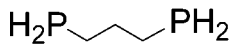
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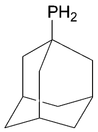
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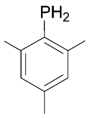
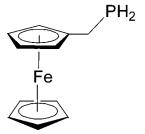

(**VI**)


(**1**)

Recently, the (ferrocenylmethyl)phosphine (**1**), a primary alkyl phosphine air stable both in the solid and solution states, has been synthesized,[10] and a few molybdenum(0)[10a] and (II),[11] tungsten(II),[11,12] ruthenium(II),[10a,13] and rhenium(I)[14] coordination compounds have been reported. The redox-active ferrocenyl group, presumably important in the kinetic stabilization against oxidation, has been associated with the surprisingly high stability.[10]

Herein, we report on the reactivity of **1** toward Pd and Pt chlorides, which led to the isolation of the novel Pd(II) and Pt(II) tetramers of formula $[M(PH_2CH_2Fc)Cl(\mu\text{-}PHCH_2Fc)]_4$ (Fc = ferrocenyl, M = Pd, **2**; M = Pt, **3**). To the best of our knowledge, **2** and **3** are the first cyclic tetranuclear Pt(II) and Pd(II) complexes having an eight-membered M_4P_4 ring.

Experimental Section

Materials and Methods. All reactions were carried out under a pure dinitrogen atmosphere using freshly distilled and oxygen-free solvents. The (ferrocenylmethyl)phosphine (**1**)[10c] and the metal precursors, $[M(cod)Cl_2]$ [cod = 1,5-cyclooctadiene, M = Pd or Pt][15] and *trans*-$[Pd(PhCN)_2Cl_2]$,[16] were prepared by literature methods. Although the primary phosphine **1** is reported to be air stable in the solid state, it was stored in the dark in a Schlenk tube under nitrogen before use.

C and H analyses were carried out on a Eurovector 3000 CHN elemental analyzer; Pd and Fe analyses were performed with a Perkin-Elmer SIMA A6000 atomic absorption spectrometer after mineralization. The chloride content of the complexes was determined by argentimetric titration using a Metrohm 716 DMS Titrino. Elemental analyses of phosphorus were carried out by spectrophotometric methods using a Kontron Uvikon 942 instrument (λ = 460 nm). IR spectra were recorded on a Bruker-Vector 22 spectrometer. NMR spectra were recorded with a BRUKER Avance 400 spectrometer; frequencies are referenced to external Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and H_2PtCl_6 (^{195}Pt). Computer simulations of the $^{31}P\{^1H\}$ experimental NMR spectra for **2** and **3** were performed using the program WINDAISY.

Synthesis of $[Pd(PH_2CH_2Fc)(\mu\text{-}PHCH_2Fc)Cl]_4$ (2). Solid **1** (80 mg, 0.344 mmol) was added to a CH_2Cl_2 (5 mL) solution of $[Pd(cod)Cl_2]$ (41 mg, 0.172 mmol), and the mixture was stirred at room temperature for 40 min. The resulting orange solution was concentrated to ca. 2 mL, and the orange residue was treated with 20 mL of Et_2O. The orange solid which separated out was isolated by filtration, washed with n-hexane (2 × 5 mL), and dried under vacuum. Yield: 88 mg (84%). Anal. Calcd for $C_{88}H_{100}Cl_4Fe_8P_8Pd_4$: C, 43.68; H, 4.17; Cl, 5.86; Fe, 18.46; P, 10.24; Pd, 17.59. Found: C, 44.11; H, 4.14; Cl, 5.51; Fe, 17.80; P, 9.82; Pd, 18.49. mp = 453 K (dec). IR (Nujol mull, cm^{-1}): ν 3089 (m), 2353 (m) and 2294 (m) ν(P−H), 1637 (m), 1462 (m), 1409 (m), 1233 (w), 1195 (w), 1105 (s), 1059 (w), 1038 (w), 1023 (s), 1001 (w), 923 (m), 865 (m), 817 (s), 482 (m), 274 (s) ν(Pd−Cl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 162 MHz): −6.8 (m, μ-$PHCH_2Fc$), −34.0 (m, PH_2CH_2Fc), $^2J_{\mu P-PH2trans}$ = 409 Hz, $^2J_{\mu P-PH2cis}$ = 5 Hz, $^2J_{\mu P-\mu Pcis}$ =

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Table 1. Crystal Data and Structure Refinement for **2**·3THF

empirical formula	$C_{100}H_{124}Cl_4Fe_8O_3P_8Pd_4$
molecular mass	2635.95
temp [K]	110(2)
wavelength [Å]	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
a [Å]	17.607(7)
b [Å]	17.944(7)
c [Å]	18.792(7)
α [°]	107.120(12)
β [°]	96.344(13)
γ [°]	117.087(15)
V [Å^3]	4839(3)
Z	2
D_{calcd} [Mg m^{-3}]	1.809
abs coeff [mm^{-1}]	2.177
F(000)	2656
θ range for data coll [°]	2.14−25.00
reflns collected	52 647
independent reflns	16 980
data/params	16 980/569
GOF on F^2	1.145
R1[a] ($I > 2\sigma(I)$)	0.1246
wR2[b] (all data)	0.2763
largest diff. peak/hole [e Å^{-3}]	1.973 and −1.498

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

13 Hz. ^{1}H NMR (CD_2Cl_2, δ, 295 K, 400 MHz): 2.97 (m, μ-PHC*H*^{c}H^{d}Fc, $^2J_{H-H} = 14.5$ Hz, $^3J_{H-H} = 8.5$ Hz, 4H), 2.78−2.90 (m, PH_2C*H*$_2$Fc, 8H), 3.36 (m, μ-PHCH^c*H*^{d}Fc, $^2J_{H-H} = 14.5$ Hz, $^3J_{H-H} = 3.9$ Hz, 4H), 3.65 (dm, μ-P*H*CH$_2$Fc, $^1J_{P-H} = 317$ Hz, 4H), 4.26 (dm, P*H*^{a}H^{b}CH$_2$Fc, $^1J_{P-H} = 360$ Hz, 4H), 3.66 (dm, PH^a*H*^{b}CH$_2$Fc, $^1J_{P-H} = 356$ Hz, 4H), 4.10−4.44 (m, ferrocenyl protons, 72H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 101 MHz): 88.0 (s, PH_2CH_2*C*), 85.4 (d, μ-PHCH$_2$*C*, $^2J_{P-C} = 6$ Hz), 69.0 (Fc), 68.9 (Fc), 68.1 (Fc), 67.9 (Fc), 67.8 (Fc), 26.4 (b, PH_2*C*H$_2$), 18.3 (d, $^1J_{P-C} = 21$ Hz, μ-PH*C*H$_2$,).

Synthesis of [Pt(PH_2CH_2Fc)(μ-$PHCH_2Fc$)Cl]$_4$ (3). Solid **1** (116 mg, 0.50 mmol) was added to a toluene (5 mL) suspension of [Pt(cod)Cl_2] (94 mg, 0.25 mmol), and the mixture was stirred at 323 K for 24 h to give a yellowish-orange suspension. Cooling to room temperature gave a yellowish-orange solid which was isolated by filtration and washed with *n*-hexane (2 × 5 mL) before being dried under vacuum. Yield: 156 mg (90%). Compound **3** could be obtained in 89% yield also from *trans*-[Pt(PhCN)$_2$Cl$_2$] instead of [Pt(cod)Cl$_2$] or by heating a toluene solution of complex **5** (see below) for 24 h at 323 K. Anal. Calcd for $C_{88}H_{100}Cl_4Fe_8P_8Pt_4$: C, 38.10; H, 3.63; Cl, 5.11; P, 8.93;. Found: C, 38.15; H, 3.65; Cl, 5.04; P, 8.90. mp = 448 K (dec). IR (Nujol mull, cm^{-1}): ν 3083 (w), 2369 (m) and 2310 (w) ν(P−H), 1601 (w), 1494 (m), 1405 (m), 1228 (w), 1188 (w), 1104 (s), 1059 (w), 1078 (w), 1036 (m), 1000 (m), 925 (m), 877 (m), 848 (s), 823 (s), 501 (s), 485 (m), 285 (s) ν(Pt−Cl). ^{31}P NMR data are reported in Table 2 (CD_2Cl_2, δ, 295 K, 162 MHz). ^{1}H NMR (CD_2Cl_2, δ, 295 K, 400 MHz): 2.68 (m, PH_2C*H*^{e}H^{f}Fc, 4H), 2.88 (m, PH_2CH^e*H*^{f}Fc, 4H), 3.05 (m, μ-PHC*H*^{c}H^{d}Fc, $^2J_{H-H} = 14.4$ Hz, $^3J_{H-H} = 9$ Hz, 4H), 3.42 (dm, μ-P*H*CH$_2$Fc, $^1J_{P-H} = 344$ Hz, 4H), 3.47 (m, μ-PHCH^c*H*^{d}Fc, $^2J_{H-H} = 14.4$ Hz, $^3J_{H-H} = 3.2$ Hz, 4H), 3.93 (dm, PH^a*H*^{b}CH$_2$Fc, $^1J_{P-H} = 360$ Hz, 4H), 4.51 (dm, P*H*^{a}H^{b}CH$_2$Fc, $^1J_{P-H} = 400$ Hz, 4H), 3.95−4.55 (m, ferrocenyl protons, 72H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 101 MHz): 87.7 (s, μ-PHCH$_2$*C*), 70.3 (s, Fc), 69.0 (s, Fc), 68.1 (s, Fc), 84.9 (s, PH_2CH_2*C*), 69.8 (s, Fc), 69.1 (s, Fc), 67.6 (s, Fc), 29.7 (b, PH_2*C*H$_2$), 24.0 (d, $^1J_{P-C} = 18$ Hz, μ-PH*C*H$_2$). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 86 MHz): −4130 (m).

Synthesis of *cis*-[Pd($FcCH_2PH_2$)$_2$Cl$_2$] (4). Addition of a CH_2Cl_2 solution (5 mL) of **1** (47 mg, 0.20 mmol) to a CH_2Cl_2 solution (10 mL) of *trans*-[Pd(PhCN)$_2$Cl$_2$] (38.3 mg, 0.10 mmol) kept at 273 K gave a red suspension which was immediately filtered while cold. Addition of cold *n*-hexane (20 mL) to the filtrate caused the precipitation of **4** as a red solid which was isolated by filtration, washed with *n*-hexane (2 × 5 mL), and dried under vacuum at 273 K for 30 min. Yield: 32 mg (50%). IR (Nujol mull, cm^{-1}): ν 2360 (w) and 2342 (w) ν(P−H), 248 (m) and 245 (m) ν(Pd−Cl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 162 MHz): −40.4 (s). ^{1}H NMR (CD_2Cl_2, δ, 295 K, 400 MHz): 3.18 (m, C*H*$_2$, 4H), 4.40 (dt, P*H*$_2$, $^1J_{P-H} = 394$ Hz, $^3J_{H-H} = 5.1$ Hz, 4H), 4.05−4.50 (m, ferrocenyl protons, 18H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, 265 K, 101 MHz): 82.1 (s, PH_2CH_2*C*), 68.3−69.2 (b, Fc), 20.8 (s, PH_2*C*H$_2$).

Synthesis of *cis*-[Pt($FcCH_2PH_2$)$_2$Cl$_2$] (5). Solid **1** (233 mg, 1.0 mmol) was added to a CH_2Cl_2 solution (15 mL) of [Pt(cod)Cl$_2$] (187 mg, 0.50 mmol), causing the formation of a yellow solution which was stirred at room temperature for 2 h. Concentration to ca. 5.0 mL of the solution and addition of Et_2O (10 mL) gave a yellow solid which was filtered off, washed with *n*-pentane (2 × 5 mL), and dried under vacuum. Yield 340 mg (93%). Anal. Calcd for $C_{22}H_{26}Cl_2Fe_2P_2Pt$: C, 36.19; H, 3.59; Cl, 5.11; P, 9.71;. Found: C, 36.53; H, 3.61; Cl, 5.01; P, 9.68. IR (Nujol mull, cm^{-1}): 2365 (w) and 2309 (w) ν(P−H), 1408 (m), 1265 (w), 1237 (w), 1105 (s), 1038 (m), 1023 (m), 1000 (m), 923 (m), 819 (s), 481 (s), 296 (m) and 285 (m) ν(Pt−Cl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 162 MHz): −51.5 (s flanked by ^{195}Pt satellites, $^1J_{P-Pt} = 3320$ Hz). ^{1}H NMR (CD_2Cl_2, δ, 295 K, 400 MHz): 2.68 (m, C*H*$_2$, $^2J_{P-H} = 11$ Hz, $^3J_{Pt-H} = 25$ Hz, 4H), 4.38 (dt, P*H*$_2$, $^1J_{P-H} = 414$ Hz, $^3J_{H-H} = 6.2$ Hz, $^2J_{Pt-H} = 43$ Hz, 4H), 4.00−4.45 (m, ferrocenyl protons, 18H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, 295 K, 101 MHz): 81.8 (s, PH_2CH_2*C*), 69.2 (s, Fc), 69.1 (s, Fc), 68.6 (s, Fc), 19.4 (d, $^1J_{P-C} = 39$ Hz, PH_2*C*H$_2$). 195Pt{^{1}H} (CD_2Cl_2, δ, 295 K, 86 MHz): −4472 (t, $^1J_{P-Pt} = 3320$ Hz).

X-ray Crystallography.[17] Suitable crystals of **2** for diffraction purposes were obtained by slow diffusion of Et_2O (3 mL) into a THF solution of [Pd(PH_2CH_2Fc)(μ-$PHCH_2Fc$)Cl]$_4$ (1 mL) at room temperature. Crystal data, parameters for intensity data collection, and convergence results are compiled in Table 1. Data were collected with Mo K$_\alpha$ radiation (graphite monochromator, $\lambda = 0.71073$ Å) on a Bruker D8 goniometer with SMART CCD area detector at 110(2) K on a crystal of approximate dimensions 0.16 × 0.04 × 0.04 mm^3. An empirical absorption correction[18] (min. trans. 0.72, max. trans 0.92) was applied before averaging symmetry equivalent data [$R_{(int)} = 0.1238$]. The structure was solved by direct methods[19] and refined with full-matrix least-squares on F^2.[20] After assignment of the electron density associated with non-hydrogen atoms of the tetranuclear Pd complex, a very large void near to a crystallographic inversion center was encountered. As attempts to model the electron density to the solvent of crystallization gave unsatisfactory results, the BYPASS procedure[21] as implemented in PLATON was used to include the contribution of the solvent to

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(17) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 295452. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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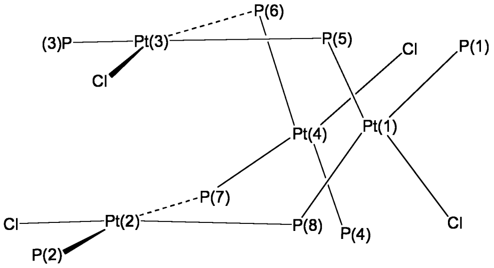
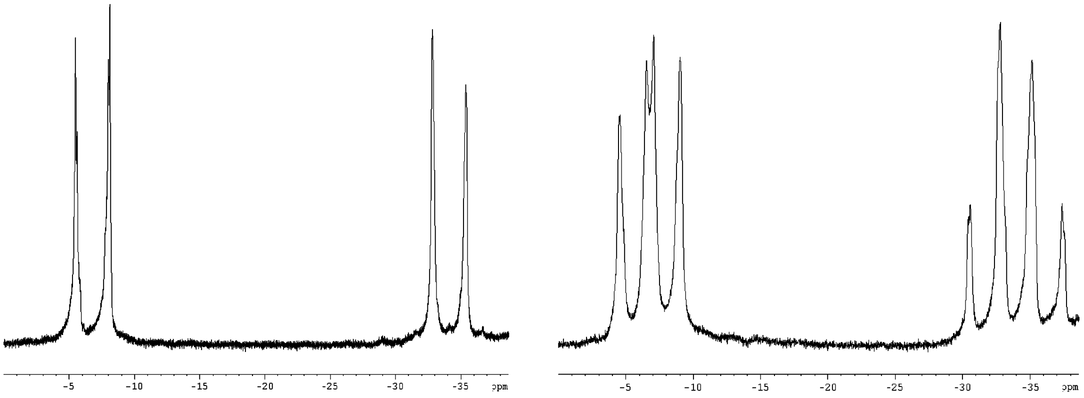
Table 2. ^{31}P and ^{195}Pt NMR Parameters for Complex **3** (CD_2Cl_2, 295 K)[a]



	P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	P(7)	P(8)	Pt(1)	Pt(2)	Pt(3)	Pt(4)
P(1)	**−29.5**				−15			389	2240	50	−40	
P(2)		**−29.5**					389	−15	−40	2240		50
P(3)			**−29.5**		389	−15			50		2240	−40
P(4)				**−29.5**		389	−15			−40	50	2240
P(5)	−15		389		**−37.2**	5		5	2496	125	2322	120
P(6)			−15	389	5	**−37.2**	5		125	120	2496	2322
P(7)		389		−15		5	**−37.2**	5	120	2322	125	2496
P(8)	389	−15			5		5	**−37.2**	2322	2496	120	125
Pt(1)	2240	−40	50		2496	125	120	2322	**−4130**			
Pt(2)	50	2240		−40	125	120	2322	2496		**−4130**		
Pt(3)	−40		2240	50	2322	2496	125	120			**−4130**	
Pt(4)		50	−40	2240	120	2322	2496	125				**−4130**

[a] Chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz.



a)

b)

Figure 1. $^{31}P\{^{1}H\}$ (a) and proton-coupled ^{31}P (b) NMR spectra of **2** (CD_2Cl_2, 295 K, 162 MHz).

the overall structure factors. The volume of 600 Å^3 and the electron count of 240 associated with the void suggests that it contains six molecules of tetrahydrofuran. The crystal data in Table 1 therefore refer to a composition of **2**·3THF.

Repeated single-crystal diffraction experiments on **3** confirmed that the compound crystallizes in the tetragonal space group $P\bar{4}$ with lattice parameters $a = 13.1576(6)$ Å, $c = 14.6717(2)$ Å, $V = 2540.00(17)$ Å^3 with one molecule per unit cell. We note that the core of the analogous Pd compound, **2**, also shows local, noncrystallographic $\bar{4}$ point group symmetry. The phase problem was readily solved, but an approximate 3:1 orientational disorder prevented us from refining a meaningful structure model.

Results and Discussion

Reactivity of 1 with Pd(II) Chloro Complexes. The reaction of 2.0 equiv of **1** with [Pd(cod)Cl_2] at 298 K in CH_2Cl_2 (or THF) gave an orange solid whose $^{31}P\{^{1}H\}$ NMR spectrum shows a second-order spin system with resonances centered at δ −34.0 and −6.8 (Figure 1a). In the proton-coupled ^{31}P NMR spectrum, these signals split into a pseudoquartet and a doublet of doublets, respectively (Figure 1b), indicating that this compound contains equimolar amounts of PH_2 and PH moieties.

The elemental analyses provided a Pd/P/Cl ratio of 1:2:1, which indicates the occurrance of dehydrochlorination and suggests, in agreement with the ^{31}P NMR spectra, the formation of a polynuclear complex of formula [Pd(PH_2CH_2-Fc)(μ-$PHCH_2$Fc)Cl]$_n$ ($n > 2$).

A single-crystal diffraction study allowed us to assign the structure [Pd(PH_2CH_2Fc)(μ-$PHCH_2$Fc)Cl]$_4$ (**2**) to the product. The high nuclearity of **2** is worth noticing, since in all the known cases, dehydrohalogenation from primary (and secondary) phosphine Pd(II) complexes led to dinuclear compounds.[5,6,8,22]

The structure of **2**, together with the atom labeling scheme, is shown in Figure 2.

Complex **2** exhibits a tetrametallic unit and can be regarded as formed by four (noncoplanar) mononuclear palladium subunits held together by bridging μ-$PHCH_2$Fc groups. The [Pd(PH_2CH_2Fc)(μ-$PHCH_2$Fc)Cl] subunits of the molecule are approximately related by an S_4 operator. The metal environ-

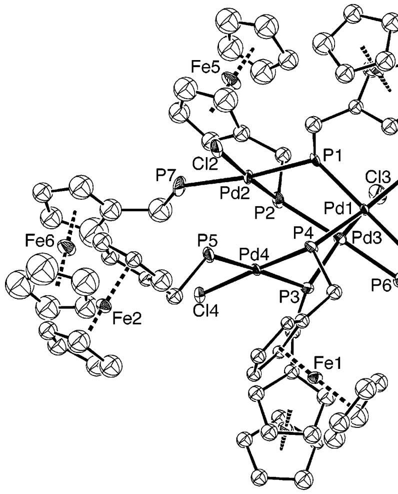
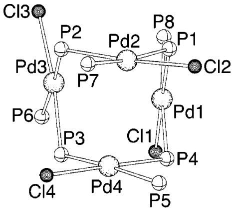


Figure 2. ORTEP drawing of **2**. The solvent molecules and hydrogen atoms have been omitted for clarity; displacement ellipsoids are scaled to 50% probability. Selected bond lengths (Å) and angles (deg): Pd(1)−P(1) 2.283(4), Pd(1)−P(8) 2.338(4), Pd(1)−P(4) 2.346(4), Pd(1)−Cl(1) 2.379(4), Pd(1)−Pd(3) 3.173(2), Pd(2)−Pd(4) 3.1206(18), Pd(2)−P(1) 2.331(4), P(1)−Pd(1)−P(8) 91.23(15), P(1)−Pd(1)−P(4) 85.25(14), P(8)−Pd(1)−Cl(1) 88.86(14), P(4)−Pd(1)−Cl(1) 94.60(14), P(1)−Pd(1)−Pd(3) 85.06(12), P(8)−Pd(1)−Pd(3) 88.92(12), P(4)−Pd(1)−P(3) 95.15(11), Cl(1)−Pd(1)−Pd(3) 95.69(12), Pd(1)−P(1)−Pd(2) 120.92(18).

Scheme 1. Core of **2** Showing the Perpendicular Arrangement of the Coordination Planes around Pd Atoms



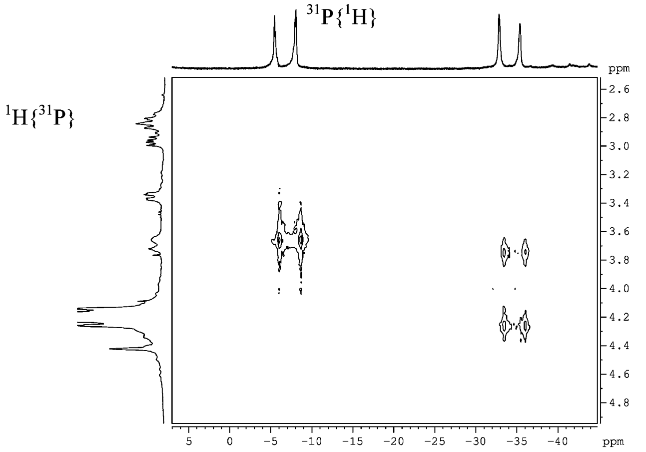


Figure 3. $^{31}P-^{1}H$ HMQC NMR spectrum of **2** (CD_2Cl_2, 295 K).

ments form alternate, almost perpendicular, planes, subtending angles of 89.4(2)°, 84.8(2)°, 90.0(2)°, and 85.63(19)° (Scheme 1). The distorted square-planar environment of each palladium atom comprises a (ferrocenylmethyl)phosphine group, two mutually cis (ferrocenylmethyl)phosphanido ligands bridging to two different adjacent metal centers, and a chlorine ligand (cis to the terminal phosphine). The angles around the metal are close to 90°, with significantly smaller μP−Pd−μP angle of 85°. Each phosphanide moiety bridges two palladium atoms and has a chlorine ligand in a trans position with respect to the first Pd (the cis position is occupied by a terminal primary phosphine) and a terminal primary phosphine in a trans position with respect to the other Pd (the cis position is occupied by a chlorine). The P(1)−Pd(1), P(2)−Pd(2), P(3)−Pd(3), and P(4)−Pd(4) bond distances are slightly shorter than P(1)−Pd(2), P(2)−Pd(3), P(3)−Pd(4), and P(4)−Pd(1), as expected on the basis of the different trans influence between the phosphine and the chlorine atom. The large Pd−μP−Pd angles (ca. 120°) are consistent with the lack of a metal−metal bond between adjacent palladium atoms.[23] The nonbonding intermetallic distances Pd(1)···Pd(3) and Pd(2)···Pd(4) [3.173(4) and 3.1206(18) Å, respectively] are long enough to preclude the possibility of metal−metal interaction between interfacing palladium atoms.

The IR spectrum of **2** showed P−H stretchings at 2353 and 2294 cm^{-1} and a Pd−Cl stretching band at 274 cm^{-1}. The signals of the $^{31}P\{^1H\}$ NMR spectrum described above can be easily attributed to the coordinated (ferrocenylmethyl)-phosphines (δ −34.0) and to the bridging phosphanides (δ −6.8). The large value of the $^2J_{P-P} = 409$ Hz is typical for coupling between trans P atoms. Additional $^2J_{P-P}$ couplings between cis phosphorus atoms (13 and 5 Hz) could be assessed by computer simulation of the experimental spectrum.

The chemical shift of the low-field resonance signal ascribed to the phosphanido groups is consistent with a system containing single phosphanido bridging ligands that support nonbonded metal centers[24] and appears at much lower field than the resonances exhibited by phosphanido ligands involved in P_2M_2 four-membered rings.[25] The ^1H NMR spectrum of **2** showed the expected signals for ferrocenyl, methylene, and P−H hydrogens, but a full assignment of the ^1H NMR features was achieved only by a perusal of a series of NMR experiments including $^1H-^1H$ COSY, $^1H\{^{31}P\}$ (at 295 and at 270 K), and $^{31}P-^{1}H$ HMQC. The spectroscopic data are consistent with the solid-state geometry and point out that each bridging phosphanido P atom is bound, apart the hydrogen and the ferrocenylmethyl moiety, to two palladium centers, one with a trans-disposed chlorine and the other with a trans-arranged terminal phosphine. Inspection of the $^{31}P-^{1}H$ HMQC NMR spectrum of **2** (Figure 3) suggests that the PH_2 protons of the terminal phosphines are diastereotopic ($PH^aH^bCH_2Fc$, $\delta_H{}^a = 4.26$, $^1J_{P-H}{}^a = 360$ Hz; $\delta_H{}^b = 3.66$, $^1J_{P-H}{}^b = 356$ Hz).

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(22) Giannandrea, R.; Mastrorilli, P.; Nobile, C. F. *Inorg. Chim. Acta* **1999**, *284*, 116−118. Gallo, V.; Latronico, M.; Mastrorilli, P.; Nobile, C. F.; Suranna, G. P.; Ciccarella, G.; Englert, U. *Eur. J. Inorg. Chem.* **2005**, 4607−4616. Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349−1354. Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188−1200.

(23) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Rosair, G. M.; Welch, A. J. *Inorg. Chem.* **1997**, *36*, 4426−4431 and references therein.

(24) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, A. G.; *Organometallics* **2003**, *22*, 2723−2728. Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, A. G. *Organometallics* **2000**, *19*, 2690−2697.

(25) Carty, A. J.; Maclaughlin, S. A.; Nucciarone, D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; p 559.

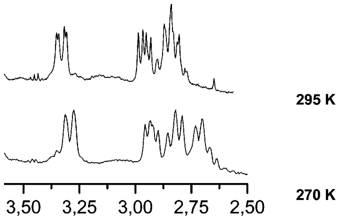
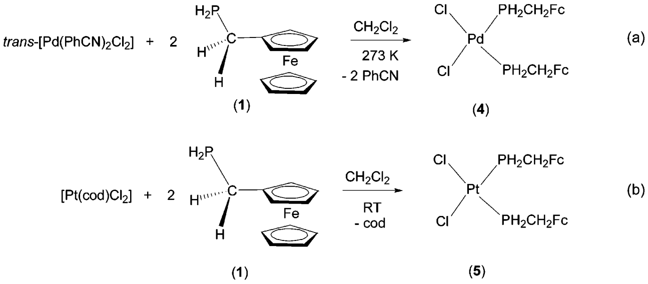


Figure 4. $^1H\{^{31}P\}$ NMR spectra of **2** (methylene region) recorded at 295 (top) and 270 K (bottom).

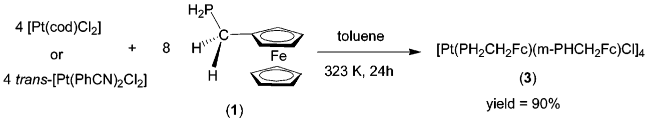
Scheme 2. Synthesis of **4** and **5**



Diasterotopic pairs are also observed for the methylene protons of both the terminal phosphines and the bridging phosphanides. Noticeably, while the CH$_2$ protons of the bridging phosphanides give rise to well-separated doublets of doublets at 295 K in the $^1H\{^{31}P\}$ NMR spectrum (μ-PHCH^cH^dFc, $\delta_{H^c} = 2.97$, $\delta_{H^d} = 3.36$, $^2J_{H^c-H^d} = 14.5$ Hz, $^3J_{H^c-H} = 8.5$ Hz; $^3J_{H^d-H} = 3.9$ Hz, Figure 4), a good separation of the methylenic protons of the terminal phosphines is evident in the $^1H\{^{31}P\}$ NMR spectrum recorded at 270 K (PH^{a}H^{b}CH^eH^fFc, $\delta_{H^e} = 2.74$ and $\delta_{H^f} = 2.76$ at 270 K, Figure 4).

Monitoring the reaction between **1** and [Pd(cod)Cl$_2$] by ^{31}P VT-NMR (CD$_2$Cl$_2$, 180 K) showed the immediate formation of **4** (singlet at δ -31) together with a series of minor products which denied a simple analysis and, similarly to **4**, disappear on heating the solution to room temperature when **2** became the only observable compound.[26] Likely, the monomer **4** is first formed in the reaction of **1** with [Pd(cod)Cl$_2$] before transforming into the tetramer **2**. Attempts to isolate **4** from the reaction of **1** and [Pd(cod)Cl$_2$] at low temperature were unsuccessful. However, pure **4** (albeit in low yield) could be isolated from the reaction between **1** and *trans*-[Pd(PhCN)$_2$Cl$_2$] at 273 K in CH$_2$Cl$_2$ (Scheme 2a). The mononuclear complex **4** was stable below 273 K in the solid state but, once dissolved in CH$_2$Cl$_2$, quickly transformed into the tetramer **2** passing through a mixture of species similar to those observed in the in situ NMR experiment. The $^{31}P\{^1H\}$ NMR spectrum at 295 K recorded immediately after dissolution in CH$_2$Cl$_2$ showed a sharp singlet at δ -40.4 (δ -31 at 180 K), which split into a triplet ($^1J_{P-H} = 394$ Hz) in the proton-coupled spectrum, indicating a negligible $^2J_{P-P}$.[27] These features suggest for **4** a cis geometry which

Scheme 3. Synthesis of **3**



was confirmed by the observation of two medium-intensity Pd$-$Cl stretching bands in the IR spectrum ($\nu_{Pd-Cl} = 245$ and 248 cm^{-1}).[28] In keeping with this structural assignment, the ^1H NMR spectrum of **4** showed three signals in a 2:2:9 ratio, ascribable to the PH$_2$ protons (δ 4.40, dt), to the methylene protons (δ 3.18, m), and to the ferrocenyl hydrogens (δ 4.05 to 4.50), respectively.

The low yield of **4** from reaction between **1** and *trans*-[Pd(PhCN)$_2$Cl$_2$] at 273 K was due to the concomitant formation of a brown precipitate insoluble in all common organic solvents. Presumably, the very unstable *trans*-[Pd(FcCH$_2$PH$_2$)$_2$Cl$_2$] which first forms can partly isomerize to *cis*-[Pd(FcCH$_2$PH$_2$)$_2$Cl$_2$], (isolable after workup at about 273 K) and partly oligomerize to other insoluble compounds. which were not further characterized.

Reactivity of 1 with Pt(II) Chloro Complexes. The 2:1 reaction[29] of **1** with [Pt(cod)Cl$_2$] at 298 K in CH$_2$Cl$_2$ (Scheme 2b) gave a yellow solution from which a yellow solid could be isolated. This showed in the $^{31}P\{^1H\}$ NMR spectrum a sharp singlet at δ -51.5 flanked by ^{195}Pt satellites ($^1J_{P-Pt} = 3320$ Hz). The value of the Pt$-$P coupling constant,[30] the triplet splitting of the ^{31}P NMR signal in the proton coupled spectrum ($^1J_{P-H} = 414$ Hz), and the two IR stretching Pt$-$Cl bands ($\nu_{Pt-Cl} = 285$ and 296 cm^{-1}), taken altogether, allow us to assign to this yellow compound the formula *cis*-[Pt(FcCH$_2$PH$_2$)$_2$Cl$_2$] (**5**). The ^1H NMR spectrum of **5** in CD$_2$Cl$_2$ showed signals for PH$_2$ and CH$_2$ at δ 4.38 and 2.68, respectively, while the $^{195}Pt\{^1H\}$ NMR spectrum consisted of a triplet centered at δ -4472. Complex **5** was more stable than its Pd analogue **4**, remaining unaltered in solution at room temperature for at least 1 day.[31]

Heating a toluene solution of **5** at 323 K for 24 h afforded the tetranuclear Pt(II) complex **3**, i.e., the Pt analogue of **2**. Complex **3** is a yellowish-orange solid insoluble in aromatic solvents but moderately soluble in halogenated solvents. This compound could be straightforwardly synthesized in high yield by reacting 2 equiv of **1** with either [Pt(cod)Cl$_2$] or *trans*-[Pt(PhCN)$_2$Cl$_2$] at 323 K in toluene (Scheme 3).

Although a crystallographic study confirmed that **3** shares with **2** an identical M$_4$P$_4$ core, we do not give here any structural detail because of extensive disorder. In keeping

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[26] Although a sound structural assignment of the minor species present in solution at low temperature is difficult, it is conceivable that these resonances are due to oligomeric palladium complexes traversing the formation of the tetramer **2**.

[27] A $^2J_{P-P}$ of hundreds of Hertz, typical for trans couplings, would have given rise to a complicated second-order spectrum. See Palmer, R. A.; Whitcomb, D. R. *J. Magn. Res.* **1980**, 39, 371$-$379.

[28] Nakamoto, K. *Infrared and Raman Spectra*, 4th ed.; Wiley: New York, 1986; pp 326$-$327.

[29] Using a P/Pt molar ratio higher than 2:1, a fast equilibrium between the bis(phosphine) complex and the cationic tris(phosphine) complex took place, as revealed by a very broad $^{31}P\{^1H\}$ NMR signal at about δ -35. A similar exchange process has been observed between L$_2$MX$_2$ complexes (X = Cl, Br; M = Pt, Pd; L = primary phosphine containing phenyl, cyclohexyl, or 2-cyanoethyl groups) and L ligand giving the cationic complex [L$_3$MX$^+$]X$^-$. See: Anand, S. P.; Goldwhite, H.; Spielman, J. R. *Transition Met. Chem.* **1977**, *2*, 158$-$160.

[30] Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979; Vol. 16, p 94.

[31] Prolonged drying of compound **5** should be avoided in order to prevent dehydroalogenation in the solid state.

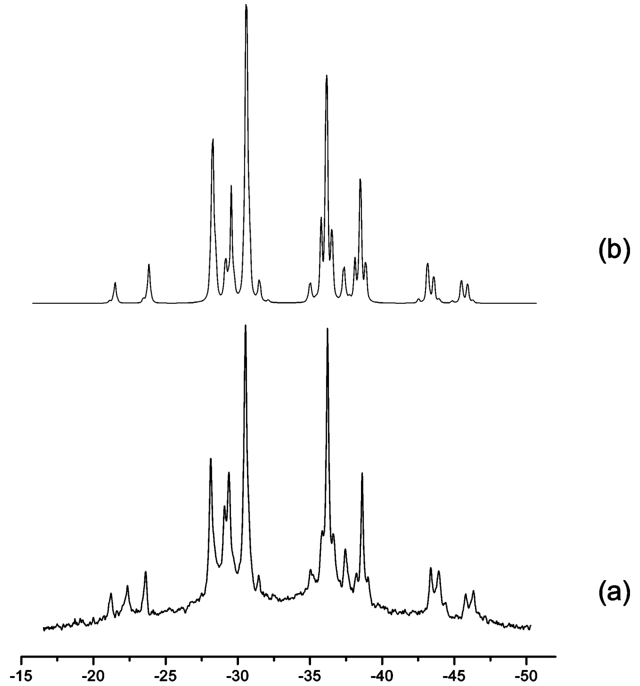

Figure 5. Experimental (a) and simulated (b) $^{31}P\{^{1}H\}$ NMR spectra of complex **3**.

with the rough crystallographic analysis and the tetrametallic structural motif, the IR spectrum of **3** in the solid state showed P−H stretchings at 2369 and 2310 cm^{-1} and a Pt−Cl stretching at 285 cm^{-1}. The $^{31}P\{^{1}H\}$ NMR spectrum of **3** is shown in Figure 5a. The seemingly complicated spectrum contains signals arising from a mixture of five isotopomers differing for the number of NMR-active ^{195}Pt nuclei incorporated in the tetrametallic core, i.e., with zero (18.97%, **A**), one (39.10%, **B**), two (30.21%, **C**), three (10.38%, **D**), and four (1.37%, **E**) ^{195}Pt nuclei. The isotopomer **A** contains 66% of total ^{31}P and gives two mutually coupled doublets ($^{2}J_{\mathrm{P-Ptrans}} = 389$ Hz) centered at δ −37.2 and −29.5 which are assigned to the bridging phosphanido ligands and to the terminal primary phosphines, respectively. Recording of the proton-coupled ^{31}P NMR spectrum, transforming the doublet at δ −37.2 into a doublet of doublets ($^{1}J_{\mathrm{P-H}} = 344$ Hz) and the doublet at δ −29.5 into a pseudoquartet, confirms this assignment. The chemical shift ascribed to the ^{31}P phosphanides P atoms is again consistent with single phosphanido bridging ligands supporting nonbonded metal centers.[24] The high-field shift of this signal with respect to **2** is consistent with the trend observed for μ-phosphanido P atoms on going down in a transition metal triad.[32] The PH$_2$ doublet at δ −29.5 is flanked by one set of ^{195}Pt satellites due to the isotopomer **B** ($^{1}J_{\mathrm{P-Pt}} = 2240$ Hz), whereas the doublet at δ −37.2, ascribed to the bridging phosphanido ligands, shows two sets of ^{195}Pt satellites, indicating the magnetic inequivalence of the two Pt atoms bridged by each phosphanide. In fact, assuming for **3** the same structure of **2**, one Pt bears a terminal phosphine trans to μ-PH, while the other Pt bears a Cl trans to the same μ-PH (see Table 2). The corresponding $^{1}J_{\mathrm{P-Pt}}$ are 2322 (P trans P) and 2496 Hz (P trans Cl), respectively, reflecting the different trans influence between phosphine and Cl.[33] Finally, the phosphanide part of the spectrum shows additional peaks flanking the central doublet due to three bonds phosphorus−platinum couplings ($^{3}J_{\mathrm{P-Pt}} \approx 120$ Hz).

The ^{31}P NMR features of the isotopomers **A**, **B**, and **C** of **3** were calculated by iterative simulation of the experimental spectra (Table 2). Figure 5b shows a comparison between experimental and simulated spectra and stresses the validity of the simulation procedure.[34]

Similar to **2**, the PH$_2$ protons of the terminal phosphines in **3** (P$H^{a}H^{b}$CH$_2$Fc, $\delta_{\mathrm{H}^{a}} = 4.51$, $^{1}J_{\mathrm{P-H}^{a}} = 400$ Hz; $\delta_{\mathrm{H}^{b}} = 3.93$, $^{1}J_{\mathrm{P-H}^{b}} = 360$ Hz), the methylene protons of both the terminal phosphines (PH$_2$C$H^{e}H^{f}$Fc, $\delta_{\mathrm{H}^{e}} = 2.68$ and $\delta_{\mathrm{H}^{f}} = 2.88$), and the bridging phophanido groups (μ-PHC$H^{c}H^{d}$Fc, $\delta_{\mathrm{H}^{c}} = 3.05$, $^{2}J_{\mathrm{H}^{c}-\mathrm{H}^{d}} = 14.4$ Hz, $^{3}J_{\mathrm{H}^{c}-\mathrm{H}} = 9$ Hz; $\delta_{\mathrm{H}^{d}} = 3.47$, $^{3}J_{\mathrm{H}^{d}-\mathrm{H}} = 3.2$ Hz) are diastereotopic.

Inspection of Figure 5a shows that the $^{31}P\{^{1}H\}$ NMR peaks of **3** are quite broad, indicating a fluxional behavior at room temperature. On lowering the temperature down to 180 K (Figure 6), four pairs of partially overlapped mutually coupled doublets, as indicated by the COSY ^{31}P−^{31}P NMR spectrum, became evident. Medium-size rings are known to give rise to conformational equilibria which were studied, for instance, in the case of seven- and eight-membered heterocycles.[35] In our case, we may envisage an equilibrium between a boat-boat conformation (as found in the solid-state structure) and a boat-chair conformation, as depicted in Scheme 4. At room temperature, the equilibrium is fast and results in the observed average broad spectrum.

Changing the conformation from boat-boat to boat-chair results in the loss of magnetic equivalency for both phosphanide and phosphine ligands so that in the slow exchange regime, when the boat-boat and boat-chair conformers are slowly interconverting, complex **3** should exhibit five pairs of mutually coupled doublets (one for the boat-boat and four for the boat-chair conformer) in the $^{31}P\{^{1}H\}$ NMR spectrum. The observation at 180 K of only four pairs of doublets may be likely attributed to the fortuitous overlapping of two of the five couples of doublets.[36]

In the case of the palladium tetramer **2**, lowering the temperature down to 180 K did not result in any new signal attributable to "frozen" conformers, presumably due to faster equilibration.

Coordination compounds containing M$_4$P$_4$ cores have many precedents in the literature. Apart from a few clusters

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(32) Barrè, C.; Boudot, P.; Kubicki, M. M.; Moïse, C. *Inorg. Chem.* **1995**, *34*, 284−291.

(33) Hartley, F. R. *Chem. Soc. Rev.* **1973**, *2*, 163−179.

(34) The peaks observed in addition to those accounted for in the simulated spectrum may be attributed to the 10.4% and 1.4% of molecules containing three and four magnetically active platinums, respectively.

(35) Pastor, S. D.; Smith, A. R.; Rihs, G. *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *115*, 169−177.

(36) $^{31}P\{^{1}H\}$ NMR NOESY-EXSY experiments carried out at 180 K were not decisive in confirming the existence of the conformational equilibrium since no clear exchange cross-peaks could be assigned. The major problem of these experiments was the shortness of the FID (ca. 30 ms) that forced us to use mixing times shorter than 20 ms, a time possibly insufficient to warrant the envisaged exchange to occur.

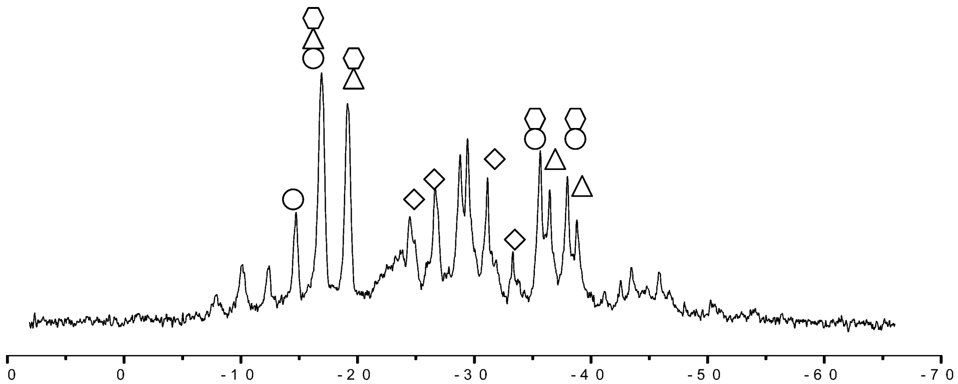
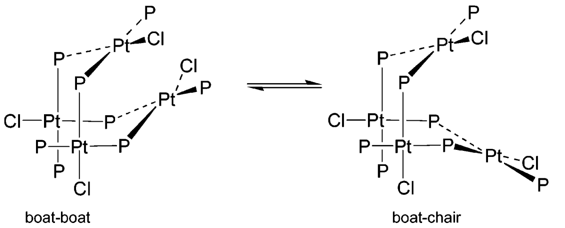
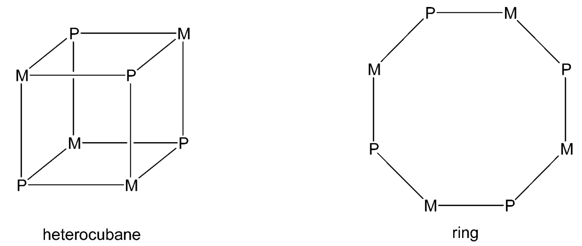


Figure 6. $^{31}P\{^1H\}$ NMR spectra of **3** in CD_2Cl_2 at 180 K (the four pairs of doublets are marked).

Scheme 4. Boat-Boat-to-Boat-Chair Conformational Equilibrium for **3**



Scheme 5. Common Geometries of M_4P_4 Cores



where at least two metals are covalently bonded,[37] the most frequent geometries deal with species containing the M_4P_4 array embedded in planar (M = Hg,[38] Cu,[39] Ag[40]) or butterfly-like (M = Au[41]) rings or in polyhedra exhibiting more or less distorted heterocubane topologies (M = In,[42] Al,[43] Rb, Ce,[44] Mg, Ca, Sr, Ba, Sn,[45] Scheme 5).

Distorted tetraphosphatetrametalla cubanes involving transition metals are much more rare and, to the best of our knowledge, are limited to the two derivatives $[\{Cp^*M(\mu_3-P)\}_4]$ (M = Co, Ni) prepared by Dahl and co-workers by thermal reaction of white phosphorus with appropriate metal cyclopentadienyl precursors[46] and to the heterotetranuclear cluster $[\{Cp''Ru\}_3\{Cp^*Fe\}(\mu_3\text{-}P)\}_4]$ obtained by co-thermolysis of $[Cp^*Fe(\eta^5\text{-}P_5)]$ and $[\{Cp''(CO)_2Ru\}_2]$ (Cp'' = 1,3-^{t}Bu$_2$Cp).[47] Tetranuclear platinum compounds featuring a Pt_4P_4 motif are extremely rare, being represented only by the spheroidal polyhydridotetraplatinum clusters $[Pt_4H_2(P^tBu_3)_4]$ and $Pt_4H_8[PPh^iPr_2]_4$.[48] No similar palladium polyhydrido cluster has been reported so that a Pd_4P_4 moiety may be recognized only in the ternary palladium phosphide $Nb_5Pd_4P_4$ prepared by arc-melting of metallic palladium with NbP.[49] Therefore, the peculiar arrangement of four metals and four phosphorus donor atoms ascertained for **2** and **3** in both the solid and solution states has no precedent in eight-membered M_4P_4 rings and cages, and likely its formation stands on steric reasons favored by the relatively small encumbrance exerted by the (ferrocenylmethyl)phosphine coligands.

Conclusions

In contrast to the known halide primary phosphine complexes which dehydrohalogenate to dimeric species, the mononuclear chloride (ferrocenylmethyl)phosphine Pd(II) and Pt(II) complexes, which are first formed in the reaction between Pd(II) or Pt(II) chlorides and **1**, easily transform into tetranuclear species of formula $[M(PH_2CH_2Fc)(\mu\text{-}PHCH_2Fc)Cl]_4$ (M = Pd, **2**; M = Pt, **3**). Both complexes adopt in the solid state the monocyclic arrangement with a M_4P_4 core, as authenticated by X-ray crystallopgraphy. In solution, the two tetrametallic complexes exhibit a fluxional behavior with several conformers interconverting on the NMR time scale. The exchange process was slowed at low temperature for the Pt(II) complex, providing evidence for a boat-boat to boat-chair equilibration, but not for the Pd(II) tetramer which shows fast exchange even at low temperature.

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Supporting Information Available: $^1H-^1H$ COSY NMR of **2**; $^{31}P\{^1H\}$ DNMR and $^{31}P-^{31}P$ COSY NMR spectra of the reaction mixture: $[Pd(cod)Cl_2] + 2$ equiv **1**; $^1H-^{31}P$ HMQC, $^1H-^1H$ COSY, and LT $^{31}P-^{31}P$ COSY NMR spectra of **3**; atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, hydrogen coordinates and isotropic displacement parameters, and anisotropic displacement parameters for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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