

p-tert-Butylcalix[4]arene Tetrakis(diphenylphosphinite) and Tetrakis(dimethylphosphinite) Acting as Phosphorus Binding Surfaces for Monometallic and Homo- and Heterodimetallic Fragments

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p-tert-Butylcalix[4]arene tetrakis(diphenylphosphinite), calix[4]-(PPh₂)₄ (**1**), and tetrakis(dimethylphosphinite), calix[4]-(PMe₂)₄ (**2**), provide a phosphorus surface consisting of four coplanar trivalent phosphorus atoms for binding two metal ions into a close geometrical proximity. Homodimetallic complexes have been obtained in the reaction of **1** with [(COD)MCl₂] [COD = cycloocta-1,5-diene], namely, [{calix[4]-(PPh₂)₄}(MCl₂)₂] [M = Pd (**3**), Pt (**4**)]. Characterizations by ¹H and ³¹P NMR were particularly informative and showed how the bridging methylene of the calix[4]arene skeleton may function as a spectroscopic probe. A dimeric complex was obtained by reacting **1** with [Rh(CO)₂Cl]₂ to give [{calix[4]-(PPh₂)₄}{Rh(CO)Cl}₂] (**5**). Reaction of **1** with excess NiCl₂ gave exclusively the monometallic complex, [{calix[4]-(PPh₂)₄}NiCl₂] (**6**), regardless of the stoichiometry used. The analogous Pd monometallic complex (**7**) undergoes a ligand disproportionation reaction, while the corresponding Pt analogue does not exist under the same conditions. Complex **6** represents a good entry to dinuclear heterodimetallic complexes. In fact, its reaction with [(NBD)Mo(CO)₄] [NBD = norbornadiene] led to [{calix[4]-(PPh₂)₄}NiCl₂{Mo(CO)₄}] (**8**). The use of the more basic and less sterically demanding ligand **2** led to the synthesis of homonuclear bimetallic complexes [{calix[4]-(PMe₂)₄}(MCl₂)₂] [M = Ni (**9**), Pd (**10**), Pt (**11**)].

Introduction

The phosphorus functionalization of calix[4]arene¹ in its cone conformation provides a rather unique planar set of four phosphorus atoms and thus mimics a binding surface for transition metals. The methodology for the exhaustive phosphorus derivatization of calix[4]arene was introduced by us a few years ago.² It consisted of converting *p*-tert-butylcalix[4]arene into the corresponding phosphinite derivative using diphenylchlorophosphane and 3-tert-butyl-2-chloro-1,3,2-oxaphospholidine.^{2a} More recently, examples of partial P-functionalization of the lower and the upper rims of the calix[4]arene skeleton were pursued, along with their use in metal complexation.^{3,4} Only very recently two approaches on calix[*n*]arene-related systems were reported, namely, the synthesis

of calix[4]phosphole by Mathey⁵ and resorcinarene phosphinites and phosphonites by Puddephatt.⁶

The objective of our investigation was to utilize the fully P-functionalized calix[4]arene for fixing dimetallic units. We felt that this should exist without the support of any bridging ligand or metal–metal bond; thus the two metal centers on the calix[4]arene phosphorus skeleton are held within cooperative distance. This, however, largely depends on the steric hindrance of the R substituent in the PR₂ fragment.

We report here the complexation of transition metal ions by both the *p*-tert-butylcalix[4]arenetetrakis(diphenylphosphinite), calix[4]-(PPh₂)₄, and *p*-tert-butylcalix[4]arene tetrakis(dimethylphosphinite), calix[4]-(PMe₂)₄. Particular attention is devoted to the structural analysis of such compounds in solution by

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NMR, particularly on the bridging methylene which can be used as a spectroscopic probe for inspecting the metal fragments attached to the P₄ system.

Experimental Section

General Procedure. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Solvents were dried and distilled by standard methods prior to use. All compounds were handled using modified Schlenk techniques under a nitrogen atmosphere or in an inert atmosphere drybox under nitrogen. ¹H NMR spectra were recorded at 200.132 MHz and ³¹P{¹H} NMR spectra at 81.015 MHz on a Bruker AC-200 instrument or on a Bruker AMX-400 instrument at 400.264 and 162.03 MHz, respectively. They are referenced to an external standard of tetramethylsilane at $\delta = 0$ with positive value to low field and to an external standard of phosphoric acid (85%) with positive value to low field, respectively. The standard for ¹⁹⁵Pt is [Na₂PtCl₆]. If not noted otherwise, the spectra were recorded in CD₂Cl₂ at 293 K. The magnitude of the coupling constant is given in positive value if not noted otherwise. IR spectra were recorded on a Perkin-Elmer 1600 FT IR instrument.

The following compounds were synthesized according to the published methods: *p*-tert-butylcalix[4]arene,⁷ calix[4]-(PPh₂)₄, [(COD)-PtCl₂]₂,^{8a} [(COD)PdCl₂]₂,^{8b} [COD = cycloocta-1,5-diene], NiCl₂,^{8c} [(NBD)-Mo(CO)₄]₂,^{8c} [NBD = norbornadiene = bicyclo[2.2.1]hepta-2,5-diene], [Rh(CO)₂Cl]₂,^{8c} and {calix[4]-(PPh₂)₄}{Fe(CO)₃}₂.

Preparation of 2. To a stirred suspension of *p*-tert-butylcalix[4]arene (12.98 g, 20.0 mmol) in THF (100 mL) was added dropwise Bu⁺Li (50 mL, 80 mmol). The resulting pale yellow solution was stirred overnight. The solution was cooled to 0 °C, and freshly distilled dimethylchlorophosphine (7.72 g, 80 mmol) in THF (20 mL) was slowly added while the reaction mixture was kept at 0 °C. A white precipitate formed immediately. The reaction mixture was allowed to come to room temperature and stirred for 4 h. Evaporation of the solvent yielded a yellow taffy product, which was redissolved in toluene (15 mL). LiCl was filtered off over a bed of Celite. The resulting yellow solution was evaporated to dryness. Adding acetonitrile (100 mL) yielded a white precipitate, which was filtered off and dried. The product was recrystallized from *n*-octane. Yield: 14.5 g (83.4%). Anal. Calcd for C₅₂H₇₆O₄P₄: C, 70.23; H, 8.62. Found: C, 70.06; H, 8.72. ¹H NMR: $\delta = 7.69$ (s, 8H); 5.49 (d, $J = 12.6$ Hz, 4H); 4.19 (d, $J = 12.6$ Hz, 4H); 2.67 (d, $J = 6$ Hz, 24H); 2.16 (s, 36H). ³¹P{¹H} NMR: $\delta = 127.3$.

Preparation of 3. To a stirred solution of **1** (1.88 g, 1.36 mmol) in dichloromethane (10 mL) was added a solution of [(COD)PdCl₂] (0.776 g, 2.72 mmol) in dichloromethane (10 mL). The solution slowly turned orange and was stirred overnight. The solvent was evaporated to dryness and the orange residue washed with cold *n*-hexane (30 mL), filtered off, and dried. Crystals suitable for X-ray analysis were obtained from toluene/acetonitrile. Yield: 2.34 g (93.4%). Anal. Calcd for C₉₂H₉₂Cl₄O₄P₄D₂C₇H₈: C, 64.89; H, 5.50. Found: C, 64.84; H, 5.72. ¹H NMR (400 MHz, CD₂Cl₂, 293 K): $\delta = 8.03$ (m, 5H); 7.53 (m, 10H); 7.26 (m, 5H); 7.17 (m, 10H); 7.06 (m, 10H); 6.53 (d, $J = 2.2$ Hz, 4H); 6.29 (d, $J = 2.2$ Hz, 4H); 5.19 (dt, $J_1 = 13.6$ Hz, $J_2 = 2.1$ Hz, 2H); 4.25 (d, $J = 14$ Hz, 2H); 2.71 (dd, $J_1 = 13.6$ Hz, $J_2 = 14$ Hz, 4H); 0.90 (s, 36H). ³¹P{¹H} NMR: $\delta = 117.7$.

Preparation of 4. To a stirred solution of **1** (1 g, 0.722 mmol) in dichloromethane (10 mL) was added a solution of [(COD)PtCl₂] (0.539 g, 1.44 mmol) in dichloromethane (10 mL). The solution slowly turned yellow and was stirred overnight. The solvent was evaporated to dryness, and the white residue was washed with cold *n*-hexane (30 mL), filtered off, and dried. Crystals suitable for X-ray analysis were obtained from toluene/acetonitrile. Yield: 1.31 g (95.5%). Anal. Calcd for C₉₂H₉₂Cl₄O₄P₄Pt₂: C, 57.62; H, 4.84. Found: C, 57.68; H, 5.00. ¹H NMR: $\delta = 8.12$ (m, 5H); 7.61 (m, 5H); 7.17 (m, 30H); 6.51 (d, $J = 2.6$ Hz, 4H); 6.30 (d, $J = 2.4$ Hz, 4H); 5.86 (dt, $J_1 = 11.4$ Hz, $J_2 = 3.4$ Hz, 2H); 4.38 (d, $J = 14$ Hz, 2H); 2.85 (d, $J = 14$ Hz, 4H); 0.90

(s, 36H). ³¹P{¹H} NMR: $\delta = 90.7$ ($J_{P-Pt} = 4368$ Hz). ¹⁹⁵Pt{³¹P, ¹H} NMR: $\delta = -1736$ ($J_{Pt-P} = 4285$ Hz).

Preparation of 5. To a stirred solution of **1** (1.0 g, 0.722 mmol) in dichloromethane (10 mL) was added a solution of [Rh(CO)₂Cl]₂ (0.28 g, 0.722 mmol) in dichloromethane (10 mL). The solution slowly turned yellow and was stirred overnight. After addition of *n*-hexane (50 mL) a white precipitate formed and was filtered off. It turned out to be free ligand (0.48 g). The solvent was evaporated to dryness. Crystals suitable for X-ray analysis were obtained on extraction with diethyl ether. Yield: 350 mg (56.6%). Anal. Calcd for C₉₄H₉₂-Cl₂O₆P₄Rh₂: C, 65.72; H, 5.40. Found: C, 65.59; H, 6.09. IR (CH₂Cl₂): ν (CO) = 1994 (s) cm⁻¹. ¹H NMR: $\delta = 8.06$ (m, 5H); 7.66 (s, 4H); 7.35 (m, 5H); 7.69 (m, 30H); 6.56 (d, $J = 13.4$ Hz, 2H); 6.08 (s, 4H); 4.88 (d, $J = 13.6$ Hz, 2H); 3.65 (d, $J = 13$ Hz, 2H); 1.85 (d, $J = 12.6$ Hz, 2H); 1.59 (s, 18H); 0.79 (s, 18H). ³¹P{¹H} NMR: $\delta = 138.1$ (d, $J_{P-Rh} = -214$ Hz), 135 (d, $J_{P-Rh} = -212$ Hz).

Preparation of 6. To a stirred suspension of **1** (5 g, 3.6 mmol) in THF (100 mL) was added solid NiCl₂ (1.0 g, 7.7 mmol). The suspension was heated at reflux for 3 days while slowly turning deep red. The hot solution was filtered in order to remove excess NiCl₂. Evaporation to half of its volume and addition of toluene (150 mL) yielded a red powder, which was filtered off and dried. Yield: 5.05 g (92.5%). Anal. Calcd for C₉₂H₉₂Cl₂NiO₄P₄: C, 72.9; H, 6.0. Found: C, 72.63; H, 6.22. ¹H NMR: $\delta = 8.22$ (m, 5H); 7.6 (m, 10H); 7.3 (m, 10H); 7.0 (m, 15H); 6.57 (dd, $J_1 = 2.4$ Hz, $J_2 = 8$ Hz, 4H); 6.40 (dt, $J = 14$ Hz, 1H); 6.44 (d, $J = 2.02$ Hz, 2H); 6.11 (d, $J = 2.02$ Hz, 2H); 4.76 (d, $J = 13$ Hz, 1H); 3.67 (d, $J = 13.8$ Hz, 2H); 3.53 (d, $J = 13.6$ Hz, 1H); 2.87 (d, $J = 12.8$ Hz, 1H); 2.11 (d, $J = 13.8$ Hz, 2H); 0.99 (s, 18H); 0.83 (s, 18H). ³¹P{¹H} NMR: $\delta = 121, 112.6$.

Preparation of 7. To a stirred solution of **1** (1.0 g, 0.722 mmol) in dichloromethane (10 mL) was added a solution of [(COD)PdCl₂] (0.206 g, 0.722 mmol) in dichloromethane (10 mL). The solution slowly turned orange and was stirred overnight. The solvent was evaporated to dryness, and the orange residue was washed with cold *n*-hexane (30 mL), filtered off, and dried. Yield: 0.95 g (84.2%). Anal. Calcd for C₉₂H₉₂Cl₂O₄P₄Pd: C, 70.7; H, 5.93. Found: C, 70.52; H, 6.30. ¹H NMR: $\delta = 8.13$ (m, 5H); 7.43 (m, 10H); 7.26 (m, 10H); 7.22 (m, 15H); 6.61 (d, $J = 2.6$ Hz, 2H); 6.51 (dd, $J_1 = 8$ Hz, $J_2 = 2.4$ Hz, 4H); 6.44 (d, $J = 2.5$ Hz, 2H); 5.9 (dt, $J = 14.1$ Hz, 1H); 4.78 (d, $J = 12.8$ Hz, 1H); 3.76 (d, $J = 14$ Hz, 2H); 3.24 (d, $J = 13.4$ Hz, 1H); 2.90 (d, $J = 12.8$ Hz, 1H); 2.18 (d, $J = 13.6$ Hz, 2H); 0.99 (s, 18H); 0.87 (s, 18H). ³¹P{¹H} NMR: $\delta = 121.1, 114.8$.

Preparation of 8. To a solution of **6** (0.54 g, 0.36 mmol) in THF (50 mL) was added solid [(NBD)Mo(CO)₄] (0.11 g, 0.36 mmol). Stirring was maintained over a period of 3 h with a concomitant color change from deep red to light red. The solution was evaporated to dryness and the residue recrystallized from toluene. Yield: 0.53 g (83.3%). Anal. Calcd for C₉₆H₉₂Cl₂MoNiO₈P₄: C, 66.91; H, 5.38. Found: C, 66.75; H, 5.97. IR (CH₂Cl₂, 293 K): ν (CO) = 2025 (vs), 1958 (b), 1905 (b) cm⁻¹. ¹H NMR: $\delta = 7.66$ (s, 5H); 7.35 (m, 5H); 7.69 (m, 30H); 6.56 (d, $J = 2.2$ Hz, 2H); 6.48 (d, $J = 2.2$ Hz, 2H); 6.29 (d, $J = 2.3$ Hz, 2H); 6.24 (d, $J = 2.3$ Hz, 2H); 5.81 (dt, $J = 13.4$ Hz, 1H); 5.59 (dt, $J = 13.7$ Hz, 1H); 5.10 (d, $J = 13$ Hz, 1H); 4.6 (d, $J = 13$ Hz, 1H); 3.2 (d, $J = 14$ Hz, 2H); 1.85 (d, $J = 12.6$ Hz, 2H); 0.97 (s, 18H); 0.80 (s, 18H). ³¹P{¹H} NMR: $\delta = 146.7, 103.2$.

Preparation of 9. To a stirred suspension of **2** (0.43 g, 0.483 mmol) in THF (50 mL) was added solid NiCl₂ (0.41 g, 3.16 mmol). The suspension was heated at reflux for 2 days and slowly turned deep red. The hot solution was filtered in order to remove excess NiCl₂. Cooling resulted in orange needles. Red cubic crystals suitable for X-ray analysis were obtained from toluene/acetonitrile. Yield: 0.41 g (73.9%). Anal. Calcd for C₅₂H₇₆Cl₄Ni₂O₄P₄: C, 54.39; H, 6.67. Found: C, 52.89; H, 6.94. ¹H NMR: $\delta = 7.01$ (s, 4H); 6.95 (s, 4H); 5.23 (d, $J = 12$ Hz, 2H); 4.18 (d, $J = 13$ Hz, 2H); 3.84 (d, $J = 13.4$ Hz, 2H); 3.29 (d, $J = 13.3$ Hz, 2H); 1.67 (s, 12H); 1.55 (s, 12H); 1.11 (s, 36H). ³¹P{¹H} NMR: $\delta = 126.5$.

Preparation of 10. To a stirred solution of **2** (0.26 g, 0.296 mmol) in dichloromethane (10 mL) was added a solution of [(COD)PdCl₂] (0.17 g, 0.592 mmol) in dichloromethane (10 mL). The solution slowly turned orange and was stirred overnight. The solvent was evaporated to dryness, and the orange residue was washed with cold *n*-hexane (30 mL), filtered off, and dried. Crystals suitable for X-ray analysis were

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Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **2**, **10**, and **11**

complex	2	10	11
empirical formula	C ₅₂ H ₇₆ O ₄ P ₄	C ₅₂ H ₇₆ Cl ₄ O ₄ P ₄ Pd ₂	C ₅₂ H ₇₆ Cl ₄ O ₄ P ₄ Pt ₂
<i>a</i> (Å)	17.853(3)	23.275(5)	23.255(3)
<i>b</i> (Å)	11.444(2)	22.856(5)	22.846(3)
<i>c</i> (Å)	14.272(2)	14.256(4)	14.207(2)
α (deg)	70.20(2)	90	90
β (deg)	93.02(2)	90	90
γ (deg)	82.58(2)	90	90
<i>V</i> (Å ³)	2706.0(9)	7584(3)	7548.0(18)
<i>Z</i>	2	4	4
<i>fw</i>	889.1	1417.9	1595.3
space group	<i>P1</i>	<i>Pnma</i>	<i>Pnma</i>
<i>t</i> (°C)	22	22	22
λ (Å)	1.541 78	0.710 69	0.710 69
ρ _{calcd} (g cm ⁻³)	1.091	1.242	1.404
μ (cm ⁻¹)	15.89	7.32	40.07
<i>R</i> ^a	0.112	0.061	0.055
<i>R</i> _w ^b	0.293	0.155	0.135

^a $R = \sum |\Delta F| / \sum |F_o|$ (calculated for the unique observed data). ^b $R_w = [\sum w(\Delta F^2) / \sum (wF_o^2)]^{1/2}$ (calculated for the unique observed data).

obtained from toluene/acetonitrile. Yield: 0.32 g (80.2%). Anal. Calcd for C₅₂H₇₆Cl₄O₄P₄Pd₂·C₇H₈: C, 53.05; H, 6.34. Found: C, 53.35; H, 6.34. ¹H NMR: δ = 7.07 (d, *J* = 2.3 Hz, 4H); 6.95 (d, *J* = 2.3 Hz, 4H); 4.72 (dt, *J*₁ = 13.2 Hz, *J*₂ = 2.5 Hz, 2H); 4.28 (d, *J* = 13.2 Hz, 2H); 3.68 (d, *J* = 13.2 Hz, 2H); 3.41 (d, *J* = 13 Hz, 2H); 2.56 (virtual triplet, 12H); 1.84 (virtual triplet, 12 H); 1.12 (s, 36 H). ³¹P{¹H} NMR: δ = 129.0.

Preparation of 11. To a stirred solution of **2** (0.30 g, 0.342 mmol) in dichloromethane (10 mL) was added a solution of (COD)PtCl₂ (0.26 g, 0.684 mmol) in dichloromethane (10 mL). The solution slowly turned yellow and was stirred overnight. The solvent was evaporated to dryness, and the white residue was washed with cold *n*-hexane (30 mL), filtered off, and dried. Crystals suitable for X-ray analysis were obtained from toluene/acetonitrile. Yield: 0.29 mg (60.1%). Anal. Calcd for C₅₂H₇₆Cl₄O₄P₄Pt₂: C, 43.95; H, 5.39. Found: C, 44.24; H, 5.63. ¹H NMR: δ = 7.07 (d, *J* = 2.2 Hz, 4H); 6.95 (d, *J* = 2.3 Hz, 4H); 5.23 (dt, *J*₁ = 13.2 Hz, *J*₂ = 2.0 Hz, 2H); 4.30 (d, *J* = 13 Hz, 2H); 3.64 (d, *J* = 13.4 Hz, 4H); 3.40 (d, *J* = 13.2 Hz, 4H); 2.57 (dd, *J*_{P-H} = 13.4 Hz, *J*_{Pt-H} = 40.8 Hz, 12H); 1.82 (dd, *J*_{P-H} = 13.4 Hz, *J*_{Pt-H} = 40.8 Hz, 12H); 1.12 (s, 36H). ³¹P{¹H} NMR: δ = 95.2 (*J*_{P-Pt} = 4170 Hz).

X-ray Crystallography for Complexes 2, 10, and 11. Suitable single crystals of complexes **2**, **10**, and **11** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with the use of TRACER.⁹ Crystal data and details associated with data collection are given in Tables 1 and S1 (Supporting Information). Data were collected at room temperature (295 K) on a single-crystal diffractometer (Siemens AED for **2**, and Enraf-Nonius CAD4 for **11**). For intensities and background, individual reflection profiles were analyzed.¹⁰ The structure amplitudes were obtained after the usual Lorentz and polarization corrections,¹¹ and the absolute scale was established by the Wilson method.¹² Intensities of compound **2** were corrected for crystal decay (68%), detected during data collection through the decay of three standard reflections. The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. Data were then corrected for absorption using the program ABSORB¹³ for all compounds. The function minimized during the least-squares refinement was $\sum w(\Delta F^2)^2$. Anomalous scattering

corrections were included in all structure factor calculations.^{14b} Scattering factors for neutral atoms were taken from ref 14a for non-hydrogen atoms and from ref 15 for H. Structure solutions and refinements were based on the observed reflections [$I > 2\sigma(I)$].

The structures were solved by direct methods using SHELX86¹⁶ for **2** and by the heavy-atom method starting from a three-dimensional Patterson map for **10** and **11**. Refinements were done by full-matrix least squares first isotropically, then anisotropically for all the non-H atoms, except for the disordered atoms. As is usually observed in calixarene compounds, some methyl carbon atoms of *tert*-butyl groups (C30–C32, C35, C38–C40 in **2**; C21–C23 in **10**; C17–C19 and C21–C23 in **11**) were affected by high thermal parameters indicating the presence of disorder. This was solved by splitting the atoms over two positions isotropically refined with a site occupation factor of 0.5. During the refinement the C–C bond distances were constrained to 1.54(1) Å. In compound **2** one PMe₂ group (P3, C49, C50) was found to be disordered over two positions sharing the C49 methyl carbon atom. The P3 and C50 atoms were split over two positions (A and B) and refined anisotropically (for P3) and isotropically (for C50) with site occupation factors of 0.6 and 0.4, respectively. In the isostructural complexes **10** and **11** the C29 methyl of the guest acetonitrile molecule and the toluene solvent molecule of crystallization (C41–C47) were found to be disordered about a mirror plane. These were isotropically refined with a site occupation factor of 0.5. Moreover the acetonitrile solvent molecule (N2, C30, C31) was found to be statistically distributed over two positions (A and B) isotropically refined with a site occupation factor of 0.25 since the two positions were in the near proximity of a mirror plane. The choice of the space group in complexes **10** and **11** was done on the basis of the *E*-statistics and confirmed by the successful structure refinements. Attempts to refine the structures in the non-centrosymmetric *Pna2*₁ space group in order to remove disorder were unsuccessful due to strong correlations between symmetry-related atoms and the persistence of disorder.

All hydrogen atoms except those associated with the disordered carbon atoms, which were ignored, were put into calculated positions for **2** and located from difference Fourier maps for **10** and **11**. They were introduced in the subsequent refinements as fixed atom contributions with isotropic *U*'s fixed at 0.10 for **2** and 0.08 Å² for **10** and **11**. In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ with $P = (F_o^2 + 2F_c^2)/3$ and $a = 0.1695, 0.1094, \text{ and } 0.0827$ for **2**, **10**, and **11**, respectively, was applied.

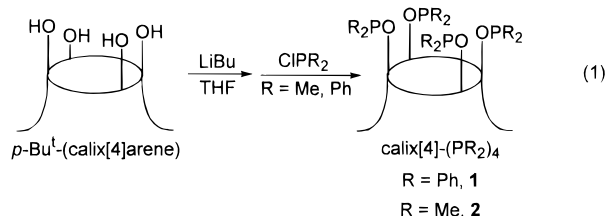
All calculations were performed by using SHELX76¹⁷ for the early stages of solution and SHELXL92¹⁸ for refinements. The final difference maps showed no unusual feature, with residual peaks about 1.00 e Å⁻³ for **10** and **11** located along the direction of M–P and M–Cl bonds. Final atomic coordinates are listed in Tables S2–S4 for non-H atoms and in Tables S5–S7 for hydrogens. Thermal parameters are given in Tables S8–S10, bond distances and angles in Tables S11–S13.¹⁹

Results and Discussion

1. *p*-tert-Butylcalix[4]arene Tetrakis(phosphinites). The syntheses of the calix[4]arene phosphinite ligands **1** and **2** were carried out by reacting the dialkyl- or diarylchlorophosphane with the lithium salts of *p*-tert-butylcalix[4]arene, which was prepared *in situ* (eq 1).² The synthesis of **1** has been detailed recently,² while the synthesis of **2** is reported here. Reaction 1 carried out with dimethylchlorophosphane²⁰ gave a white solid, which is very soluble in the majority of the solvents, including

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- (19) See the paragraph at the end of the paper regarding the Supporting Information.
- (20) Parshall, G. W. *Org. Synth.* **1965**, *45*, 102.



aliphatic hydrocarbons. The NMR spectrum of the crude product showed a mixture of all conformers, with the prevalence (*ca.* 90%) of the cone conformer. Fortunately, the cone conformer is insoluble in acetonitrile, which results in simple purification and isolation.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** consists of a singlet at $\delta = 127.3$. In the ^1H NMR spectrum, the signals assigned to the bridging methylene protons are split into two doublets with a coupling constant of $^2J = +12.6$ Hz. This nonequivalency (diastereotopicity) is due to the fact that one proton is oriented out of the calixarene macrocycle (the *exo* proton) and the other oriented inward (the *endo* proton). In addition, the *endo* proton is influenced by the dipolar moments of the neighbouring oxygen atoms. This splitting is clear evidence for the cone conformation.²¹ The signal of the methyl groups bonded to phosphorus appears as a doublet due to the coupling of the methylene protons with phosphorus; the magnitude of the coupling constant is $^2J_{\text{P-H}} = +6$ Hz.

The solid state structure of **2** (Figure 1) confirmed the results in solution derived from the NMR data, and it shows that there is a close solid state–solution structural correlation. Selected bond distances and angles are given in Table 2, and relevant conformational parameters are compared in Table 3. The O_4 core is nearly planar; the displacement from the mean plane ranges from $-0.053(5)$ to $0.072(6)$ Å. It is parallel to the reference plane defined by the C7, C14, C21, and C28 bridging methylene carbon atoms, the dihedral angle between them being $2.6(1)^\circ$. The mean plane through the P1, P2, P3A, P3B, and P4 atoms shows remarkable distortions ranging from $-0.601(4)$ to $0.310(3)$ Å. The dihedral angles it forms with the reference plane and the O_4 core are $5.5(1)$ and $2.9(1)^\circ$, respectively. The torsion angle of the O_4 plane (O1-O2-O3-O4) is $4.31(3)^\circ$. The corresponding angle for the P_4 plane (P1-P2-P3A-P4) is $-17.45(6)^\circ$. In contrast to the ligand calix[4]-(PPh_2)₄ (**1**)²² the O_4 and P_4 planes are no longer almost planar and parallel. This is due to the increased flexibility of the dimethylphosphino groups in calix[4]-(PMe_2)₄ (**2**) as compared to the diphenylphosphino groups in **1**. The A and B positions of the P3 phosphorus atom are symmetrically arranged with respect to a local mirror plane running perpendicular to the $\text{P2}\cdots\text{P4}$ line without giving rise to inconsistent intramolecular contacts. The contact distances between adjacent phosphorus atoms are $5.320(3)$ and $4.988(3)$ Å for $\text{P1}\cdots\text{P2}$ and $\text{P1}\cdots\text{P4}$, respectively, and range from $4.367(7)$ to $5.669(6)$ Å for those involving the P3 disordered atom. The functionalization of the oxygen atoms by the dimethylphosphino groups removes the C_4 symmetry of the calix[4]arene, which assumes an elliptical cone section conformation, two aromatic rings (A, C) being pushed outward and two (B, D) inward with respect to the cavity of the macrocycle (Table 3). This reflects in the separation between opposite *para* carbon atoms, the $\text{C4}\cdots\text{C17}$ and $\text{C10}\cdots\text{C24}$ distances being $9.222(15)$ and $5.443(9)$ Å. The overall conformation of the macrocycle should be attributed to the flexibility of calixarene and the steric hindrance of the PMe_2

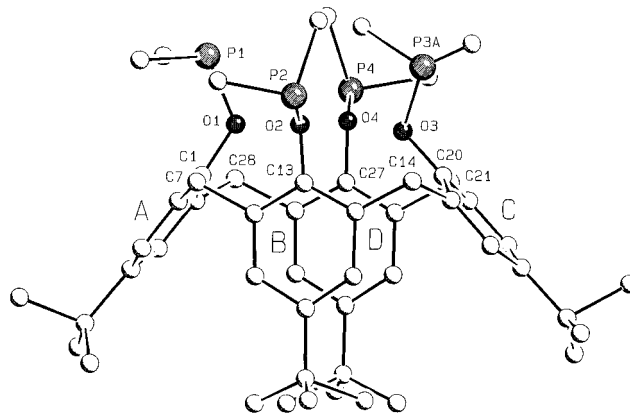


Figure 1. A SCHAKAL view of compound **2**. Disorder omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **2**

P1–O1	1.663(5)	P3B–C49	1.919(11)
P1–C45	1.793(10)	P3B–C50B	1.81(4)
P1–C46	1.793(11)	P4–O4	1.664(4)
P2–O2	1.663(4)	P4–C51	1.784(16)
P2–C47	1.798(13)	P4–C52	1.816(12)
P2–C48	1.773(13)	O1–C1	1.389(14)
P3A–O3	1.717(7)	O2–C13	1.396(10)
P3A–C49	1.800(11)	O3–C20	1.394(8)
P3A–C50A	1.82(2)	O4–C27	1.410(11)
P3B–O3	1.677(10)		
C45–P1–C46	95.9(6)	O3–P3B–C50B	101.0(12)
O1–P1–C46	105.6(4)	O3–P3B–C49	91.0(5)
O1–P1–C45	105.2(4)	C51–P4–C52	97.3(6)
C47–P2–C48	97.3(6)	O4–P4–C52	96.5(5)
O2–P2–C48	102.6(5)	O4–P4–C51	100.3(4)
O2–P2–C47	97.3(4)	P1–O1–C1	122.5(4)
C49–P3A–C50A	99.0(8)	P2–O2–C13	116.3(4)
O3–P3A–C50A	99.9(7)	P3B–O3–C20	115.4(5)
O3–P3A–C49	93.9(4)	P3A–O3–C20	117.3(5)
C49–P3B–C50B	100.3(11)	P4–O4–C27	115.9(5)

Table 3. Comparison of Conformational Parameters for Compounds **2**, **10**, and **11**

dihedral angle ^a (deg)	2	10	11
E– O_4	2.6(1)	0.2(1)	1.1(2)
E–A	127.7(2)	113.1(2)	112.1(2)
E–B	90.7(2)	116.8(2)	116.6(3)
E–C	133.1(2)	113.1(2)	112.1(2)
E–D	91.1(2)	116.8(2)	116.6(3)
A–C	99.3(3)	101.9(2)	101.7(2)
B–D	179.6(2)	105.1(2)	103.7(3)

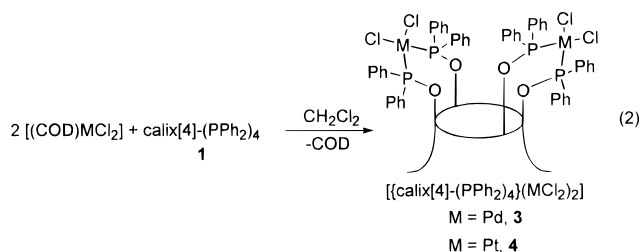
^a E refers to the reference plane C7, C14, C21, C28 in **2**; C7, C14, C7', C15 in **10** and **11**. O_4 refers to the plane through the four phenolic oxygens. A, B, C, and D refer to the aromatic rings bonded to O1, O2, O3, and O4, respectively (O3 and O4 should be read O2' and O1' respectively for **10** and **11**).

groups. In this respect it is worth noting that only one of these methyl groups is oriented toward the columnar axis of calixarene giving rise to the shortest $\text{C}\cdots\text{P}$ intraligand contact: $\text{C49}\cdots\text{P1}$, $3.728(12)$ Å. Unfortunately the C49 methyl is bonded to the disordered P3 atom, preventing thorough conclusions on possible interactions between the methyl protons and the P1 lone pair.

2. Metal Complexation by *p*-tert-Butylcalix[4]arene Tetraakis(diphenylphosphinite). **2A. Homodimetallic Complexes.** The displacement of a labile ligand has been used for the metalation of **1** according to eq 2. Complexes **3** and **4** have been obtained as crystalline solids (yield >95%). Their syntheses, without any structural information, have been briefly mentioned.²³ The structures were assigned on the basis of a

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comparison of their ^1H NMR spectra with that of $\{[\text{calix[4]-(PPh}_2)_4]\{\text{Fe}(\text{CO})_3\}_2\}$, for which we reported the X-ray analysis.^{2b} In order to simplify the understanding of the spectroscopic data, we should mention that the overall structure of **3** and **4** consists of two 10-membered metallacycles, bridged by two methylene groups. The phosphametallacycle is shown in Figure 2 with the numbering scheme of relevant protons. Additional support to the proposed structures comes from their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

The detailed analysis of the NMR data of **3** also applies to **4** and analogous derivatives. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of a singlet assigning the four phosphorus atoms as equivalents ($\delta = 117.7$ ppm), which is in agreement with the singlet observed for the four Bu^t signals in the ^1H NMR spectrum ($\delta = 0.90$). These data are consistent with the proposed structure of **3**. The signals which were assigned to the protons of the aryl groups were split into two doublets with a coupling constant of $^4J = +4$ Hz. This nonequivalency is due to the fact that two aryl protons are inside the 10-membered metallacycle (H_1) and two are pointing outside the metallacycle (H_2) (see Figure 2). The doublet ($^2J = +14$ Hz) at 2.71 ppm has been assigned to the *exo* proton of the bridging methylene (Figure 2), while the *endo* proton appears at 5.19 ppm as a doublet of triplets with coupling constants of $^2J = +13.6$ Hz (coupled to the geminal *exo*) and of $J = +2.1$ Hz. The latter coupling may be due to coupling between H_{endo} and the two equivalent phosphorus atoms of the metallacycle (a similar P–H coupling in a phosphaoxetane derivative was observed by Pastor *et al.*²⁴) or to coupling with the aryl protons. The latter possibility was excluded, on the basis of magnitude of the corresponding $^4J_{\text{H-H}}$ coupling constant (~ 1 Hz).²⁵

Apparently, the metal atom forces the metallacycle into a favorable geometry where P– H_{endo} coupling can occur either “through bonds” or “through space”.²⁶ A two-dimensional hetero-COSY (or HETCOR) experiment for ^{31}P – ^1H determines J -coupled protons to the phosphorus nuclei.²⁷ This would allow one to see whether the P–H coupling was a $^5J_{\text{P-H}}$ coupling through bonds or not. In spite of several mixing times, only the protons from the adjacent phenyl rings in **3** appeared to be coupled to phosphorus. This result rules out the possibility of through-bond coupling. To confirm this conclusion, a hetero-TOCSY (total correlation spectroscopy) ^{31}P – ^1H experiment was performed on **3** (Figure 3).

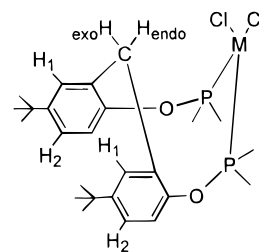


Figure 2. The metallacycle formed within the phosphacalix[4]arene.

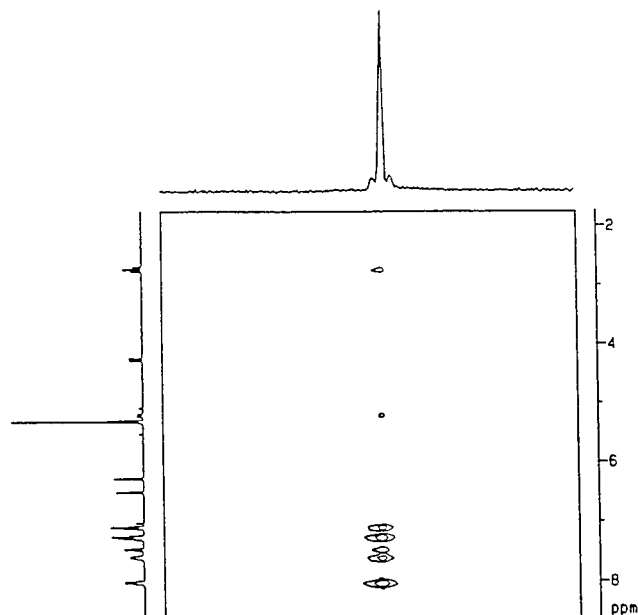


Figure 3. Hetero-TOCSY (^{31}P – ^1H) NMR spectrum of **3** (400/162.030 MHz, CDCl_3 , 298 K).

The singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum correlates with the signals of two doublets assigned to the methylene protons in the ^1H NMR spectrum. These signals were assigned as follows: the first correlated signal was assigned to the doublet of H_{exo} at $\delta = 2.71$ and the second correlated signal to the doublet of triplets of H_{endo} at 5.19 ppm. A through-space interaction²⁸ between H_{endo} and the two equivalent phosphorus atoms of the metallaphosphacycle can therefore be postulated. This effect was observed for the corresponding platinum, **4**, nickel, **6**, and iron, $\{[\text{calix[4]-(PPh}_2)_4]\{\text{Fe}(\text{CO})_3\}_2\}$, derivatives.^{2b} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** consists of a singlet with the corresponding ^{195}Pt satellites at $\delta = 90.7$ and a coupling constant of $^1J_{\text{P-Pt}} = +4368$ Hz. The ^{195}Pt spectrum showed one peak at $\delta = -1736$ with a coupling constant of $^1J_{\text{P-Pt}} = +4285$ Hz. The splitting pattern of the ^1H NMR spectrum was identical to that of the palladium analogue **3**, the major difference being the chemical shift of the *endo* proton of the methylene group, moving from 5.19 to 5.86 ppm.

The use of ligand **1** allowed the generation of another interesting starting material for this reactivity study, namely, the dimetallic rhodium *cis* analogue of the Vaska compound. The synthesis was achieved in CH_2Cl_2 according to eq 3, and complex **5** was obtained from Et_2O as a yellow crystalline solid.

The IR spectrum shows a single CO stretching vibration at 1994 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of two doublets at $\delta = 138.1$ and 135 ($^1J_{\text{P-Rh}} = -214$ and -212 Hz). In the ^1H NMR spectrum two singlets of equal intensity are

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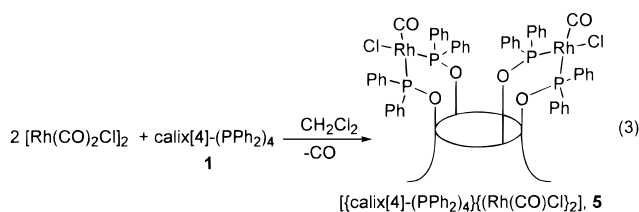
(24) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Steinhubel, L. *Phosphorus Sulfur Relat. Elem.* **1983**, *15*, 9.

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(26) See, for a related example: Goddard, J. D.; Payne, A. W.; Cook, N.; Luss, H. R. *J. Heterocycl. Chem.* **1988**, *25*, 575.

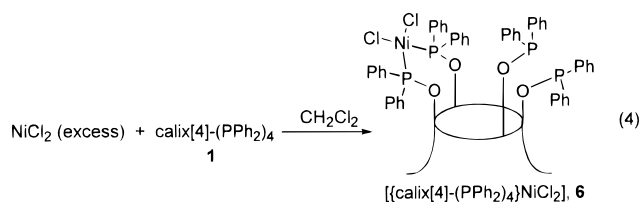
(27) (a) Bampos, N.; Field, L. D.; Messerle, B. *Organometallics* **1993**, *12*, 2529. For general reference: (b) Martinand, G. E.; Zektzer, A. S. *Two dimensional NMR Methods for Establishing Molecular Connectivity*; VCH: Weinheim, Germany, 1988. (c) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987.

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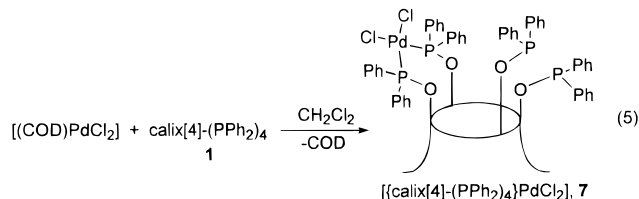


observed for the Bu^t groups (1.59 and 0.79 ppm), as well as the nonequivalence of the phosphorus atoms in the ³¹P{¹H} NMR spectrum. The signals assigned to the H_{endo} were shifted downfield, as compared to the platinum and palladium derivative at $\delta = 6.56$ ($^2J = +13.4$ Hz). This doublet was not further split in a triplet as observed for **3** and **4**, because the two phosphorus atoms of the phosphametallacycle are no longer magnetically equivalent. It should be mentioned that, on the basis of our spectroscopic data, it would be difficult to determine the exact spatial arrangement of the two [Rh(CO)Cl] moieties, though our NMR data allow one to conclude that we have a single isomer among the possible *cis* and *trans* dispositions of the two CO groups. The *cis* isomer is shown as **5** in eq 3.

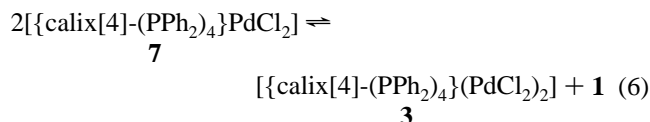
2B. Monometallic and Heterodimetallic Complexes. The entry into this area was made possible by observing that reaction of **1** with NiCl₂ gave only the monometalated species, regardless of the large excess of NiCl₂ used (eq 4). In the case of



palladium, the monometalated form is accessible by running reaction 2 or using PdCl₂ as the starting material with the appropriate 1:1 ligand:metal stoichiometric ratio (eq 5). The



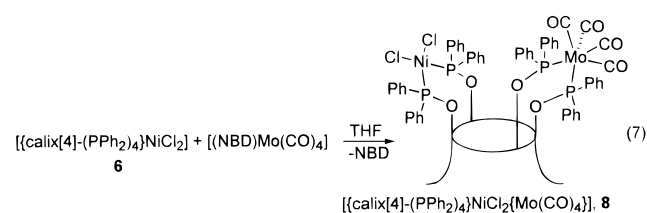
monometalated form in the case of Pd is, however, the kinetic product. Keeping **7** in solution for 2 weeks resulted in the slow ligand disproportionation reaction, according to eq 6.



In the case of platinum, regardless of the starting material, PtCl₂ or [(COD)PtCl₂], or the ligand:metal stoichiometric ratio, we obtained exclusively the bimetallic complex **4**. The same observation was made by mixing equimolar amounts of **3** and **1**. The equilibrium shown in eq 6 explains the traces of **3** always found in the synthesis of **7**. The disproportionation reaction has been monitored by ³¹P{¹H} NMR spectroscopy. One singlet appears at $\delta = 117.7$ for **3**, while in the case of **7** we observe two singlets at $\delta = 121.1$ and 114.8. The similar ³¹P{¹H} and ¹H spectra of **6** and **7** (see Experimental Section) suggest similar structures. Further support comes from an approximate X-ray analysis on **6**.²² Details are given for the

NMR spectra of **7**. The downfield peak ($\delta = 121.1$) in the ³¹P{¹H} NMR spectrum of **7** was assigned to the two noncoordinated phosphorus atoms on the basis of the value for the free ligand at 121 ppm. The high-field signal ($\delta = 114.8$) was assigned to the two phosphorus atoms bonded to palladium. The shift to high field for the latter peak was greater than for the corresponding bimetallic compound **3** ($\delta = 117.7$). This may be indicative of an increased bond strength due to less steric strain.²⁹ The two phenyl groups of the noncomplexed phosphorus, which are *endo* to the macrocyclic cavity, relieve steric strain by twisting to a more favorable geometrical arrangement. The corresponding ¹H NMR spectrum of **7** shows two signals at 0.99 and 0.87 ppm for different *tert*-butyl groups. This is consistent with the data from the ³¹P{¹H} NMR spectrum. The signals assigned to the methylene groups are split into six doublets due to the low symmetry of **7**.

The synthetic relevance of complexes like **6** and **7** stays on their potentiality as precursors of heterodimetallic complexes. This is particularly true for **6**, due to its easy preparation on a large scale. The first problem to be faced in the synthesis of heterodimetallic complexes is the metal-ion exchange process observed in the reaction of **6** with [(COD)MCl₂] [M = Pd, Pt]. In this case we observed a complete transmetalation reaction. The synthesis of a heterodimetallic complex was however successful in a number of cases, one of them being exemplified by reaction 7. The ³¹P{¹H} NMR spectrum of **8** shows two



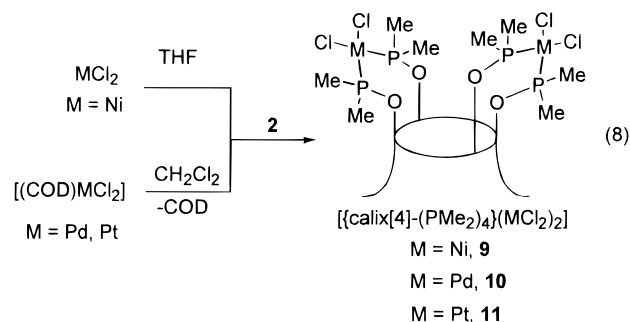
singlets at $\delta = 146.7$ and 103.2 ppm, which are assigned to phosphorus complexed to molybdenum and nickel, respectively. The latter peak shows a large shift to high field ($\Delta = 9.4$ ppm), which may be due in part to the increased steric hindrance and/or the electronic changes caused by the presence of Mo(0). The [Mo(CO)₄] should have a C_{2v} local symmetry, for which four IR active C—O stretching bands (2A₁ + B₁ + B₂) are expected, rather than the three which are observed (2025, 1958, and 1905 cm⁻¹). In a number of cases, however, the two A₁ bands in [L₂Mo(CO)₄] complexes fall very close.³⁰ The rather high frequency of the CO stretching vibrations allows us to show that the σ -donor properties of our bidentate system are quite close to those of bis(diphenylphosphino)ethane, dppe.³¹

3. Metal Complexation Using *p*-tert-Butylcalix[4]arene Tetrakis(dimethylphosphinite). The steric hindrance of the P₄ set of donor atoms and the phosphorus basicity change remarkably from **1** to **2**, and it is these features which have allowed the formation of particularly promising phosphorus derivatives of Ni(II), Pd(II), and Pt(II) starting materials. Their syntheses were achieved as shown in eq 8. We attribute the formation of a dimetallic derivative to the increased basicity and the decreased steric demand of **2**, compared to **1**. There is only a slight influence of the metal on the phosphorus resonance in the ³¹P{¹H} NMR spectrum of **9** (from $\delta = 127.3$ to 126.5 ppm), contrary to what was observed for **6** and **8** in comparison with **1**, with a much larger shift difference.

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The signals in the ^1H NMR spectrum of **9** are broader than those of **10** and **11**. This is due to the well-documented square planar (diamagnetic)—tetrahedral (paramagnetic) equilibria for $[(\text{R}_3\text{P})_2\text{NiCl}_2]$ complexes in solution. The signals assigned to the aryl protons appeared either as a broad singlet in CDCl_3 (6.98 ppm) or as a broad doublet in CD_2Cl_2 (7.01 and 6.95 ppm). The signals assigned to the methylene protons appeared as broad doublets at 5.23, 4.18, 3.84, and 3.29 ppm. The signal at 5.23 ppm was assigned to the *endo* proton. The signals which were assigned to the protons of the methyl groups at the phosphorus atoms appeared as two broad singlets at 1.67 and 1.55 ppm. They are more split up, compared to the free ligand **2**, where only one doublet was observed. This is due to the complexation to nickel, which makes the methyl groups at phosphorus nonequivalent. The Bu^t groups give rise to a singlet at 1.11 ppm.

The structures proposed for **9–11** are supported by the X-ray analysis carried out on **10** and **11**, which are isostructural. The structural parameters discussed refer to **10**, while the values of complex **11** are given in square brackets in the text (Table 4).

The crystals contain solvents of crystallization in a 1:1:2 complex:toluene:acetonitrile molar ratio. The complexes have an imposed *m* symmetry, the mirror plane running through the bridging C14 and C15 methylene carbon atoms of calixarene (Figures 4 and 5). The four phosphorus atoms define a binding surface for two metal atoms, each one bonded to a pair of adjacent P atoms. Coordination around each metal is completed to square planar by two *cis* chlorine atoms. The coordination plane shows a small but significant tetrahedral distortion around palladium (displacements ranging from $-0.037(7)$ to $0.018(3)$ Å) and around platinum (displacements ranging from $-0.024(4)$ to $0.020(4)$ Å). Such a plane forms a dihedral angle of $53.8(1)$ [$52.9(1)$]° with the mean reference plane (C7, C14, C7', C15), which is tetrahedrally distorted (displacements from $-0.320(12)$ [$-0.332(16)$] to $0.146(8)$ [$0.155(11)$] Å). The O_4 and P_4 cores, which are planar for symmetry requirements, are parallel to each other (dihedral angle $1.1(1)$ [$0.3(1)$]°) and parallel to the mean reference plane (dihedral angles $1.1(2)$ [$0.2(1)$] and $1.4(2)$ [$0.9(1)$]° for O_4 and P_4 , respectively).

The chelating behavior of the macrocycle ligand toward two metal atoms results in a $\text{P1}\cdots\text{P2}$ bite distance of $3.449(4)$ [$3.434(4)$] Å, the other $\text{P}\cdots\text{P}$ distances between adjacent phosphorus atoms being $\text{P1}\cdots\text{P1}'$, $5.751(4)$ [$5.721(3)$] Å, $\text{P2}\cdots\text{P2}'$, $5.623(4)$ [$5.606(3)$] Å, and between opposite phosphorus atoms being $\text{P1}\cdots\text{P2}'$, $6.650(4)$ [$6.623(3)$] Å. The distance between the two metal ions is $7.437(2)$ [$7.324(2)$] Å, while the minimum distance they can eventually achieve is $3.447(2)$ [$3.433(3)$] Å. This distance would allow cooperative effects between the two metal centers. The metal freezes the cone conformation of calixarene as is seen from the dihedral angles given in Table 3 and from the distance between opposite *para* carbon atoms ($\text{C4}\cdots\text{C10}'$, $7.819(12)$ [$7.781(16)$] Å). The behavior and conformation of the macrocycle are similar to those observed for the $[\text{p-Bu}^t\text{-calix}[4]\text{-(PPh}_2\text{)}_4\text{}\{\text{Fe}(\text{CO})_3\}_2]^{2b}$ com-

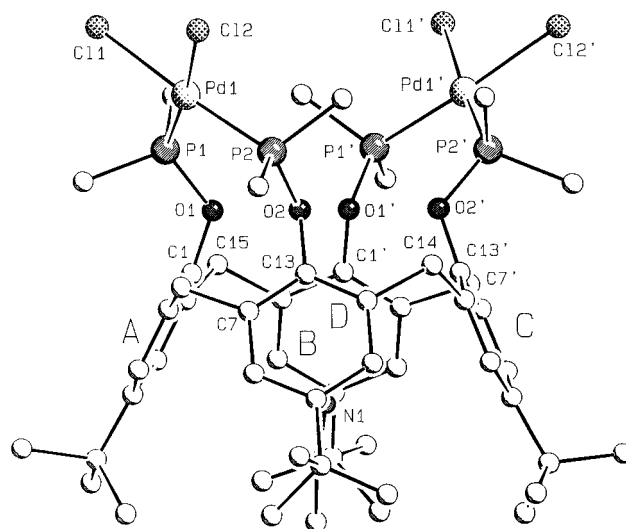


Figure 4. A SCHAKAL view of complex **10**. Prime denotes a transformation of $x, 0.5 - y, z$. Disorder omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complexes **10** (M = Pd) and **11** (M = Pt)

	10	11
M—C12	2.353(3)	2.351(4)
M—C11	2.366(3)	2.360(3)
M—P1	2.242(3)	2.217(3)
M—P2	2.241(3)	2.216(2)
P1—O1	1.615(5)	1.620(7)
P1—C24	1.785(12)	1.798(14)
P1—C25	1.814(10)	1.811(13)
P2—O2	1.635(5)	1.632(7)
P2—C26	1.777(11)	1.762(13)
P2—C27	1.773(9)	1.784(13)
O1—C1	1.399(8)	1.387(11)
O2—C13	1.388(8)	1.441(11)
P1—M—P2	100.5(1)	101.5(1)
C11—M—P2	174.6(1)	173.0(1)
C11—M—P1	84.8(1)	85.5(1)
C12—M—P2	83.4(1)	84.4(1)
C12—M—P1	175.5(1)	174.0(1)
C12—M—C11	91.2(1)	88.6(1)
M—P1—C25	112.2(3)	111.2(5)
M—P1—C24	110.6(4)	112.3(4)
M—P1—O1	117.5(2)	117.0(3)
C24—P1—C25	107.0(5)	105.1(5)
O1—P1—C25	107.0(4)	103.2(5)
O1—P1—C24	101.8(4)	107.0(5)
M—P2—C27	111.0(3)	112.2(4)
M—P2—C26	112.4(3)	111.4(4)
M—P2—O2	118.2(2)	116.9(2)
C26—P2—C27	105.9(5)	104.7(6)
O2—P2—C27	102.2(4)	102.4(5)
O2—P2—C26	106.0(4)	108.2(5)
P1—O1—C1	122.3(4)	123.3(6)
P2—O2—C13	122.9(4)	121.7(6)

plex, indicating that the ordering role of the metal atoms is a primary factor in determining the calix[4]arene conformation. The size and conformation of the cavity are suitable for hosting an acetonitrile molecule, which shows a disordered C29. The extent of inclusion of the guest molecule into the cavity is indicated by the distance of the N1 atom from the O_4 core, which is $4.001(18)$ [$3.97(2)$] Å.

The singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum moves slightly in **10** compared to the free ligand **2** (129.0 and 127.3 ppm, respectively). An analogous spectral change was also observed for **3** compared to **1** (117.7 and 121 ppm, respectively). This may be indicative of the weak P—Pd interaction, compared to the strong interaction for Pt—P in **11**, which has a singlet at $\delta = 95.2$ ppm ($^1J_{\text{P-Pt}} = 4170$ Hz). The splitting pattern of the

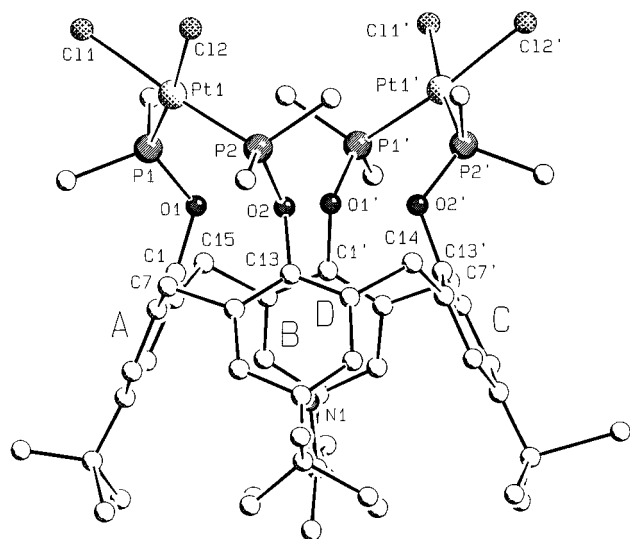


Figure 5. A SCHAKAL view of complex **11**. Prime denotes a transformation of x , $0.5 - y$, z . Disorder omitted for clarity.

PMe_2 group in the ^1H NMR spectra of **9–11** may be an indication of the tetrahedral distortion from the normal square planar coordination around the metal. In the ^1H NMR spectrum of **11**, the signals assigned to the protons of the dimethylphosphino group appear as two doublets at $\delta = 2.57$ and 1.82 with a coupling constant of $^2J_{\text{P-H}} = +13.4$ Hz (the second coupling constant $^3J_{\text{Pt-H}}$ of $+40.8$ Hz was also observed). This is indicative of a *cis* product. In the solid state structure of **11** (Figure 5) the P-M-P angle is, as a matter of fact, $101.4(2)^\circ$. Apparently, the calixarene skeleton is quite flexible in solution and allows a more regular square planar arrangement of the P_2PtCl_2 moiety than in the solid state. The ^1H NMR spectrum of the corresponding palladium derivative **10** shows two virtual triplets, which are assigned to the dimethylphosphino protons at $\delta = 2.56$ and 1.84 (in the extreme case of a *trans* chelating ligand, a triplet would have been observed).^{27c,32} The distorted triplet with a broad central peak is an example of virtual coupling. The $^2J_{\text{P-P}}$ coupling of this compound is larger than when the two phosphorus atoms are bonded *cis* to the metal; this eventually can be used as a criterion for a tetrahedral distortion in **10**. This is in agreement with the data obtained from the solid state structure of **10** (Figure 4), where the P-M-P angle is $100.5(1)^\circ$ (see Table 4). Complex **9** displays only two broad singlets at 2.58 and 1.67 ppm; this feature, together with its paramagnetism, is indicative of a distorted geometry around the nickel atom. The interpretation of the

splitting pattern of the protons of the methyl groups at phosphorus allows the assignment of the structure in solution for the corresponding P_2MCl_2 fragments in the derivatives **9–11**. The metal with the smallest radius, Ni (**9**), adopts partly a tetrahedral structure, and the metal with the largest radius, Pt (**11**), a *cis* square planar one. Palladium in **10** displays a behavior between those of the two limiting cases.

At this stage we should comment on the spectroscopic visibility of the bridging methylene signals. In the calix[4]arene skeleton they serve as a spectroscopic probe for structural correlations in complexes **3–5**, particularly considering the changes in chemical shift and the magnitude of the $J_{\text{P-H}}$ coupling constant of the *endo* hydrogen (see Figure 2). A remarkable downfield shift was observed for the sequence **3** \rightarrow **4** \rightarrow **5**, the free ligand **1** being the reference. A further downfield shift was observed on going from **4** to **11**, according to an increase of electron density at the metal (phenyl *vs* methyl substituents at phosphorus). The same downfield shift is found on going from di- to monometallic species, *i.e.*, from **3** to **7** with a $\Delta = 0.71$ ppm. The first argument is based on geometrical constraints and postulates a sort of weak interaction between the metal center and the H_{endo} proton. However, this kind of interaction was not further specified. An agostic type of interaction can be excluded, because this would result in a high-field shift for the proton which undergoes the agostic interaction.³³ This is clearly not the case. Instead, the opposite trend was observed, a downfield shift of the signal assigned to H_{endo} , compared to the free ligand. This phenomenon may be explained in terms of an increased deshielding of the *endo* proton, because the formation of a metallacycle results in an additional ring current which opposes the external field.³⁴ Additional electron density increases the deshielding and leads to a further downfield shift, compared to the electron-poor derivatives.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, fractional atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations for **2**, **10**, and **11** (19 pages). Ordering information is given on any current masthead page.

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