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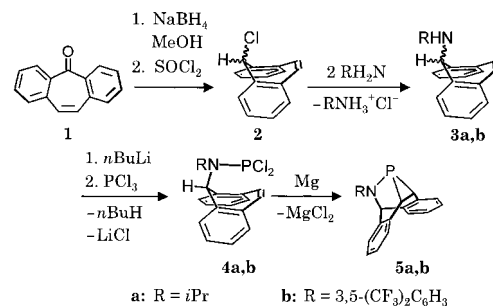
Very Stable Phosphiranes**

Jürgen Liedtke, Sandra Loss, Gilles Alcaraz, Volker Gramlich, and Hansjörg Grützmacher*

Dedicated to Professor Edgar Niecke on occasion of his 60th birthday

Phosphiranes are strained three-membered PC_2 -heterocycles^[1] which are potentially interesting ligands for homogeneous transition metal catalyst complexes. Their small sum of bond angles at the phosphorus center ($\Sigma \angle (\text{P})$: 240–275) should make them good π acceptors; however, these heterocycles are usually labile towards [2+1] cycloreversions into phosphinidines, RP, and olefins.^[2] Although in recent years some rather stable phosphiranes bearing bulky substituents at the phosphorus center (i.e. *t*Bu, adamantyl, mesityl, supermesityl, $\text{N}(\text{SiMe}_3)_2$) have been prepared,^[3] their use in catalysis was found to be limited because of ligand decomposition.^[4] In order to suppress this undesired cycloreversion reaction, we searched for a simple high-yield synthesis of phosphiranes, in which the PC_2 ring is embedded in a polycyclic framework.^[5]

Starting from the dibenzoannelated tropolone **1**, amines **3a** and **3b** are obtained following known literature procedures.^[6] After lithiation and subsequent reaction with PCl_3 the dichloroaminophosphanes **4a** and **4b** are isolated as colorless crystals in more than 90% yield. Using commercially available magnesium turnings and thf as solvent, dehalogenation of **4a** and **4b** led to gram quantities of the amino-substituted^[7] phosphiranes **5a** and **5b** in excellent yields (> 90%; Scheme 1).



Scheme 1. Synthesis of **5a** and **5b**.

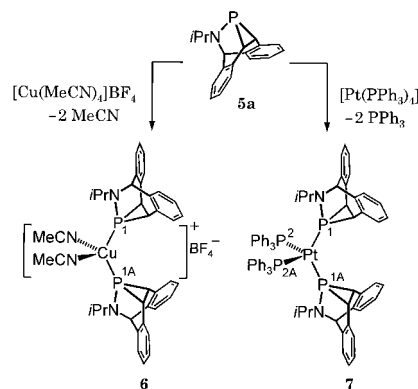
Formally these compounds are formed by an intramolecular [2+1] cycloaddition of an R_2NP phosphinidene unit to the C–C double bond of the central seven-membered ring of

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the dibenzotropyliidene unit, which has a rigid boat conformation as shown for **4a** and **4b**.^[8] In **5a** and **5b** the PC₂ ring is part of a tetracyclic cage and, with reference to the analogous hydrocarbon C₉H₁₀ (barbarlane), we name these phosphiranes phosphazabarbaralanes (*BABAR*-Phos). They form colorless crystals which melt without decomposition and can be handled in air. In contrast to 1-phenylphosphirane, PhP(CH₂)₂, **5a** and **5b** do not react even with an excess of strong alkylating agents such as MeOSO₂CF₃ to form phosphiranium salts,^[9] nor do they react with sulfur in refluxing toluene to give thiophosphoranes.

To answer the question, how *BABAR*-Phos binds to d¹⁰ transition metal centers, we treated **5a** with [Cu(MeCN)₄]BF₄ and [Pt(PPh₃)₄]. The bis(*BABAR*-Phos) complexes **6** and **7** were obtained quantitatively (Scheme 2). While d⁸ platinum(II) metal complexes of the unsaturated phosphirene PhP(CPh)₂ are known, attempts to prepare electron-rich d¹⁰ complexes containing intact phosphiranes gave only ring-opened products.^[10]

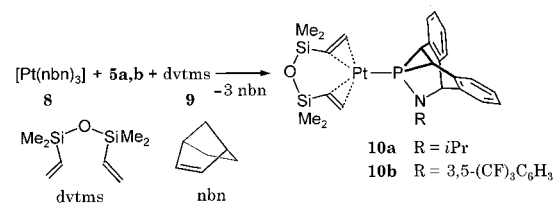


Scheme 2. Complexes with the ligand **5a**.

The binding properties of *BABAR*-Phos **5a** were qualitatively compared: triphenylphosphane, Ph₃P [$\Sigma \chi(P) \approx 303$], as the better σ donor, readily displaces the phosphirane **5a** from the copper complex **6**. Consequently, attempts to prepare *BABAR*-Phos complexes from triphenylphosphane coinage metal complexes, [(Ph₃P)_nM]⁺ (M = Cu, Ag, Au) failed. However, in solutions of platinum complex **7**, free PPh₃ is observed by ³¹P NMR spectroscopy in addition to [Pt(*BABAR*-Phos)₂(PPh₃)] ($\delta(^{31}\text{P}) = -109$, $^2J(\text{P,P}) = 74$ Hz,

$^1J(\text{Pt,P}) = 4454$ Hz; $^{15}J(\text{P,P}) = 74$ Hz, $^1J(\text{Pt,P}) = 4374$ Hz)); thus the *BABAR*-Phos ligand remains bonded to platinum. It is assumed that phosphorus to metal σ donation is the more important component in the complexation of phosphanes in coinage metal complexes. On the other hand, metal-to-ligand π donation is believed to make the predominant electronic contribution in the binding of phosphanes to zero-valent platinum.^[1b] Thus our experiments suggest a poor σ -donating but rather high π -accepting strength for **5a**.

As shown in Scheme 3, the d¹⁰ platinum *BABAR*-Phos olefin complexes **10a** and **10b** are readily accessible by substitution of norbornene (nbn) in [Pt(nbn)₃] (**8**). The



Scheme 3. Synthesis of the complexes **10a** and **10b** from **5a** and **5b**, respectively.

compound **10a** was isolated and characterized by single-crystal X-ray structure analysis (Figure 1).^[11a] The structures of **5b**, **6**, and **7**^[11b] have also been determined and selected bond lengths and angles are listed in Table 1.

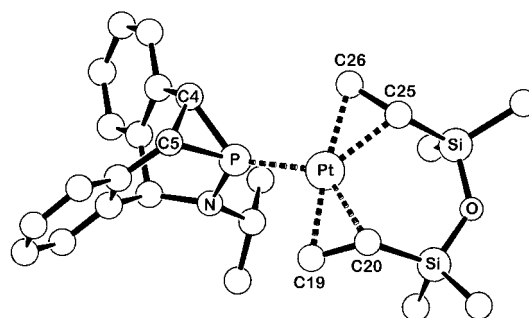


Figure 1. Molecular structure of **10a**. Selected bond lengths [Å] and angles [°] (see also Table 1; X1 = midpoint of the C19–C20 bond, X2 = midpoint of the C25–C26 bond): Pt–C19 2.141(7), Pt–C20 2.133(6), Pt–C25 2.152(7), Pt–C26 2.127(7), C19–C20 1.405(9), C25–C26 1.416(11); P–Pt–X1 111.95(6), P–Pt–X2 114.15(6), X1–Pt–X2 133.90(4).

Table 1. Selected structural data of **5b**, **6**, **7**, and **10a**.

	<i>a</i> ₁ [Å]	<i>a</i> ₂ [Å]	<i>b</i> [Å]	<i>c</i> [Å]	<i>d</i> [Å]	α [°]	β_1 [°]	β_2 [°]	$\Sigma \chi$ [°]	γ_1 [°]	γ_2 [°]	γ_3 [°]
5b	1.850(3)	1.863(3)	1.532(4)	1.738(2)	–	48.8(1)	98.8(1)	99.0(1)	246.5	–	–	–
6 Cu ^[a]	1.821(5)	1.849(5)	1.544(6)	1.676(4)	2.269(1)	49.8(2)	101.5(2)	103.1(2)	254.4	119.8(1)	127.2(2)	134.2(2)
7 Pt ^[a]	1.831(5)	1.856(5)	1.558(7)	1.699(4)	2.281(1)	49.9(2)	99.5(2)	101.0(2)	250.4	124.8(1)	125.2(2)	131.5(2)
10a Pt	1.812(6)	1.821(7)	1.576(9)	1.684(6)	2.241(2)	51.4(3)	101.7(3)	103.1(3)	256.2	119.8(2)	130.0(2)	131.4(2)

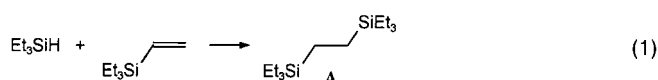
[a] Averaged data of both *BABAR*-Phos ligands are given.

Table 2. Selected physical data for **4a,b**, **5a,b**, **6**, **7**, and **10a,b** (δ in ppm, J in Hz).

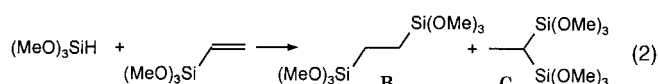
	$\delta(^{31}\text{P})$	$\delta(^1\text{H})$ PCHCH	$\delta(^{13}\text{C})$ PCHCH	M.p. [$^{\circ}\text{C}$]
4a	168.7	7.12	130.7	114
4b	154.7	7.21	130.6	122
5a	–153.5	2.65, $^2J(\text{P,H}) = 22$	21.3, $^1J(\text{P,C}) = 38$	85
5b	–146.0	3.12, $^2J(\text{P,H}) = 20$	22.4, $^1J(\text{P,C}) = 38$	147
6	–133.5	3.08, $^2J(\text{P,H}) = 15$	20.7, $^1J(\text{P,C}) = 30.2$	(decomp) > 176
7	–111, $^2J(\text{P,P}) = 66$, $^1J(\text{Pt,P}) = 4038$ (P1, 1A); 13.5, $^2J(\text{P,P}) = 66$, $^1J(\text{Pt,P}) = 4254$ (P2, 2A).	2.3 (m)	27.7, $^1J(\text{P,C}) = 23$	(decomp) > 180
10a	–74, $^1J(\text{Pt,P}) = 4203$	2.85, $^2J(\text{P,H}) = 5.7$, $^3J(\text{Pt,H}) = 13.8$	23.1, $^1J(\text{P,C}) = 15$, $^2J(\text{Pt,C}) = 18$	(decomp) > 95
10b	–76, $^1J(\text{Pt,P}) = 4218$	3.02, $^2J(\text{P,H}) = 6.0$, $^3J(\text{Pt,H}) = 12.8$	25.2, $^1J(\text{P,C}) = 18$, $^2J(\text{Pt,C}) = 15$	–

The bond parameters show the expected trends: The Pt–P1/1A lengths (2.281(1) Å in **7**, 2.241(2) Å in **10a**) are shorter than the Pt–P2/2A (PPh₃) bond lengths (2.324(1) Å) in **7**. In all compounds the ring internal P–C bonds (a_1, a_2) and P–N (c) bonds become shorter when the phosphorus lone pair is involved in complexation. At the same time, the basal C–C bond, b , becomes longer and the sum of bond angles, $\Sigma\angle$, at phosphorus becomes larger. These effects are most pronounced in the three-coordinate platinum(0) complex **10a**.

Given that Pt⁰ olefin complexes are known hydrosilylation catalysts, we mixed [Pt(nbn)₃] (**8**) with a slight excess of dtms **9** in benzene as solvent and then added one equivalent of phosphane to afford the catalyst precursor. By ³¹P NMR spectroscopy, the complexes **10a** and **10b** were the only species detected in these solutions. For the hydrosilylation reaction (1) 14 mol %, and for reaction (2) 1.4 mol % catalyst were used, respectively



	Conversion to A [%]	t [h]	T [$^{\circ}$]
Pt/PPh ₃	< 3	72	25
Pt/ 5a	100	72	25
Pt/ 5b	100	< 24	25



	Conversion [%]	B [%]	C [%]	t [h]	T [$^{\circ}$]
Pt/PPh ₃	100	> 90	< 10	24	25
Pt/ 5a	100	83	17	< 24	25
Pt/ 5b	100	78	22	< 8	25

The phosphirane ligands **5a** and **5b** significantly enhance the catalytic activity when compared to PPh₃ under identical conditions. Specifically, 1) no conversion was observed in reaction (1) with PPh₃ and 2) use of BABAR-Phos **5b** bearing an electron-withdrawing group bound to the nitrogen center, reduces the conversion time by a factor of about 3. In the mixtures, the intact complexes **10a** and **10b** were observed by ³¹P NMR spectroscopy even after longer time periods (> 5 d). The formation of elemental platinum was not observed.

Summarizing the results described above, we have shown that very stable, nonsensitive phosphiranes may be easily prepared in high yields when the three-membered PC₂ ring is incorporated into a polycyclic cage. BABAR-Phos ligands allow the synthesis of low-valent platinum metal complexes to which they tightly bind. Some of these complexes are indeed effective hydrosilylation catalysts and their activity may be tuned by the substituents bound to the nitrogen center.

Experimental Section

Selected physical data of all compounds described in the following are given in Table 2.

General procedure for 4a,b: *n*BuLi (25 mL of a 1.6 M hexane solution; 40 mmol) was added to a solution of the amine **3a** or **3b** (40 mmol) in Et₂O at –30 °C. The reaction mixture was allowed to warm to room temperature, and then added dropwise to a solution of PCl₃ (5 mL, 57 mmol) in Et₂O (20 mL) at –20 °C. All solvents were removed in vacuum, the residue was suspended in toluene (50 mL), and then filtered over celite. Subsequently the solvent was removed in vacuum to give nearly pure compounds which were recrystallized from Et₂O (**4a**) or toluene (**4b**) (yields > 90 %).

5a,b: A solution of **4a** or **4b** (29 mmol) in THF (100 mL) was stirred in the presence of Mg turnings (1 g, 41 mmol) at room temperature. After 5 h, dry dioxane (5 mL) was added to precipitate MgCl₂. The solvents were evaporated, the residue was dissolved in toluene (100 mL), and filtered over celite. The toluene phase was concentrated to 10 % of its volume and hexane was added to precipitate spectroscopically pure **5a** or **5b** as slightly yellow powders (95 % yield; **5a**: 7.7 g, **5b**: 12.4 g), which were recrystallized from Et₂O/hexane.

6: Complex **6** was obtained quantitatively by mixing [Cu(CH₃CN)₄]BF₄ (100 mg, 0.3 mmol) and **5a** (168 mg, 1.2 mmol) in CH₃CN (15 mL). Crystals suitable for an X-ray structure analysis were obtained at –20 °C.

7: Complex **7** was prepared from [Pt(PPh₃)₄] (0.2 g, 0.4 mmol) and **5a** (0.225 g 0.8 mmol) in toluene (10 mL). After the solvent had been dried in vacuum, the remaining yellow powder was washed with hexane (3 × 5 mL) to remove free PPh₃. Drying in vacuum gave pure **6** as a yellow powder in 92 % yield.

10a: Complex **10a** was obtained in 70 % yield (97 mg) from [Pt₂(dvtms)₃]^[12] (100 mg, 0.11 mmol) and **5a** (60 mg, 0.21 mmol) in toluene (2 mL). Crystals were grown from concentrated hexane solutions.

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Study of the Interactions between Poly(vinyl pyrrolidone) and Sodium Dodecyl Sulfate by Fluorescence Correlation Spectroscopy

Ralf Nörenberg,* Jürgen Klingler, and Dieter Horn

Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

Interactions between polymers and surfactants in aqueous solutions are attracting much attention at present as many formulations and industrial processes make simultaneous use of polymers and surfactants for their complementary or even synergistic roles.^[1] In many of these applications the optimization of the properties of the polymer in the presence of interference from other chemicals demands a method that is capable of monitoring the association behavior in complex media, in a wide concentration regime, and with less effort than the presently available methods permit. There have been a lot of experimental techniques explored in the past to study the complex formation.^[2–6] All of them, however, have their specific limitations. The first method used to study the complex formation was NMR-self-diffusion by monitoring the hydrodynamic size of surfactant molecules.^[7] However, this method is limited in the concentration range accessible and also takes a lot of effort.

With the ongoing development of optical correlation techniques, measurements of the self-diffusion coefficient of fluorescing molecules by fluorescence correlation spectroscopy (FCS)^[8] became a practical laboratory technique in the last few years.^[9] Since fluorescence is a very sensitive technique measurements of the self-diffusion coefficient can be extended to very low concentrations.^[10] We present herein the first study of the complex formation of sodium dodecyl sulfate (SDS) with poly(vinyl pyrrolidone) (PVP) by FCS to demonstrate its applicability for associating colloidal systems. The complexes of SDS with PVP belong to the best studied model systems in the literature and often serve as a reference system.

Fluorescence correlation spectroscopy uses fluctuations in the numbers of fluorescent molecules (or particles) in a very small observation volume to obtain information on the diffusive properties of these molecules.^[11] The resulting autocorrelation functions $G(t)$ were fitted to the theoretical Equation (1).^[10]

$$G(t) = 1 + \frac{1}{N} \left(\frac{1}{1 + \frac{4Dt}{r^2}} \right) \quad (1)$$

In this equation N is the average number of fluorescent molecules, D the thermal diffusion coefficient of the molecules and r the radial width of the laser focus. The value of r was obtained by calibrating the instrument with the dye Rhodamin 6G, by assuming a diffusion coefficient of this dye of $2.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The diffusion coefficients in this study

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