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A 14-VE Platinum(0) Phosphabarrelene Complex in the Hydrosilylation of Alkynes

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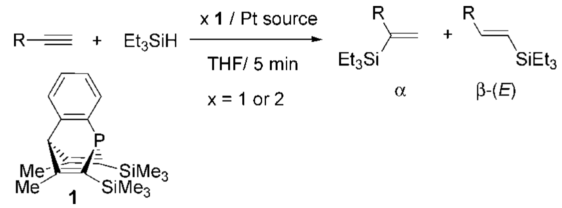
Summary: A bulky phosphabarrelene ligand is used in the platinum-catalyzed hydrosilylation of alkynes. High regioselectivities were achieved under mild conditions from an in situ formed catalyst at low catalyst loadings. Furthermore, a rare 14-VE PtL_2 complex was isolated, which equally proved to be a highly reactive catalyst precursor.

Sterically crowded tertiary phosphines have found important applications in the kinetic stabilization of unsaturated low-valent transition-metal complexes.[1−3] Some of these complexes proved to be among the most active catalysts in organic transformations of synthetic relevance such as the Pd-catalyzed cross-coupling reactions.[2,4] In some instances, the unsaturation of the metal coordination sphere could be used for the stabilization of reactive species.[5] Controlling the steric environment of tertiary phosphines thus allows us to finely tune the degree of coordinative unsaturation of a metal center and in turn its reactive behavior, yet this remains an important challenge. In most cases, bulky phosphines are available through multistep synthesis from halogenated derivatives or through metal-catalyzed phosphination or phosphinylation processes.[6,7] In this perspective, low-coordinated phosphorus species featuring either $C\equiv P$ or $C=P$ bonds, which exhibit reactivity close to that of their carbon counterparts, were shown to behave as efficient precursors of cyclic phosphines and phosphorus-containing cage compounds.[8] Among these, 1-phosphabarrelenes, which are easily prepared through [4 + 2] classical Diels−Alder reactions between phosphinines and alkynes, have recently appeared as a very promising new class of ligands in catalysis for several reasons.[9] First, these bicyclic phosphines are well-suited for the stabilization of low-valent transition-metal complexes, as they combine rigidity and a modular steric crowding. Second, they possess electronic properties significantly different from those of bulky trialkylphosphines, as they are in fact good π-acceptor ligands.[10] Herein we wish to report on the successful use of one of these phosphabarrelene ligands in the platinum(0)-catalyzed hydrosilylation of alkynes.[11] We also show that the ligand allows the stabilization of a rare 14-electron Pt(0) species.

Scheme 1. Pt-Catalyzed Hydrosilylation of Alkynes using Ligand 1



All our experiments were carried out with ligand **1**, which is easily obtained through the [4 + 2] cycloaddition of in situ generated benzyne with the 2,6-bis(trimethylsilyl)-3,5-dimeth-

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Table 1. Substrate and Silane Screening[a]

entry	Pt source	L/Pt	S/Pt	substrate	silane	t (min)	conversn (%)	$\beta(E)/\alpha$[b]
1	[(COD)PtCl$_2$]	0	100	PhCCH	Et$_3$SiH	60	100	80/20
2	[(COD)PtCl$_2$]	2	1000	PhCCH	Et$_3$SiH	5	100	99/1
3	[(COD)PtCl$_2$]	2	10000	PhCCH	Et$_3$SiH	1440	100	92/8
4	[Pt$_2$(DVDS)$_3$]	1	100	PhCCH	Et$_3$SiH	60	85	97/3
5	[Pt(PCy$_3$)$_2$]	2	100	PhCCH	Et$_3$SiH	5	100	92/8
6	[(COD)PtCl$_2$]	2	1000	PhCCH	PhMe$_2$SiH	5	100	99/1
7	[(COD)PtCl$_2$]	2	1000	PhCCH	Ph$_3$SiH	60	0	n.d.
8	[(COD)PtCl$_2$]	2	1000	1-hexyne	Et$_3$SiH	5	99	99/1
9	[(COD)PtCl$_2$]	2	1000	1-hexyne	PhMe$_2$SiH	5	98	99/1
10	[(COD)PtCl$_2$]	2	1000	HCCHCH$_2$OH	Et$_3$SiH	5	99	99/1
11	[(COD)PtCl$_2$]	2	1000	3-hexyne	Et$_3$SiH	5	99	
12	[(COD)PtCl$_2$]	2	1000	PhCCPh	Et$_3$SiH	5	99	

[a] Conditions: alkyne (1 mmol), silane (1.2 mmol), THF (0.5 mmol). Abbreviations: n.d. = not determined; S = substrate; L = ligand. [b] The ratio of isomers was determined by GC; the $\beta(Z)$ isomer was not detected.

ylphosphinine at room temperature. Preliminary experiments were conducted in the case of the silylation of phenylacetylene with triethylsilane, a transformation which is well documented and often used as a benchmark (Scheme 1). In a standard experiment **1** (0.2 equiv) was reacted first with [Pt(COD)Cl$_2$] (0.1 equiv) in the presence of triethylsilane (120 equiv) in THF at 60 °C for 2 min prior to the addition of phenylacetylene (100 equiv). The resulting mixture was then placed in a water bath at 20 °C and the progress of the reaction monitored by GC analysis. As can be seen in Table 1, entry 2, the presence of ligand **1** results in an important increase of both the reaction rate and the selectivity, compared to those for the [Pt(COD)Cl$_2$]-based catalyst (entry 1), despite a 10 times lower catalyst loading. A complete conversion with a β-(E)/α ratio of 99/1 was obtained after only 5 min (entry 2). Note that, at lower catalyst loadings (0.01%), the catalytic activity decreased while the regioselectivity was slightly altered (entry 3). As the first catalytically active species in this transformation involves a Pt(0) complex, the combination of 1 equiv of **1** with the Kartstedt catalyst [Pt$_2$(DVDS)$_3$] was tested. The 16-electron species formed in situ resulted in a less efficient catalytic system (entry 4). To the best of our knowledge, the combination of **1** and [Pt(COD)Cl$_2$] turns out to be the most efficient phosphine-based catalyst reported to date and shows superior selectivity compared to [Pt(PCy$_3$)$_2$] under our reaction conditions (Table 1, entry 5). To evaluate the scope of our catalyst, further experiments were conducted with other silanes and alkynes (see Table 1). Apart from the case of triphenylsilane, where no reaction was observed (entry 7), conversions were complete within 5 min and good regioselectivities were obtained.

In order to get further insight into the mechanism of this transformation, observation/isolation of intermediates was sought. The reaction was therefore carried out with higher catalyst loading (5% [(COD)PtCl$_2$], 10% **1**), allowing the direct observation of Pt species by NMR spectroscopy. As expected from the first results (cf. Table 1), the reaction of Et$_3$SiH with phenylacetylene is complete within 5 min and a single new platinum complex is observed in the ^{31}P NMR spectrum (δ −15.56 ppm, s wit sat, $J_{\mathrm{P-Pt}} = 3120$ Hz), as shown by the presence of Pt satellites ($I = {}^1/_2$, natural abundance 33%). This complex, **2**, was isolated from the reaction mixture (see the Supporting Information) and fully characterized. In particular, it is characterized by a high-field resonance in the ^{1}H spectrum (δ −15.56 ppm, t with sat, $J_{\mathrm{P-H}} = 15.3$ Hz, $J_{\mathrm{Pt-H}} = 588.4$ Hz), indicating the presence of a hydride ligand, coupled with two equivalent phosphorus ligands. The X-ray crystal structure analysis confirmed the complex to be the *trans*-[Pt(**1**)$_2$HCl] complex (Figure 1).

This complex, which was also synthesized independently from the reaction **1** with [Pt(COD)Cl$_2$] with triethylsilane in THF at 60 °C in good yields (Scheme 2), is a deactivated form of the catalyst. Indeed, according to ^{31}P NMR spectroscopy, in a first attempt, heating a solution of **2** in a NMR tube in the presence of triethylsilane in excess (10 equiv) in THF at 60 °C resulted in the appearance of the new platinum complex **3**, characterized by a signal of weak intensity at δ 5.6 ppm (s with sat, $J_{\mathrm{PPt}} = 4644.0$ Hz). However, under these conditions, complex **3**, which was only formed in a small amount, could not be isolated. Supposing that complex **3** could be the corresponding 14-VE complex which equilibrates with **2** through the oxidative addition of HCl in solution, experiments were conducted under a stream of nitrogen. Under these new conditions, the slow but quantitative formation of **3** was observed. This complex could be prepared in a straightforward manner from the reaction of **1** (2 equiv) with [Pt(COD)Cl$_2$] in the presence of [CoCp$_2$] (2 equiv) as a reducing agent in acetonitrile as solvent (Scheme 2). The structure of **3** was further confirmed by an X-ray crystal structure analysis (Figure 2).

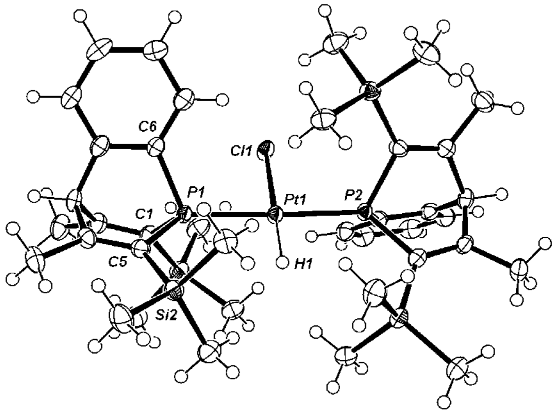

Figure 1. Molecular structure of **2** in the crystal (ORTEP representation, thermal ellipsoids set to the 50% probability level, two THF molecules omitted for clarity). Selected bond distances (Å) and angles (deg): Pt1−P1, 2.293(1); Pt1−P2, 2.293(1); Pt1−Cl1, 2.413(2); Pt1−H1, 1.68(1); P1−Pt1−P2, 177.03(5); P1−Pt1−Cl1, 88.52(3).

Complex **3** is a rare example of a PtL$_2$ complex.[3,12] Interestingly, the Pt−P bonds at 2.243(4) and 2.239(1) Å are close to those of the [(PCy$_3$)$_2$Pt] complex (2.231(4) Å), though the two ligands display different electronic capacities (note: due to the higher π-acceptor properties of the phosphabarrelene compared to a trialkylphosphine, a shorter Pt−P bond length should be expected). Accordingly, the P−Pt−P bite angles are comparable in the two complexes (162.62(4)° in **3** vs 160.0(5)° in [(PCy$_3$)$_2$Pt]) and markedly different from that of the [(P(t-Bu)$_2$-Ph)$_2$Pt] complex, where agostic interactions between the central Pt atom and alkyl C−H groups are found. As expected, **3** is

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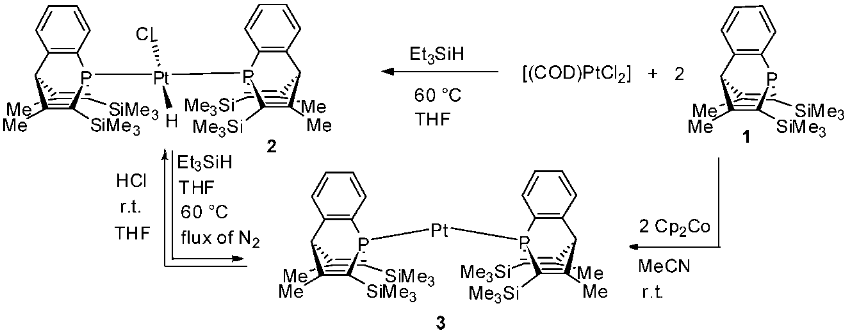
Scheme 2. Syntheses of Complexes 2 and 3



indeed a very good catalytic precursor and the experiments reported in Table 1 were successfully reproduced using 0.1% of catalyst under the same experimental conditions.

In order to get further insight into the initial steps of the catalytic pathway, complex **3** was reacted with Et_3SiH. Surprisingly, no reaction occurred, even at elevated temperature (in a THF solution at reflux). This result contrasts sharply with the well-known reactivity of the $[Pt(PCy_3)_2]$ complex with silanes between −78 and 0 °C.[13] On the other hand, **3** reacted readily at room temperature with phenylacetylene to afford a new complex characterized by a AX spin system pattern in ^{31}P NMR spectroscopy (δ −11.2 ppm, d + sat ($J_{PP} = 35.9$ Hz, $J_{PtP} = 3680$ Hz), −17.7 ppm, d + sat ($J_{PP} = 35.9$ Hz, $J_{PtP} = 3640$ Hz)). This characteristic spin pattern of complex **4** correlates well with the formation of a 16-VE alkyne adduct.[14] Importantly, this complex subsequently reacted with 1 equiv of Et_3SiH at 60 °C to yield complex **3** and the *trans*-triethylstyrylsilane according to ^1H and ^{31}P NMR data. Overall, these results led us to conclude that, unlike for other Pt complexes reported so far, the first step of the catalytic cycle with complex **3** might involve coordination of the alkyne and not the oxidative addition of silane on a low-valent Pt(0) complex.

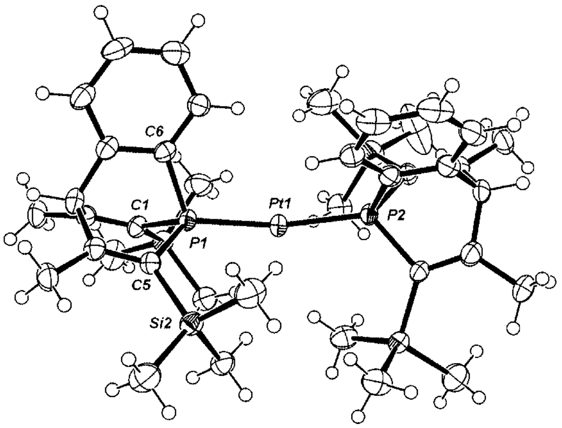
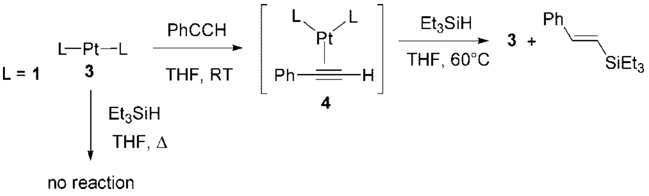


Figure 2. Molecular structure of **3** in the crystal (ORTEP represenatation, thermal ellipsoids set to the 50% probability level). Selected bond distances (Å) and angles (deg): P1−Pt1, 2.239(1); P2−Pt1, 2.243(1); P1−Pt1−P2, 162.62(4).

Scheme 3. Reactivity of 3 toward PhCCH and Et_3SiH



In summary, we have shown here that bulky phosphabarrelene ligands act as very efficient ligands in the Pt(0)-catalyzed hydrosilylation of alkynes under mild conditions. Though some structural analogy exists between complex **3** and $[(PCy_3)_2Pt^0]$, a significant difference in reactivity toward Et_3SiH is observed. The basis of this difference resides in the electronic properties of the ligand (π acceptor). Further studies will now focus on the reactivity and use of this complex and its derivatives in other catalytic processes. The use of these new ligands in the stabilization of other electron-deficient complexes will also be addressed.

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Supporting Information Available: Text, figures, tables, and CIF files giving full experimental details, references for vinylsilanes, the ^{31}P NMR spectrum of **4**, and crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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