

A Diaminocarbene–Phosphonium Ylide: Direct Access to C,C Chelating Ligands**

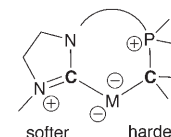
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For a long time, the main neutral spectator ligands used in catalysts with late transition metals (such as Ru, Rh, Ir, Ni, and Pd) were phosphines and amines.^[1] More recently, carbon-centered ligands have appeared as a competing category. Two kinds of such spectator carbon ligands can be distinguished. Unsaturated ligands centered at an sp²-hybridized carbon atom are represented by a wide range of carbenes,^[2] and in particular by N-heterocyclic carbenes (NHCs).^[3] Examples of saturated ligands centered at an sp³-hybridized carbon atom have been limited until now to specific phosphonium ylides.^[4] Although these types of neutral carbon ligands differ in their formal character according to the Green formalism (L = two-electron ligand for NHCs, X = one-electron ligand for ylides), they share two noticeable common features in terms of their bonding mode: 1) They act as σ donors (rather than π acceptors), and 2) they are intrinsically α -zwitterionic ($^-\text{C}=\text{N}^+$, $^-\text{C}-\text{P}^+$), which results in a formal β -zwitterionic form of the coordinated unit ($^-\text{M}-\text{C}=\text{N}^+$, $^-\text{M}-\text{C}-\text{P}^+$). The latter feature should induce electrostatic distortion in the metal coordination sphere and thus play a special role in the control of metal-mediated processes, for example, in catalysis. However, the effective σ donation and charge separation induced by the ligands should be less pronounced with soft, phosphine-like, carbene ligands than with harder ylide ligands. (All phosphonium ylides described to date were indeed reported to act as η^1 carbon-centered ligands rather than as η^2 C=P ligands.)^[4]

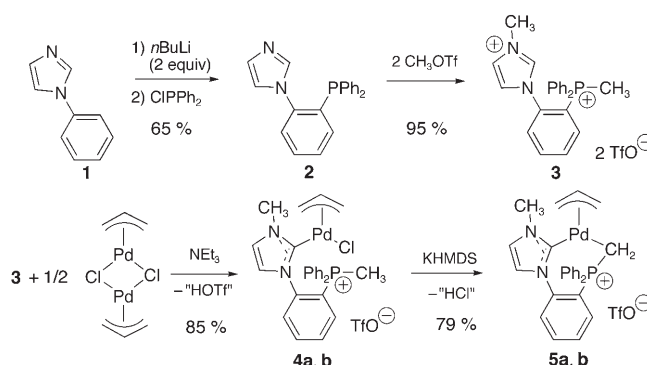
A large number of homo- and heteroleptic bidentate ligands, in particular with a diaminocarbene functionality (NHC–X: X = N, O, P, S), have been devised to increase the efficiency and fine-tune the stereoselectivity of complexation.^[5] Electrostatic distortion and electronic σ donation should also be enhanced with bidentate C,C ligands. Symmetrical soft–soft dicarbon ligands are exemplified by biscarbene ligands,^[6] which have been used as alternatives to diphosphine ligands in catalysis. Symmetrical hard–hard dicarbon ligands can be found in doubly zwitterionic com-

plexes of ω bisylides.^[7] Owing to the promising properties of both types of dicarbon ligand, hybrid soft–hard dicarbon ligands are natural targets for investigation. We describe herein the development of a carbene–ylide ligand of a palladium complex (Scheme 1).

A rigid phenylene bridge occurs in many bidentate ligands, and in particular in ylides of phosphonio(phosphino)benzenes, as the bridge can not undergo undesired deprotonation.^[8] The (imidazolylphenyl)diphenylphosphine **2** was prepared in 65 % yield by the double deprotonation of 1-phenylimidazole (**1**) with *n*BuLi in THF, followed by monophosphinylation of the most nucleophilic lithiated carbon atom (at one *ortho* position of the phenyl substituent; Scheme 2). A single equivalent of the hard methylating



Scheme 1. Generic zwitterionic formula of complexes of soft–hard C,C ligands.



Scheme 2. Straightforward synthesis of the two cationic phosphonio-carbene-palladium complexes **4a,b** (with a monodentate ligand) and **5a,b** (chelated). The letters **a** and **b** refer to stereoisomers of complexes **4** and **5**.

reagent methyl triflate (MeOTf) reacted selectively with **2** in CH₂Cl₂ to give the *N*-methylated monocation, the treatment of which with a second equivalent of MeOTf afforded the iminio–phosphonio dication **3** in 95 % yield. The conjugated diacid **3** of the targeted ligand precipitated from the reaction mixture and was thus obtained simply in pure form. Compound **3** was fully characterized, including by X-ray diffraction analysis of a single crystal (Table 1, Figure 1).^[9]

Despite the similarity of the pK_a values of the imidazolium and methylphosphonium salts (pK_a 22–24 in DMSO), the heteroleptic nature of the targeted ligand prompted us to investigate a sequential complexation route. We found that standard transmetalation through an NHC–Ag intermediate can be avoided.^[3] Instead, the direct and mild treatment of **3**

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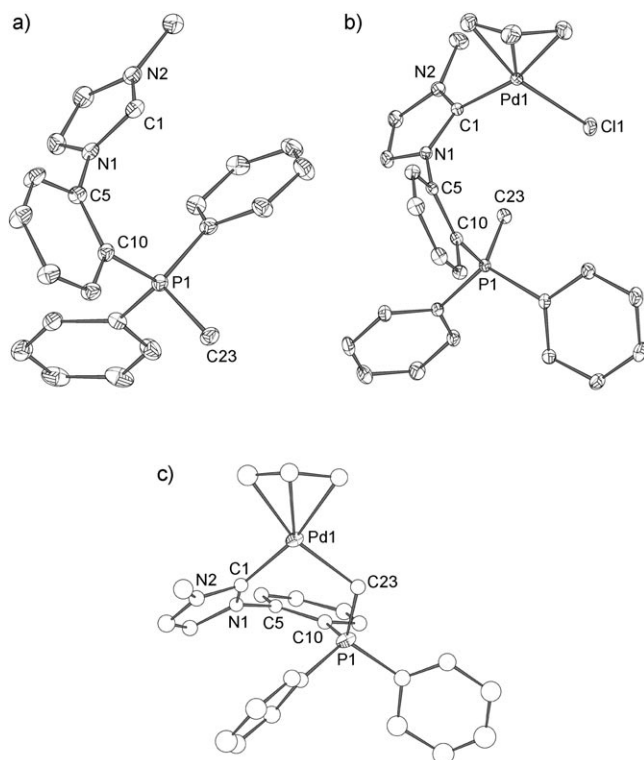
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Supporting information for this article, including synthetic procedures, characterization data for all new compounds, catalytic procedures, and crystal-structure data, is available on the WWW under <http://www.angewandte.org> or from the authors.

Table 1: Comparison of structural data (selected bond lengths [Å] and angles [°]) from X-ray diffraction studies of dication **3** and complexes **4a,b** and **5a,b**.

	3	4a,b	5a,b ^[a]
P ⁺ –CH ₂	1.783(3)	1.788(2)	1.73(1); 1.71(1)
ArN–CN	1.330(4)	1.358(2)	1.38(2); 1.37(2)
CH ₃ N–CN	1.321(4)	1.345(3)	1.36(2); 1.36(2)
Pd–CN ₂	–	2.037(2)	2.01(1); 2.02(2)
A...CH ₂ P ⁺	–	A=Cl: 3.539(2)	A=Pd: 2.10(1); 2.15(1)
P ⁺ C–C–N–CN dihedral angle	89.8	103.3	45.7; 55.6
N ₂ C–Pd...CH ₂	–	45.6	99.9; 97.9
(Ph ₂ P ⁺ CH ₂)...imidazole interaction	π–π stacking (x=3)	weak CH...p/π interaction? (x=3)	π–π stacking (x=2)
P ⁺ C ^α ...NAr	C ^α =C _{ipso} : 3.153(4)	C ^α =CH ₃ : 3.056(3)	C ^α =C _{ipso} : 3.12(2); 3.08(2)
P ⁺ C ^α ...CN ₂	C ^α =C _{ipso} : 3.145(4)	C ^α =CH ₃ : 3.290(3)	C ^α =C _{ipso} : 3.00(2); 3.10(2)

[a] The left-hand value corresponds to one of the molecules in the asymmetric unit, and the right-hand value to the other molecule in the same asymmetric unit (see CCDC files).^[9]

**Figure 1.** ORTEP views of the X-ray crystal structures of compounds a) **3**, b) **4a,b**, and c) **5a,b** with thermal ellipsoids drawn at the 30% probability level (for representative bond lengths and angles, see Table 1).

with half an equivalent of allylchloropalladium dimer $[(\text{PdCl}(\pi\text{-allyl}))_2]$ and triethylamine in acetonitrile afforded cleanly a phosphonocarbene mononuclear complex as a 1:1 mixture of the stereoisomers **4a** and **4b** in 85% yield. The chemical shift observed for the phosphorus atom in **4a,b** in the ^{31}P NMR spectrum ($\delta_{\text{P}} = 21.70\text{--}21.73$ ppm) is indeed very similar to that for **3** ($\delta_{\text{P}} = 20.50$ ppm), whereas in the ^{13}C NMR spectrum the

chemical shift of the carbon atom directly bonded to both nitrogen atoms in the imidazolyl moiety shifted from $\delta_{\text{C}} = 137.1$ ppm in **3** to $\delta_{\text{C}} = 181.8\text{--}182.0$ ppm in **4a,b**. The existence of two stereoisomers of **4** is possibly a result of restricted rotation about the Pd–CN₂ or N–aryl bond. On the basis of data in the literature,^[10] the observed stereochemical disorder can be attributed reasonably to the flip of the π -allyl ligand with respect to the disymmetric diaminocarbene ligand, whereby the MePh_2P^+ group lies *anti* to the π -allyl ligand. This hypothesis and the overall structure of the complex were confirmed by X-ray diffraction analysis of colorless single crystals of **4a,b** deposited from ethanol (Table 1,

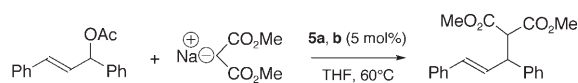
Figure 1). The air-stable complex **4a,b** is stable on silica gel and, more interestingly, soluble and stable in water.

The preliminary complexation of the carbene enabled the preparation of a new type of phosphonocarbene complex and was also expected to facilitate the chelation of the palladium center by the ylide of the appended phosphonium ion. Although examples of the C–H activation or deprotonation of *N*-alkyl substituents of NHC ligands have been reported,^[11] the treatment of **4a,b** with potassium bis(trimethylsilyl)amide (KHMDs) in THF afforded cleanly a dehydrochlorinated complex (electrospray MS: m/z 503) as a 7:3 mixture of stereoisomers in 79% yield. As the signal in the ^{31}P NMR spectrum was shifted significantly to $\delta_{\text{P}} = 34.2\text{--}34.1$ ppm (from $\delta_{\text{P}} = 21.70\text{--}21.73$ ppm for **4a,b**), the complex was believed to be the expected carbene–ylide complex in the form of a mixture of the stereoisomers **5a** and **5b**. The presence of a Pd–CH₂ methylene group was confirmed by multinuclear NMR spectroscopy, in particular on the basis of the high-field ^{13}C NMR signals $\delta_{\text{C}} = -11.2$ and -10.9 ppm. The geometrically constrained chelate configuration was deduced from the coupling constants observed in the ^{13}C NMR spectrum for the coupling of the carbene carbon center ($\delta_{\text{C}} = 180.7$ and 181.2 ppm) with the positively charged phosphorus center through the shortest pathway between the two nuclei (C–Pd–CH₂–P⁺; $^3J_{\text{PC}} = 7.8$ and 8.6 Hz).

The structure of complex **5a,b** was confirmed by X-ray diffraction analysis of colorless single crystals deposited from a $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ mixture (Table 1, Figure 1). As commonly observed,^[10] the π -allyl ligand was found to be disordered over two orientations with respect to the frozen $\text{N}_2\text{C–Pd–CH}_2\text{P}^+$ chelated core. The seven-membered palladacycle is boat-shaped, the prow occupied by the phosphorus center and the stern by the C–NAr bond. Although this conformation is dictated mainly by steric constraints, an auxiliary driving force is a π stacking of the imidazolyl ring with a phenyl ring of the $^+\text{PPh}_2$ unit (Table 1). A similar π -stacking interaction was also observed in the free dication **3**. In the nonchelated phosphonocarbene complex **4a,b**, this interaction is replaced by short

contacts between the methyl group on the phosphorus atom and the C=NAr bond, and between the same methyl group and the chloride ligand. The formation of these contacts is probably directed by weak CH $\cdots$ X interactions (X = N, C, Cl). In complex **5a,b**, the P $^+$ –CH $_2$ bond (ca. 1.73 Å) is markedly shorter than that in **4a,b** (ca. 1.79 Å); however, the P $^+$ CH $_2$ –Pd bond length (ca. 2.10 Å) is comparable to classical P $^+$ CH(R)–Pd distances.^[8b] The chelating substitution of the chloride ligand in **4a,b** by the ylide ligand in **5a,b** results in a slight shortening of the N $_2$ C–Pd bond (ca. 2.04 Å in **4a,b** versus 2.01 Å in **5a,b**) and a slight lengthening of the ArN–C bond (ca. 1.36 Å in **4a,b** versus 1.38 Å in **5a,b**). These data suggest that the strong σ donation of the hard ylide is absorbed by the residual π acceptance of the softer diamino-carbene ligand.

The catalytic properties of the air-stable complex **5a,b** were tested in the Tsuji–Trost allylation of the dimethyl malonate anion by 3-acetoxy-1,3-diphenylpropene. The reaction in the presence of **5a,b** (5 mol %) in THF as the solvent was complete within 12 h at 60 °C to give the desired product with 100% conversion and 100% selectivity according to 1 H NMR spectroscopic analysis of the crude material (Scheme 3).



Scheme 3. 1,3-Diphenylallylation of dimethyl malonate under the catalysis of complex **5a,b**.

In summary, we have developed an efficient short sequential synthesis of two novel π -allyl–palladium complexes, monodentate **4a,b** and bidentate **5a,b**, from the readily accessible dication **3**. The diaminocarbene–phosphonium-ylide complex **5a,b** contains a novel type of strongly σ -donating C,C chelating ligand. This PdC $_5$ -type complex is “homoleptic” in the first coordination sphere: The palladium atom is bonded to five carbon atoms of three different types: allylic (sp 2 /sp 3), carbenic (sp 2), and phosphonioalkyl (sp 3). Preliminary experiments illustrated the catalytic properties of complex **5a,b**. The solubility and stability in water of **4a,b** and **5a,b**, which are readily accessible on a multigram scale, suggest the possibility of catalytic applications in aqueous media. Finally, the ligands might be made intrinsically atropoisomeric with respect to the central C(Ar)–N bond,^[12] and applications in asymmetric catalysis can be envisaged. Efforts toward the development of such chiral ligands are in progress.

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