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Carbon Ligands

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

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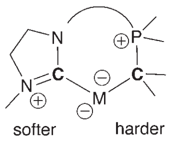
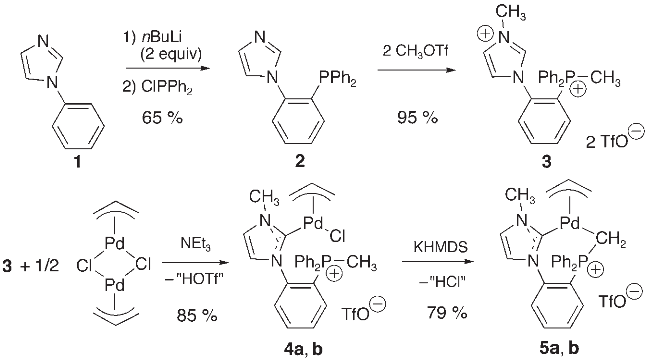
For a long time, the main neutral spectator ligands used in catalysts with late transition metals (such as Ru, Rh, Ir, Ni, and Pd) were phosphines and amines.[1] More recently, carbon-centered ligands have appeared as a competing category. Two kinds of such spectator carbon ligands can be distinguished. Unsaturated ligands centered at an sp^2-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 sp^3-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 ($^{-}\mathrm{C{=}N}^{+}$, $^{-}\mathrm{C{-}P}^{+}$), which results in a formal β-zwitterionic form of the coordinated unit ($^{-}\mathrm{M{-}C{=}N}^{+}$, $^{-}\mathrm{M{-}C{-}P}^{+}$). 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 complexes 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).



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

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 reagent methyl triflate (MeOTf) reacted selectively with **2** in CH_2Cl_2 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]



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**.

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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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)
$CH_3N{-}CN$	1.321(4)	1.345(3)	1.36(2); 1.36(2)
$Pd{-}CN_2$	–	2.037(2)	2.01(1); 2.02(2)
$A\cdots CH_2P^+$	–	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_2C-Pd$\cdots CH_2$	–	45.6	99.9; 97.9
$(Ph_2P^+CH_x)\cdots$imidazole interaction	π–π stacking ($x=3$)	weak CH···p/π interaction? ($x=3$)	π–π stacking ($x=2$)
$P^+C^\alpha\cdots NAr$	$C^\alpha = C_{ipso}$: 3.153(4)	$C^\alpha = CH_3$: 3.056(3)	$C^\alpha = C_{ipso}$: 3.12(2); 3.08(2)
$P^+C^\alpha\cdots CN_2$	$C^\alpha = C_{ipso}$: 3.145(4)	$C^\alpha = CH_3$: 3.290(3)	$C^\alpha = C_{ipso}$: 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]

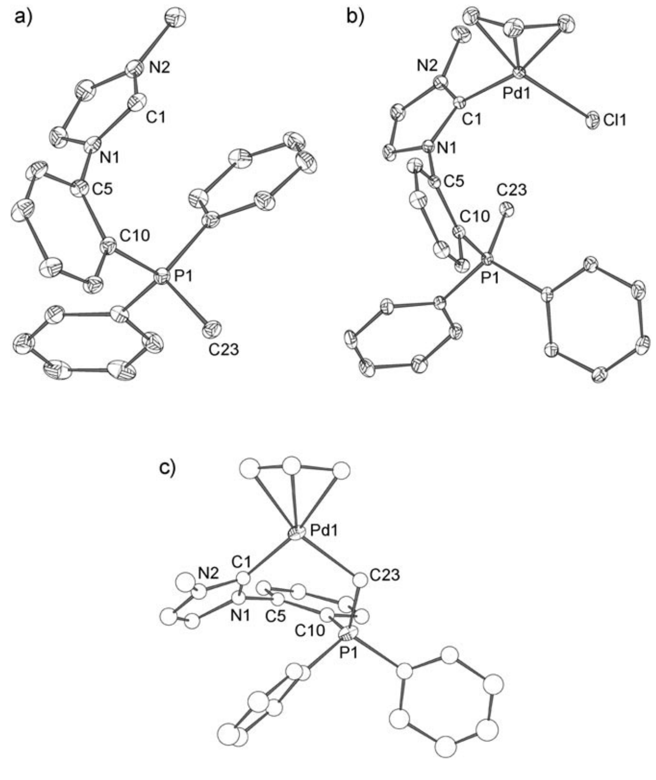


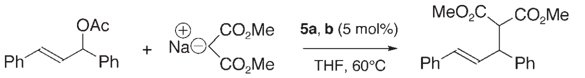
Figure 1. ORTEP views of the X-ray crystal structures of compounds a) **3**, b) **4a**,**b**, and c) **5a**,**b** with thermal ellipsoids drawn at the 30% probability level (for representative bond lengths and angles, see Table 1).

with half an equivalent of allylchloropalladium dimer [{PdCl(π-allyl)}$_2$] and triethylamine in acetonitrile afforded cleanly a phosphoniocarbene 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 ($\delta_P = 21.70$–21.73 ppm) is indeed very similar to that for **3** ($\delta_P = 20.50$ 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 $\delta_C = 137.1$ ppm in **3** to $\delta_C = 181.8$–182.0 ppm in **4a**,**b**. The existence of two stereoisomers of **4** is possibly a result of restricted rotation about the $Pd{-}CN_2$ 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 phosphoniocarbene 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 $\delta_P = 34.2$–34.1 ppm (from $\delta_P = 21.70$–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 $Pd{-}CH_2$ methylene group was confirmed by multinuclear NMR spectroscopy, in particular on the basis of the high-field ^{13}C NMR signals $\delta_C = -11.2$ 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 ($\delta_C = 180.7$ and 181.2 ppm) with the positively charged phophorus center through the shortest pathway between the two nuclei (C–Pd–CH_2–P^+; $^3J_{P,C} = 7.8$ and 8.6 Hz).

The structure of complex **5a**,**b** was confirmed by X-ray diffraction analysis of colorless single crystals deposited from a CH_3CN/Et_2O 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 N_2C–Pd–CH_2P^+ 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 $^+PPh_2$ unit (Table 1). A similar π-stacking interaction was also observed in the free dication **3**. In the nonchelated phosphoniocarbene 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···X interactions (X = N, C, Cl). In complex **5a**,**b**, the $\mathrm{P^+{-}CH_2}$ bond (ca. 1.73 Å) is markedly shorter than that in **4a**,**b** (ca. 1.79 Å); however, the $\mathrm{P^+CH_2{-}Pd}$ bond length (ca. 2.10 Å) is comparable to classical $\mathrm{P^+CH(R){-}Pd}$ 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 $\mathrm{N_2C{-}Pd}$ 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 diaminocarbene 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 $\mathrm{PdC_5}$-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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