Synthesis and Catalytic Application of Palladium Pyrazolin-3-ylidene Complexes†

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Summary: Oxidative addition of a 3-halo 1,2-disubstituted pyrazolium salt to a palladium(0) complex leads to the formation of the first reported palladium pyrazolin-3-ylidene complex. Comparison of the new system with the analogous imidazolin-2-ylidene complex in Heck catalysis shows higher yields for the new system by a factor of 2.

The Mizoroki−Heck reaction has proven to be a versatile tool in organic synthesis that involves the coupling of haloarenes and olefins.[1] Recent developments have led to catalysts of mixed N-heterocyclic carbene (NHC)/phosphine complexes of palladium(II).[2] These catalysts are more easily reduced during catalysis than bis-NHC complexes, while the Pd(0) complexes generated undergo oxidative addition with aryl halides less easily. NHC ligands are strong coordinating ligands which undergo little to no dissociation from the metal center in solution.[3] The increased electron density compared to phosphines on the palladium center provides an easier activation of the halogen−aryl bonding. Most NHC palladium Mizoroki−Heck catalysts are based on imidazolin-2-ylidenes or 1,2,4-triazolin-3-ylidenes.[4] Therefore, it seems appropriate to develop alternative NHC ligands which promise to be stronger σ-donors than the conventional imidazoline or triazoline ligands. For this purpose a suitable carbene is pyrazolin-3-ylidene. In a theoretical work it has been shown that these carbenes are stronger σ-donors than imidazolin-2-ylidenes.[5] So far the free pyrazolin-3-ylidene has not yet been reported. The difficulty in obtaining the free carbene might derive solely from inductive effects, because the carbene center in pyrazolin-3-ylidenes is attached to just one electron-withdrawing N atom, in contrast to imidazole or triazole systems with electron-withdrawing N atoms on each side of the carbene carbon. The difficulty in obtaining the free pyrazolin-3-ylidene is consistent with the lower C−H acidity of pyrazolium salts compared to imidazolium salts.[6] So far research has concentrated typically on imidazolin-2-ylidenes or imidazolidin-2-ylidenes, and surprisingly the pyrazolin-3-ylidenes have not attracted much interest.

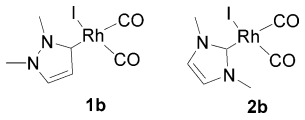

Figure 1. Iododicarbonyl(azolinylidene)rhodium(I) complexes **1b** and **2b** for comparison of their CO stretching frequencies.

The only known pyrazolin-3-ylidene complexes up to now have been reported by Öfele et al.[7] and much later by Herrmann and co-workers.[8] The syntheses of carbene−carbonyl metal complexes by Öfele are only applicable to carbonyl compounds and are not suitable to obtain catalytic Heck-active pyrazolin-3-ylidene complexes. Although the method described by Herrmann which requires an alkoxide as a base to deprotonate the pyrazolium salt is widely applicable for many imidazolium salts, the conditions used to generate the carbene seem only to be successful for complex **1a**. All attempts to apply this method to different metal centers or different pyrazolium salts were unsuccessful.

Iodo(η^4-1,5-COD)(1,2-dimethylpyrazoline-5-ylidene)-rhodium(I) (**1a**) has been synthesized in order to obtain the corresponding dicarbonyl complex **1b** (Figure 1). The CO stretching frequencies are sensitive to the electron density at the metal. Hence, comparison of the CO stretching frequencies of complex **1b** with those from the analogous imidazolin-2-ylidene complex **2b** allow us to evaluate the donor strength of the pyrazolin-3-ylidene in contrast to the corresponding imidazolin-2-ylidene. This method was recently performed by Herrmann et al. and Bertrand et al. for a variety of carbenes.[9]

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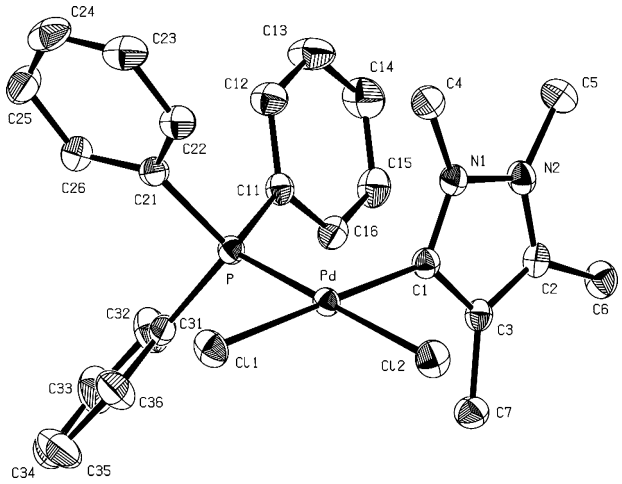
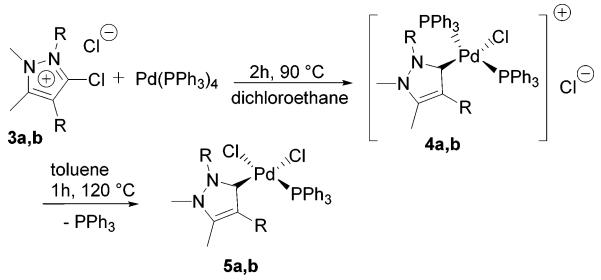


Figure 2. Molecular structure of **5b**.

Scheme 1. Synthesis of 5a (R = Ph) and 5b (R = Me)



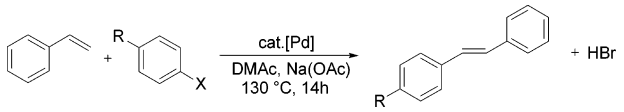
The observed frequencies for complex **1b** are 2066 and 1993 cm^{-1}, in contrast to 2073 and 1999 cm^{-1} for complex **2b**. Thus, pyrazolin-3-ylidenes induce a significant higher electron density at the rhodium center than the corresponding imidazolin-2-ylidenes.

It has been shown that oxidative addition of a low-valent metal precursor to a carbon−halogen bond is possible.[10] Due to the difficulty in obtaining the free pyrazolin-3-ylidene, the oxidative addition of a low-valent metal to a 3-halo 1,2-disubstituted pyrazolium salt opens the way to various pyrazolin-3-ylidene complexes.

Treatment of $Pd(PPh_3)_4$ with an equimolar amount of the pyrazolium salt **3a**,**b** in refluxing dichloroethane leads to the first palladium pyrazolin-3-ylidene complex **4a**,**b** in 70% yield with traces of the complex **5a**,**b**. To form the neutral palladium dichloride complex **5a**,**b**, a suspension of complex **4a**,**b** in toluene is heated for an additional 1 h (Scheme 1). The formation of **5a**,**b** can be monitored by ^{31}P NMR spectroscopy. In the case of **4b** and **5b**, respectively, the signal at δ(P) 22.7 ppm decreases while the signal at δ(P) 28.8 ppm slowly increases and 1 equiv of PPh_3 is simultaneously released.

Subsequent workup of the filtered suspension afforded the complexes **5a**,**b** in yields between 55 and 60%. Colorless crystals of **5b** suitable for X-ray diffraction studies were obtained from an ethanol/diethyl ether solution at ambient temperature (Figure 2).[11]

Table 1. Mizoroki−Heck Reaction: Coupling of Different Aryl Halides and Styrene Using Complexes 5a,b and 6 as Catalysts[a]



entry	R	X	Pd (mol %)	catalyst	yield (%)[b]
1	$C(O)CH_3$	Br	1.0	**5a**	98
2	$C(O)CH_3$	Br	1.0	**5b**	98
3	$C(O)CH_3$	Cl	1.0	**5b**	9
4	H	Br	1.0	**5a**	94
5	H	Br	1.0	**5b**	86
6	H	Br	0.1	**5b**	79
7	H	Br	1.0	**6**	40
8	H	Cl	1.0	**5b**	6
9	OCH_3	Br	1.0	**5a**	69
10	OCH_3	Br	1.0	**5b**	59
11	OCH_3	Br	0.1	**5b**	53
12	OCH_3	Br	1.0	**6**	26
13	OCH_3	Cl	1.0	**5b**	0

[a] Conditions: 1 equiv of aryl bromide, 1.5 equiv of styrene, 1.5 equiv of Na(OAc), dimethylacetamide (DMAc), T = 130 °C, t = 14 h. [b] GC yields using diethylene glycol di-*n*-butyl ether as the internal standard.

The catalytic activity of **5a**,**b** was investigated in detail for the Pd-catalyzed Mizoroki−Heck olefination of aryl halides with olefins and compared to the analogous known complex diiodo(1,3-dimethylimidazolin-2-ylidene)(triphenylphosphine)palladium(II) (**6**).[2,12] Experiments with bromoarenes and styrene show that these novel Pd−pyrazolin-3-ylidene complexes are active catalysts (Table 1). For example, 4-bromoacetophenone is coupled with styrene to *trans*-stilbene in the presence of 1 mol % of **5a**,**b** and 1.5 equiv of NaOAc in 98% yield at 130 °C in 14 h in both cases. Deactivated haloarenes such as bromoanisole show the expected lower yields, but there is an increased activity observed for the bulkier NHC **5a**, as is described in the literature for bulky imidazolin-2-ylidene ligands in Pd complexes.[4] The change of the catalyst concentration from 1 to 0.1 mol % using bromoarenes seems not to affect the yields

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(11) Crystal structure analysis of compound **5b**: $C_{25}H_{27}Cl_2N_2PPd$, M_r = 563.78, colorless fragment (0.13 × 0.28 × 0.30 mm^3), orthorhombic, *Pbca* (No. 61), a = 10.6000(1) Å, b = 16.0669(1) Å, c = 27.8350(2) Å, V = 4740.56(6) $Å^3$, Z = 8, d_{calcd} = 1.580 g cm^{-3}, F_{000} = 2288, μ = 1.092 mm^{-1}. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems cooling system at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data collection was performed at 173 K within the θ range of 1.46° < θ < 25.33°. A total of 110 029 reflections were integrated. Raw data were corrected for Lorentz, and polarization and, arising from the scaling procedure, for latent decay and absorption effects. After merging (R_{int} = 0.041), 4336 (3965 with $I_o > 2\sigma(I_o)$) independent reflections remained, and all were used to refine 388 parameters. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with R1 = 0.0225 ($I_o > 2\sigma(I_o)$), wR2 = 0.0535 (all data), GOF = 1.094, and a shift/error of <0.001. The final difference Fourier map shows no striking features ($\Delta e_{min/max}$ = +0.34/−0.37 e $Å^{-3}$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-255379 (**5b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk.

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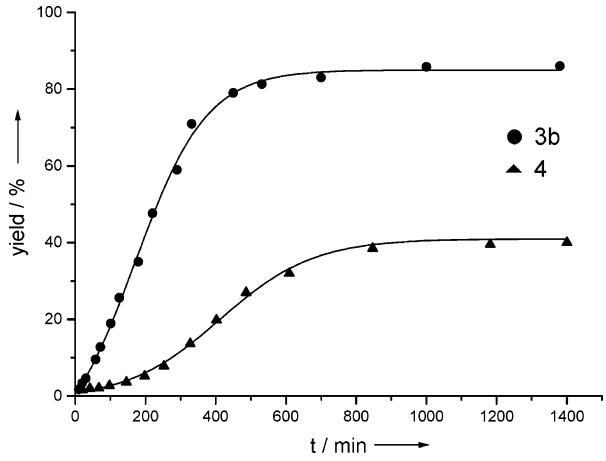

Figure 3. Time−yield comparison of **5b** and **6** in the Mizoroki−Heck reaction of bromobenzene and styrene.

significantly. However, chloroarenes do not appear to be active enough for these catalysts. Most interesting is the comparison to the analogous imidazolin-2-ylidene complex **6**. The different halogens on the palladium may also influence the activity of the complex.

To our knowledge, there has been no such considerable difference in activity observed thus far for the change of the halogens on an NHC palladium Heck catalyst. The increase of the yield by a factor of 2 is therefore mostly ascribable to pyrazolin-3-ylidene as a stronger donor (see entries 10 and 12 in Table 1). This shows clearly the superiority of the strong donating pyrazolin-3-ylidene to the weaker imidazolin-2-ylidene donors.

To evaluate the differences in activity, the coupling of bromobenzene with styrene was followed over time (Figure 3). The imidazole system **6** shows an initial activity being lower than that of complex **5b**. Thus, it appears that the induction period is evidently larger for a conventional imidazole system such as **6** than for the new pyrazole system **5b**.

This report demonstrates the synthetic route to pyrazolin-3-ylidene complexes which may introduce this NHC into homogeneous catalysis. The two complexes are the first palladium pyrazolin-3-ylidene complexes reported in the literature. It is very probable that for any catalysts containing an imidazolin-2-ylidene which promise to be more active with strong donating ligands, substitution of the imidazolin-2-ylidene by pyrazolin-3-ylidene will result in a significant increase in activity of the catalyst. Its superior role as compared to standard imidazolin-2-ylidene complexes in Heck catalysis was demonstrated as being due to its nucleophilic carbene center acting as a strong σ-donor ligand.

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Supporting Information Available: Text giving experimental procedures for the synthesis of pyrazolium salts **4a**,**b** and the new palladium complexes together with the analytical and spectral data of all new compounds and structural data for complex **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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