Facile Synthesis of Highly Substituted Pd–η³-Allyl Complexes Containing Nitrogen Ligands

Richard E. Rülke,[a] Dave Kliphuis,[a] Cornelis J. Elsevier,[a] Jan Fraanje,[b] Kees Goubitz,[b] Piet W. N. M. van Leeuwen[a] and Kees Vrieze*[a]

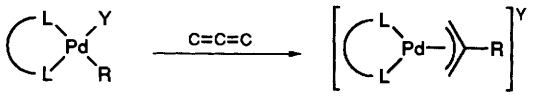
[a] *Anorganisch Chemisch Laboratorium, J. H. van't Hoff Research Institute and*
[b] *Department of Crystallography, Universiteit van Amsterdam, Nieuwe Achtergracht 166, NL 1018 WV Amsterdam, The Netherlands*

The first examples of quantitative migratory insertion of allene, 1,1-dimethylallene (DMA) and tetramethylallene (TMA) into alkyl and acyl palladium complexes containing bidentate and terdentate nitrogen ligands are presented; very stable palladium η³-allyl compounds containing 2,2'-bipyridine and 2-(2-{[(6'-methyl-2-pyridyl)methylene]amino}ethyl)-pyridine and an exceptional η¹-allyl palladium complex containing terpy have been obtained.

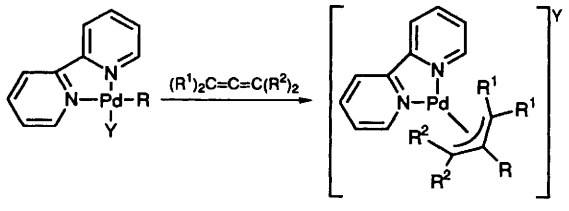
It has recently been reported in the course of our studies into the details of the formation of polyketones homogeneously catalysed by Pd^{II} complexes[1] that alkenes may readily insert into palladium–acyl bonds.[2] This prompted us to turn our attention to other unsaturated substrates such as allenes, mainly because by using substituted allenes, like tetramethylallene, access to pentasubstituted allyl palladium complexes, as outlined in Scheme 1, could be achieved. Such highly substituted compounds are less easy to obtain *via* known routes.[3] Insertion of allenes into chloro- and organo-palladium complexes have been reported in the past by several groups, *e.g.* reversible formation of the 2-chloroallyl palladium compounds,[4] insertions of allene into alkyl, vinyl and phenyl palladium complexes[5,6] and studies by Cazes on the catalytic insertion–allylation reaction.[7] In all these cases phosphine ligands were used.

Considering these studies we were interested in the possibilities of (*i*) insertion of highly substituted allenes into organopalladium compounds, (*ii*) insertion of allenes into alkyl and acyl palladium compounds and (*iii*) insertion of allenes into organopalladium complexes containing nitrogen ligands.

The allene insertion was studied for complexes σ²-(bipy)-Pd(R)(Y),[8] (Scheme 2), [σ³-(mmap)Pd(R)]CF_3SO_3[9] (Scheme 3) and [σ³-(terpy)Pd(R)]Cl·$2H_2O$[10] (Scheme 4), [R = Me, C(O)Me, $CH_2C_6H_5$, $C(O)C_6H_5$, $CH_2C(O)OMe$; Y = Cl, Br, CF_3SO_3, BF_4]† with allene (propadiene), DMA (3-methylbuta-1,2-diene, dimethylallene) and TMA (2,4-dimethylpenta-2,3-diene, tetramethylallene). The insertion of allenes proved very easy and quantitative yields have been obtained by this method at room temperature in dichloromethane, acetonitrile or methanol. The ¹H NMR data of the products of the reaction of allenes with selected palladium compounds are listed in Table 1. The allyl palladium compounds formed were all very stable at room temperature in solution and as a solid, except for the terpy allyl palladium complexes, which decompose within a few hours.



Scheme 1 Presentation in outline of the insertion of an allene into an organopalladium compound

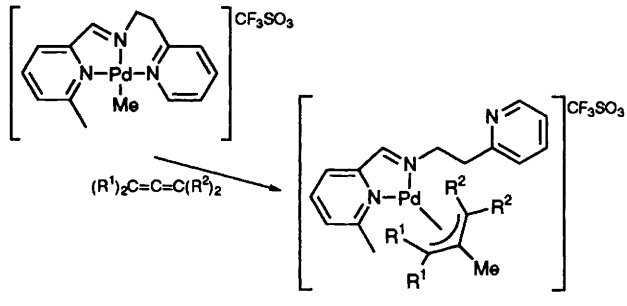


Scheme 2 Allene insertion into bipy complexes. R = Me, C(O)Me, $CH_2C_6H_5$, $C(O)C_6H_5$, $CH_2C(O)OMe$; R^1 = H, Me; R^2 = H, Me; Y = Cl^-, $CF_3SO_3^-$, BF_4^-

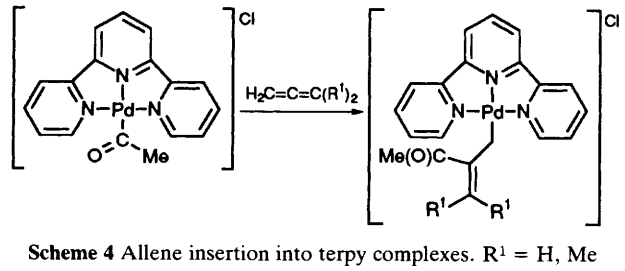
No complexes containing coordinated allene have been observed and in all cases R migrates to the electrophilic central carbon atom of the allene, see Scheme 2. In the case of the bipy palladium complexes, as expected, the allene insertions resulted in ionic η³-allyl products, whereas the strong tendency of terpy to maintain terdentate coordination resulted in η¹-allyl complexes which have rarely been observed for palladium. At room temperature the ¹H NMR spectrum shows broadened signals which sharpen upon cooling to 213 K, clearly showing a η¹-allyl group (see Table 1). Interestingly, the palladium complexes of the more flexible trinitrogen ligand mmap, upon insertion of allene or DMA, change from terdentate coordination in the ionic starting complex to bidentate coordination in the product with a pendant ethylpyridyl arm, as shown in Scheme 3.

Crystals suitable for X-ray diffraction were obtained of η³-(2-acetyl-1,1,3,3-tetramethylallyl)palladium(II)(bipyridyl)-trifluoromethylsulfonate and the molecular structure is presented in Fig. 1.‡ The structure displays the known conformation of η³-allyl complexes, except for the acetyl group which is, unexpectedly perpendicular to the allyl moiety and is pointing towards the palladium atom (Pd–O, 3.18 Å).

As expected, the ease of insertion of the allene proved to be dependent on the number of substituents. This is nicely demonstrated in the case of the complexes [(terpy)Pd-{C(O)Me}]Cl and [(bipy)Pd($CH_2C_6H_5$)]BF_4 for which insertion of allene and DMA was observed within a few minutes, while no insertion of TMA occurred, even after a week.



Scheme 3 Allene insertion into mmap complexes. R^1 = H, Me; R^2 = H, Me



Scheme 4 Allene insertion into terpy complexes. R^1 = H, Me

Table 1 Selected spectral data of the complexes (ligand)Pd(allyl)(Y)

					^{1}H NMR[b]		
L	R	Y	Allene[a]	t[c]	R_{syn}	R_{anti}	R
bipy	Me	BF_4	TMA	mins	1.88	1.86	2.25
bipy	C(O)Me	Cl	DMA	mins	1.74, 4.45	1.49, 4.08	2.51
bipy	C(O)Me	OTf	TMA	mins	1.88[d]	1.70[d]	2.56[d]
bipy	$CH_2C_6H_5$	BF_4	DMA	mins	1.86, 3.97	1.49, 3.93	3.78, 3.93
bipy	$C(O)C_6H_5$	BF_4	DMA	mins	1.69, 4.32	1.63, 4.24	
bipy	CH_2CO_2Me	BF_4	DMA	7 d	1.81, 4.18	1.52, 3.98	3.40, 3.73
mmap	Me	OTf	TMA	hs	1.59	1.40	2.78
					R^α	R^γ	R^β
terpy	C(O)Me	Cl	DMA	mins	2.50[e]	1.56, 1.60[e]	2.41[e]

[a] Only the highest substituted allene that inserts is presented. [b] ^{1}H NMR in CD_3CN at 300.13 MHz and 293 K unless noted otherwise. [c] Approximate time needed for quantitative conversion. [d] In CD_3OD. [e] In CD_3OD at 213 K.

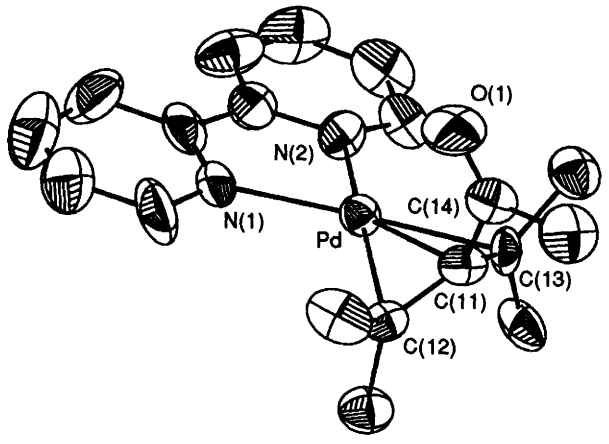


Fig. 1 Molecular structure of η^3-(2-acetyl-1,1,3,3-tetramethylallyl)-palladium(II)bipyridyl trifluoromethylsulfonate. The triflate anion is omitted for clarity. Selected bond lengths: Pd–N(1) 2.13(2), Pd–N(2) 2.10(1), Pd–C(11) 2.08(1), Pd–C(12) 2.15(1), Pd–C(13) 2.18(2). Selected bond angles: N(1)–Pd–N(2) 78.2(6), C(12)–C(11)–C(13) 124(1), Pd–C(11)–C(14) 115.7(9).

The influence of the nucleophilic character of the organic ligand in the starting compound on the reactivity towards migratory insertion of the allene is reflected in the observation that the acetyl group [R = C(O)Me], which is a very strong nucleophile, gives a very rapid allene insertion even with neutral palladium complexes containing good coordinating anionic ligands like Cl^-. However, if less nucleophilic alkyl ligands are used [R is Me, $CH_2C_6H_5$ or $CH_2C(O)OMe$ in decreasing order of basicity] allene insertion for the (neutral) bipy complexes was not observed. Rapid insertion may be induced by the use of poorly coordinating ligands *e.g.* BF_4^- and OTf^-. Only in the case of the weakly basic alkyl ligand R = $CH_2C(O)OMe$ the insertion of allene and DMA remained slow (see Table 1).

In the complexes used, the allene insertion proceeds considerably faster than the insertion of alkenes and is approximately equally fast as has been observed for the formation of acyl palladium complexes from methyl palladium compounds containing nitrogen ligands.[2,10,11]

The complexes obtained by this facile route successfully fulfil the aims we had. It is well possible to perform allene insertion in palladium compounds with both bidentate and terdentate nitrogen ligands. With few exceptions, the insertion of (substituted) allenes proceeds quantitatively. The introduction of many possible alkyl and acyl substituents on the 2-position gives access to the synthesis of a great variety of allyl palladium complexes using readily available starting complexes. A possible disadvantage might be that the insertion of TMA, a representative of the tetrasubstituted allenes, proceeds preferably for compounds which contain a strongly nucleophilic R-group, like acyls. Yet, by choosing appropriate R-groups, several pentasubstituted allyl palladium complexes are accessible by this method, which may be preferred over known routes.

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Footnotes

† The methyl complexes have been synthesized starting from (cod)Pd(CH_3)(Cl)[9] while the acetyl palladium complexes have been prepared by reacting the methyl complexes with CO. All other complexes were obtained *via* the oxidative addition of the halides on $(DBA)_4Pd_2$ in the presence of the nitrogen ligand.

‡ *Crystal data* for η^3-(2-acetyl-1,1,3,3-tetramethylallyl)palladium(II)-bipyridyl trifluoromethylsulfonate, $C_{20}H_{23}F_3N_2SO_4Pd$, triclinic, spacegroup *P*1 with a = 13.962(2), b = 14.546(3), c = 13.496(2) Å, α = 111.92(2), β = 107.26(1), γ = 62.08(2)°, V = 2222(1) Å^3, Z = 4, D_c = 1.65, $F(000)$ = 1112, μ(Cu-Kα) = 82.5 cm^{-1}; (2.5° < θ < 60°, T = 248 K, graphite monochromator, λ = 1.5418 Å) on an Enraf Nonius CAD-4 diffractometer. The structure was solved *via* Direct Methods and ΔF synthesis, refined anisotropically for all non-hydrogens by full-matrix least squares. Empirical absorption correction was applied (DIFABS). 6592 unique reflections ($-15 \leq h \leq 0$, $-16 \leq k \leq 14$, $-14 \leq l \leq 15$), 4725 significant [$I_{obs} > 2.5\sigma(I)$] resulted in R = 0.089, R_w = 0.121 with a weighting scheme $w = (7.6 + F_{obs} + 0.0114 \cdot F_{obs}^2)^{-1}$. The secondary isotropic extinction coefficient[12] refined to Ext = 0.02(1). The triflate moieties have very high temperature factors thus indicating some disorder. Scattering factors were taken from the literature.[13,14] All calculations were performed with XTAL,[15] unless stated otherwise.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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