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Diaryltriazenido Palladium(II) Complexes Derived from 1-(2-Bromo-4ethoxycarbonylphenyl)-3-phenyltriazenes

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Abstract. 1-(2-Bromo-4-ethoxycarbonylphenyl)-3-phenyltriazene (**1**) can easily be deprotonated yielding the corresponding triazenides of lithium, silver, or triethylammonium. The equimolar metathesis reaction of $[(Ph_3P)_2PdCl_2]$ with these triazenides leads to the formation of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)Cl]$ (**3**). The addition of another equivalent yields mixtures of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)Cl]$ (**3**) and $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (**4**). The reaction of 1-(2-bromo-4-ethoxycarbonylphenyl)-3-methyl-3-phenyltriazene (**2**) with one quivalent of $[Pd(PPh_3)_2]$ leads to an oxidative addition of the C-Br-bond and the formation of $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (**5**). The palladium atoms are in square planar environments.

Keywords: Palladium(II), Triazenides, Metathesis reactions, Oxidative addition, X-ray structures

Introduction

1,3-Diaryltriazenides of palladium(II) represent a scarce substance class despite the long tradition. Already in 1971, the reaction of Pd(PPh₃)₄ with 1,3-di(*para*-tolyl)triazene yielded red [(Ph₃P)₂Pd(*p*Tol-N₃-*p*Tol)₂] with monodentate triazenido ligands.¹ First hints toward bridging triazenido ligands were reported for [Cl(Me₂PhP)Pd(Ph-N₃-Ph)]₂ shortly thereafter, prepared via a deprotonation of 1,3-diphenyltriazene with a palladium-bound acetate.² The first crystal structure determination of such a complex revealed the monodentate binding mode of the triazenido ligand in square planar [Cl(Ph₃P)₂Pd(*p*Tol-N₃-*p*Tol)] (Pd-N 203.3(4) pm) with slight delocalization of the negative charge (N1-N2 133.6(8), N2=N3 128.6(7) pm).³ These complexes show dynamic behavior with the Pd atoms binding at N1 and N3 showing coalescence in NMR solution studies.

Based on these initial investigations, efforts to elucidate chemical and physical properties of triazenido-palladium complexes were intensified. Monodentate,⁴ bidentate⁵ and bridging coordination modes⁵⁻⁷ were verified by X-ray crystallographic studies at single crystals as depicted in Scheme 1. Electroneutral triazenes represent suitable Lewis bases for palladium(II) ions.^{8,9} These triazenido-palladium(II) moieties are stable toward moisture (hydrolysis) and air (oxidation). Monodentate triazenide ligands can adopt *syn-E, syn-Z, anti-E* or *anti-Z* configuration as also shown in Scheme 1. In addition, palladium(II) complexes of the type [(Ph₃P)₂Pd(R-N₃-R')X] (X = Cl, Br, R-N₃-R') can show *cis*- or favored *trans*-positioned phosphane bases.¹⁰ Despite the fact that these triazenide ligands show comparable coordination behaviour as isoelectronic formamidinates and also carboxylates, the triazenide chemistry of palladium remained strongly underdeveloped.



Scheme 1: Monodentate (left), bidentate (middle) and bridging (right) binding modes of triazenido ligands in their palladium(II) complexes (top row) and configuration of the triazenide ligands (R, R' = aryl).

Based on this rudimentary knowledge, there are almost no applications known for these palladium(II) triazenide complexes. During palladium-mediated conversion of 1,3-diaryl-3-methyltriazene into benzotriazoles,¹¹⁻¹³ such palladium complexes were discussed as intermediates in the catalytic cycle. These studies attracted our interest and we intended to elucidate the influence of ester and bromo substituents on the synthesis and structures of palladium-based triazenide complexes. In addition, the formation of carboxylic amides from triazenes in the presence of carbon monoxide succeeded via palladium(II) catalysis with yields between 70 and 93 %.^{14,15} Here the proposed mechanism contains intermediately formed triazenes bound to palladium(II) followed by insertion of the Pd(II) fragment into the N-N bond.

In this study, we investigated palladium complexes, derived from 1-(2-bromo-4ethoxycarbonylphenyl)-3-phenyltriazene (1)¹¹ and 1-(2-bromo-4-ethoxycarbonylphenyl)-3-methyl-3phenyltriazene (2)^{12,13} in order to compare the products of oxidative addition of the C-Br bond on Pd with the triazenide complexes.

Results and discussion

For a metathetical approach, 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazene (1) was deprotonated with *n*BuLi or triethylamine and the triazenides of lithium, silver(I) or triethylammonium were reacted with $[(Ph_3P)_2PdCl_2]$ in tetrahydrofuran according to Scheme 2. Silver triazenide was prepared according to literature protocols from AgNO₃, triethylamine and triazene.^{7,16} Potassium triazenides also represent suitable triazenide transfer reagents.



Scheme 2: Synthesis of the 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazenide complexes of palladium(II) via metathetical approaches ($R' = C_6H_3$ -2-Br-4-COOEt).

Depending on the stoichiometric ratio, either the monotriazenide palladium(II) complex **3** or a mixture of **3** and **4** were obtained. A quantitative conversion to the bis(triazenido) palladium(II) congener **4** did not succeed via this route. The results of the metathesis reaction in dependency of E and the stoichiometric ratio of **1** to $[(Ph_3P)_2PdCl_2]$ are summarized in Table **1**. The route via the reaction of silver triazenide with equimolar amounts of $[(Ph_3P)_2PdCl_2]$ gave the best yield (73 % of isolated complex **3**) and therefore is the preferred procedure. With the metathetical approach via lithium triazenide, yields of only 52 % were achieved. The metathetical approach via the triethylammonium intermediate is highly disadvantageous because unknown side products were detected in the NMR spectra and isolation of the pure complex was very challenging leading to a low yield of only 18 %. Mixtures of complexes **3** and **4** (obtained by metathetical approaches of $[(Ph_3P)_2PdCl_2]$ with two equivalents of triazenide) could not be separated quantitatively due to very similar solubility properties in common organic solvents like diethyl ether, alkanes, and aromatic hydrocarbons.

Table 1: Product composition in % for the metathetical approach according to Scheme 2.

E	Amount of 1	Product 3	Product 4	Yield (%)
Li	1 equiv.	100	-	52
Li	2 equiv.	52	48	-
Ag	1 equiv.	100	-	73
Ag	2 equiv.	78	22	-
Et₃NH	1 equiv.	100	-	18

For the reaction of triazenes with palladium(0) species diverse reactivity patterns are known. Oxidative addition of the N-H bond leads to the formation of hydridopalladium(II) triazenides which can dismutate to palladium(II) bis(triazenides).¹ The palladium-mediated oxidative addition of the N-N bond of a triazene is discussed as an intermediate step in the cabonylative synthesis of carboxylic acid amides from triazenes.¹⁴ Activation of aromatic C-H groups can also be achieved with palladium compounds.^{4,17-19} The oxidative addition of the C-Br bond yields arylpalladium(II) bromides and represents a well-known step in cross-coupling reactions. In all these examples, Lewis bases like e.g. phosphanes saturate the coordination spheres of the palladium atoms. In order to prevent the favored oxidative N-H addition we blocked this functionality by a methyl group and used 1-(2-bromo-4-ethoxycarbonylphenyl)-3-methyl-3-phenyltriazene (**2**) for our experiments.

The reduction of $[(Ph_3P)_2Pd(OAc)_2]$ with *n*BuLi or preferably with hydrazine hydrate in THF led to intermediate formation of $[Pd(PPh_3)_2]$ which subsequently reacted with one equivalent of **2** as depicted in Scheme 3, yielding $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (**5**). The use of butyllithium as a reductant also gave minor amounts of unknown side products whereas hydrazine hydrate reduced palladium(II) smoothly to palladium(0). However, an excess of N_2H_4 ·H₂O was disadvantageous because the released acetic acid readily formed crystalline hydrazinium acetate (the molecular structure is shown in the ESI), hampering purification procedures. Therefore, an electron-precise amount of half an equivalent of N_2H_4 ·H₂O was employed as shown in Scheme 3. The substrate $[(Ph_3P)_2PdCl_2]$ proved to be disadvantageous because the reduction proceeded significantly slower and slightly sluggish and under these conditions no complete reduction was achieved.



Scheme 3: Synthesis of the 1-(2-bromo-4-ethoxycarbonylphenyl)-3-methyl-3-phenyltriazene complex of palladium(II) via an oxidative addition of the C-Br bond.

Separation of triazene **2** and the palladium(II) complex $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (**5**) was quite challenging due to similar solubility in diethyl ether and ethanol. Recrystallization from toluene allowed the complete removal of substrate **2** and enabled the isolation of pure crystalline **5**.

There are only very few X-ray crystal structure studies reported for triazenido palladium(II) complexes. Therefore, we determined the structures of the complexes **3** to **5** and for comparison reasons also from triazene **2**.

The molecular structure and atom labelling scheme of 1-(2-bromo-4-ethoxycarbonylphenyl)-3-methyl-3-phenyltriazene (**2**) are depicted in Figure 1. The small differences between the N1-N2 single and N2=N3 double bonds of only 4.4 pm and the slightly shortened N1-C6 and N3-C7 bonds to the aryl substituents with an average value of 141.5 pm support the presence of charge delocalization within the extended π -system. This electronic interaction leads to a planar arrangement of the 1,3-diaryltriazene subunit.



Figure 1: Molecular structure and atom labelling scheme of 1-(2-bromo-4-ethoxycarbonylphenyl)-3methyl-3-phenyltriazene (**2**). The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii. Selected bond lengths (pm): N1-N2 132.5(3), N2-N3 128.1(3), N1-C6 141.9(3), N1-C16 146.6(4), N3-C7 141.1(4), Br1-C8 189.3(3); bond angles (deg.): N2-N1-C6 116.4(2), N2-N1-C16 121.0(2), C6-N1-C16 122.6(2), N1-N2-N3 113.3(2), N2-N3-C7 112.1(2); dihedral angles (deg.): N2-N1-C6-C1 -6.9(4), C6-N1-N2-N3 -179.2(2), N1-N2-N3-C7 180.0(2), N2-N3-C7-C8 173.3(2).



Figure 2: Structural motif and atom labelling scheme of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)Cl]$ (3). The nonhydrogen atoms are drawn with arbitrary radii, H atoms are neglected for the sake of clarity. Selected bond lengths (pm): Pd1-Cl1 231.3(3), Pd1-P1 231.8(3), Pd1-P2 232.2(3), Pd1-N1 201.8(11), N1-N2 129.6(16), N2-N3 130.9(16), N1-C10 144.6(17), N3-C1 141.4(17), Br1-C2 189.9(14); angles (deg.): P1-Pd1-P2 178.42(13), Cl1-Pd1-N1 178.5(4), N1-Pd1-P1 90.2(4), N1-Pd1-P2 90.9(4), Cl1-Pd1-P1 89.59(12), Cl1-Pd1-P2 89.27(12), Pd1-N1-N2 122.0(9), Pd1-N1-C10 122.5(9), N2-N1-C10 115.4(11), N1-N2-N3 112.8(10), N2-N3-C1 109.3(10).

The molecular structures of the triazenido palladium(II) complexes contain metal centers in square planar coordination spheres. The molecular structure and atom numbering scheme of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)CI]$ (3) are shown in Figure 2. The anionic chloride and triazenide bases are *trans*-positioned. The negative charge is delocalized within the triazenide moiety leading to an average N-N distance of 130.3 pm.



Figure 3: Molecular structure and atom labelling scheme of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (4). The ellipsoids represent a probability of 30 %, H atoms are omitted for clarity reasons. Symmetry-related atoms (-x+1.5, -y+1.5, -z+1) are marked with the letter "A". Selected bond lengths (pm): Pd1-N1 204.8(2), Pd1-P1 236.31(9), N1-N2 130.8(4), N2-N3 130.3(4), N1-C10 142.2(4), N3-C1 140.9(4), Br1-C2 189.6(3); bond angles (deg.): N1-Pd1-P1 90.50(8), Pd1-N1-N2 121.3(2), Pd1-N1-C10 123.7(2), N2-N1-C10 113.9(2), N1-N2-N3 114.6(2), N2-N3-C1 109.9(3).

The molecular structure and atom labelling scheme of centrosymmetric $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (4) are depicted in Figure 3. The crystallographic center of symmetry enforces *trans*-arranged triazenide ligands which show very similar N1-N2 and N2-N3 bond lengths verifying delocalization of the negative charge within this triazaallyl substructure. The Pd1-P1 bond is elongated compared to complex **3**, most probably a steric consequence due to substitution of the small chloride by another rather bulky triazenide ligand. In agreement with this interpretation also an elongation of the Pd1-N1 distances in the more strained complex **4** is observed

The molecular structure and atom labelling scheme of $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (5) is depicted in Figure 4. The palladium(II) atom is bound to the aryl moiety and the triazene subunit shows no short contacts to the metal atom. The N-N single and N=N double bonds differ by almost 10 pm, a significantly larger difference than in substrate 2. This finding can be explained by larger deviation of the diaryltriazene subunit from planarity and hence by a less effective charge delocalization. The N-C bonds are in the same order of magnitude as observed for triazene 2. The Pd1-C9 bond length lies in the expected range as also observed for unstrained $[(Ph_3P)_2Pd(Ph)Br]$ (199.5(6) pm)²⁰ and dinuclear $[(dppm)Pd(Ph)Br]_2 (204.1(7) pm).^{21}$



Figure 4: Molecular structure and atom labelling scheme of $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (5). The ellipsoids represent a probability of 30 %, H atoms are omitted for clarity reasons. The ethoxy group O2, C15, and C16 is disordered on two position, only one position is shown. Selected bond lengths (pm): Pd1-Br1 251.91(8), Pd1-P1 231.99(18), Pd1-P2 234.52(18), Pd1-C9 202.9(6), N1-N2 125.7(7), N2-N3 135.4(7), N1-C8 141.8(8), N3-C6 140.7(9), N3-C7 146.2(8); bond angles (deg.): Br1-Pd1-P1 89.69(4), Br1-Pd1-P2 93.75(5), Br1-Pd1-C9 174.36(17), P1-Pd1-P2 175.35(6), P1-Pd1-C9 89.47(18), P2-Pd1-C9 87.41(18), C8-N1-N2 112.6(5), N1-N2-N3 114.4(5), N2-N3-C6 116.8(5), N2-N3-C7 120.1(6), C6-N3-C7 122.8(6).

In Table 2 selected structural parameters of palladium(II)-bound triazenides are compared. Preferably, the triazenide ligands bind as monodentate ligands in mononuclear complexes (entries 1-10) or as bridging ligands in di- (entries 12-20) and even tetranuclear (entry 21) palladium(II) compounds. In contrast, the bidentate binding fashion in mononuclear derivatives is quite unique (entry 11). The compounds $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (4) (entry 8) and $[(py)_2Pd(2-FC_6H_4 N_3-C_6H_4-4-NO_2_2$ (entry 10) are the only known mononuclear complexes with two triazenide ligands. In all these derivatives, the triazenide ligands have (syn-E) configuration. In mononuclear complexes with monodentate triazenide ligands the Pd-N bond lengths vary within a rather narrow range of 202 to 205 pm (exception being entries 3 and 5 with trans-positioned aryl groups). Larger distances and a broad variation of the Pd-N values are observed for bridging triazenide ligands. Regardless of the binding mode, the negative charge is largely delocalized within the triazenide functionalities supporting largely ionic interactions between the palladium(II) cation and the triazenide anion. Furthermore, the NNN bond angles are smaller than 120° and vary in the range between 111° and 118°; steric strain induced by the bidentate coordination of the triazenide to one palladium(II) atom leads to a smaller angle of only 106.2(4)° (entry 11) whereas in the tetranuclear congener larger values of approx. 120° are found due to intramolecular electrostatic repulsion between the palladium(II) cations on the one hand and between the chloride anions on the other (entry 21).

<< Insert Table 2 >>

Selected NMR data are summarized in Table 3 to elucidate the influence of the coordination of the triazenides at palladium(II) atoms on the chemical shifts. Formation of the palladium(II) complexes leads to very small shifts of the ¹H resonances of the N-bound methyl substituents (compounds **2** and **5**) whereas the ethyl group of the ester functionality shows a larger shift toward higher field. ¹³C{¹H} resonances of the phenyl group of **2** are not influenced by formation of complex **5** whereas the ipso-carbon atom of the ester-functionalized aryl substituent shows a low field shift. Formation of triazenides **3** and **4** leads to slightly low field shifted resonances of the *ipso*-carbon atoms of the phenyl group. ³¹P{¹H} NMR shifts of **3** and **5** with palladium-bound halide ligands are very similar, whereas the substitution of chloride by another triazenide ligand leads to a high field shifted resonance. Resonances of very small intensity (see Figures S4 and S6 of the ESI) belong to the isomeric form with palladium(II) bound to the nitrogen atom adjacent to the 2-bromo-4-ethoxycarbonylphenyl group.

	1	2	3	4	5
Solvent	[D ₈]THF	[D ₈]THF	CDCl ₃	CDCl ₃	[D ₈]THF
¹ H					
δ(NMe)	-	3.77	-	-	3.73
δ(Me _{Et})	1.36	1.37	1.39	1.45	1.21
δ(CH _{2,Et})	4.33	4.34	4.35	4.42	4.08
¹³ C{ ¹ H}					
δ(Me _{N3})	-	33.8	-	-	32.9
δ(Me _{Et})	14.4	14.5	14.6	14.6	14,7
δ(CH _{2,Et})	61.4	61.5	60.9	61.0	60.0
δ(<i>i</i> C _{Ph})	142.1	145.5	149.4	148.8	146.0
$\delta(iC_{PhCOOEt})$	152.1	151.9	153.4	154.0	158.4
³¹ P{ ¹ H}					
δ(PPh₃)	- /		22.0	17.2	23.6

Table 3: Comparison of selected NMR parameters (chemical shifts, ppm) of triazenes 1 and 2 with those of palladium(II) complexes 3 to 5.

The cyclic voltammogram of triazene **2** shows a reversible reduction wave at -1.24 V and palladation leads to a slight positive shift to -1.20 V in **5**. An irreversible oxidation process is indicated at 0.96 V in case of ligand **2** and 0.88 V for **5**. Cyclic voltammograms of complexes with Pd–Cl bonds exhibit a different behavior: complex **3** shows a broad irreversible oxidation wave at 0.23 V due to several oxidation processes. Besides the oxidation of palladium(II) species, also oxidation of the chloride ion Cl⁻ to Cl₂ occurs. This behavior was observed earlier for several dinuclear palladium(II) triazenides.⁷

Complex $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (5) was also studied by ESI mass spectrometry and an intensive mass was found at m/z = 650.1166 Da. In agreement with the isotopic pattern of this signal a formula of $C_{34}H_{31}N_3O_2PPd$ (deviation from calculated high resolution mass 1.7 ppm) can be deduced due to loss of one PPh₃ ligand and the bromide anion.

TGA measurements showed that the triazenes **1** and **2** decomposed above 150 °C and 190 °C, respectively. Formation of the palladium-bound triazenide stabilized this unit and degradation of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)Cl]$ (**3**) started above 210 °C. Contrary to this observation, the

influence of the insertion of Pd into the C-Br bond of the aryl group on the stability of the triazene unit was negligible and weight loss of $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (5) was detected already above 140 °C. This finding verified the structural data which showed no significant changes of the bonding parameters of the triazene substructure upon palladation of the aryl substituent. The high decomposition temperatures of these diaryltriazenes are contrary to earlier observations at 1-(2,4,6-triisopropylphenyl)-3-(2-pyridylmethyl)triazene, which eliminated dinitrogen already under very mild conditions in hot *n*-pentane.²⁷

Conclusions

The metathetical approach is a suitable pathway to prepare palladium(II) triazenides. Thus, the equimolar reaction of $[(Ph_3P)_2PdCl_2]$ with deprotonated 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazene (1) as lithium, silver, or triethylammonium salt yields the palladium(II) complex $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)Cl]$ (3). The second reaction step with another equivalent of triazenide proceeds less straightforward and mixtures of 3 and doubly triazenide substituted $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (4) are obtained.

The oxidative addition of the C-Br bond of 1-(2-bromo-4-ethoxycarbonylphenyl)-3-methyl-3-phenyltriazene (**2**) on the palladium(0) species $[Pd(PPh_3)_2]$ in THF yields $[(Ph_3P)_2Pd\{C_6H_3-2-(N=N-N(Me)Ph)-5-COOEt\}Br]$ (**5**). The *N*-methylated derivative has been used to avoid competitive oxidative addition of the N-H bond on palladium.

In the molecular structures of complexes **3** and **4**, the palladium-bound triazenide ligands show (*syn-E*)-configuration. The negative charge of these anions is largely delocalized, leading to quite similar N-N and N=N bond lengths and supporting a mainly ionic bonding situation in the respective palladium complexes. In mononuclear palladium(II) compounds, the monodentate coordination mode is preferred, the very rare bidentate binding fashion has not been observed for this 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazenide ligand.

Experimental

General Considerations: All manipulations were carried out in a nitrogen atmosphere using standard Schlenk techniques. The solvents THF and toluene were dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. The indicated yields are not optimized and refer to crystalline yields. ¹H and ¹³C(¹H) NMR spectra were recorded on Bruker Avance 600, 400 and Avance 250 spectrometers. Chemical shifts are reported in parts per million relative to SiMe₄ as external standard. ¹H, ¹³C(¹H)-HSQC, ¹H, ¹³C(¹H)-HMBC, and H,H-COSY NMR experiments were performed for the assignment of the resonances. The residual signals of $[D_8]$ THF, CDCl₃ and C₆D₆ were used as internal standards. For mass spectrometric investigations the spectrometers ThermoFinnigan MAT95XL and Finnigan SSQ710 were at our disposal. IR spectra were recorded with a Bruker ALPHA FT-IR spectrometer. The compounds 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazene (1)¹¹ and 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazene

Synthesis of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)Cl]$ (3): This complex can be prepared by three methods via intermediate silver triazenide (A), via lithium triazenide (B) and via triethylammonium triazenide. The preferred method proceeded via intermediately prepared silver triazenide. Method A: Silver 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazenide: Sodium methanolate (0.29 g, 5.4 mmol) was dissolved in 50 mL of anhydrous ethanol and added dropwise to 1-(2-bromo-4ethoxycarbonylphenyl)-3-phenyltriazene (1, (1.725 g, 5.0 mmol), dissolved in 50 mL of anhydrous dichloromethane. The resulting deep yellow-brown solution was stirred for 20 min and a solution of silver nitrate (0.84 g, 4.9 mmol) in 13 mL of deionized and degassed water was added. Stirring overnight led to a yellow-green suspension. The precipitate was collected and washed three times with 12 mL of ethanol. After drying in high vacuum the crude product of silver 1-(2-bromo-4ethoxycarbonylphenyl)-3-phenyltriazenide (1.55 g, yield: 69%) was used without further purification. This silver triazenide (0.19 g, 0.42 mmol) was suspended in 9 mL of dichloromethane. A suspension of 0.293 g of bis(triphenylphosphane)-dichloro-palladium(II) (0.42 mmol) in 9 mL of toluene was added at once to the silver triazenide mixture. During stirring overnight at r.t. the color of the reaction mixture turned brown-orange and became clear. The solution was filtered through a Schlenk frit covered with diatomaceous earth. All volatiles were removed in vacuo from the filtrate. The remaining orange powder was extracted twice with *n*-hexane. After removal of the solvent, the product was dried in vacuo. Recrystallization was possible from a saturated toluene solution by diffusion with *n*-hexane. Yield: 0.31 g of 3 (73%). The methods B (52 %) and C (18 %) are described in the ESI. Physical data of **3**: Dec. without melting. ¹H NMR (400 MHz, CDCl₃, 297 K): δ = 1.39 (t, J = 7.1 Hz, 3H, COOEt <u>CH</u>₃), 4.35 (q, J = 7.1 Hz, 2H, COOEt <u>CH</u>₂), 6.11 (d, J = 8.5 Hz, 1H, BrArH <u>4-CH</u>), 6.79 (t, J = 7.3 Hz, 1H, ArH <u>4-CH</u>), 6.95 (t, J = 7.9 Hz, 2H, ArH <u>3,3´-CH</u>), 7.23 (t, 12H, J = 7.6 Hz PPh₃ <u>3,3´-CH</u>), 7.35 (t, 6H, J = 7.4 Hz PPh₃ <u>4-CH</u>), 7.47 (m, 2H, ArH <u>2,2'-CH</u>), 7.54 (dd, J = 8.5 Hz 1.9 Hz, 1H, BrArH <u>5-CH</u>), 7.69 (m, 12H, PPh₃ 2,2[′]-CH), 8.19 (d, J = 1.9 Hz, 1H, BrArH <u>3-CH</u>). ¹³C{¹H} NMR (100 MHz, CDCl₃, 297 K): δ = 14.6 (COOEt CH₃), 60.9 (COOEt CH₂), 117.2 (BrAr 2-CBr), 119.6 (Ar 2,2'-CH), 119.7 (BrAr 6-CH), 122.7 (Ar 4-<u>CH</u>), 125.2 (BrAr <u>4-C</u>), 128.1 (t, ${}^{2}J_{PC}$ = 5.2 Hz, PPh₃ <u>2,2 -CH</u>), 128.3 (BrAr <u>5-CH</u>), 130.0 (t, ${}^{1}J_{PC}$ = 24.2 Hz, PPh₃ <u>1-C</u>), 130.6 (PPh₃ <u>4-CH</u>), 134.4 (BrAr <u>3-CH</u>), 135.0 (t, ³J_{PC} = 5.2 Hz, PPh₃ <u>3,3'-CH</u>), 149.4 (Ar <u>1-CN</u>), 153.4 (BrAr <u>1-CN</u>), 166.2 (<u>C</u>OOEt), ³¹P{¹H} NMR (162 MHz, CDCl₃, 297 K): δ = 22.0. ¹H NMR (400 MHz, [D₈]THF, 297 K): δ = 1.33 (t, J = 7.1 Hz, 3H, COOEt <u>CH₃</u>), 4.28 (q, J = 7.1 Hz, 2H, COOEt <u>CH₂</u>), 6.11 (d, J = 8.5 Hz, 1H, BrArH <u>6-CH</u>), 6.77 (t, J = 7.3 Hz, 1H, ArH <u>4-CH</u>), 6.93 (t, J = 8.0 Hz, 2H, ArH <u>3,3´-CH</u>), 7.22 (t, 12H, J = 7.6 Hz PPh₃ 3,3'-CH), 7.36 (t, 6H, J = 7.4 Hz PPh₃ 4-CH), 7.50 (m, 3H, ArH 2,2'-CH, BrArH 5-CH), 7.71 (m, 12H, PPh₃ <u>2,2'-CH</u>), 8.11 (d, J = 1.9 Hz, 1H, BrArH <u>3-CH</u>), ¹³C{¹H} NMR (101 MHz, [D₈]THF, 297 K): δ = 14.6 (COOEt <u>CH₃</u>), 60.8 (COOEt <u>CH₂</u>), 117.7 (BrAr <u>2-CBr</u>), 120.1 (Ar <u>2,2'-CH</u>), 120.3 (BrAr <u>6-CH</u>), 123.3 (Ar <u>4-CH</u>), 126.1 (BrAr <u>4-C</u>), 128.46 (t, ²J_{PC} = 5.2 Hz, PPh₃ <u>2,2'-CH</u>), 128.55 (BrAr <u>5-CH</u>), 128.7 (Ar <u>3,3'-CH</u>) 131.1 (t, ${}^{1}J_{PC}$ = 24.2 Hz, PPh₃ <u>1-C</u> and s, PPh₃ <u>4-CH</u>), 134.6 (BrAr <u>3-CH</u>), 135.7 (t, ${}^{3}J_{PC}$ = 6.5 Hz, PPh₃ <u>3,3'-CH</u>), 150.4 (Ar <u>1-CN</u>), 154.0 (BrAr <u>1-CN</u>), 165.2 (<u>C</u>OOEt), ³¹P{¹H} NMR (162 MHz, [D₈]THF, 297 K): δ = 25.6 (*E*-N1), tiny signal at δ (ppm) = 26.9 (*E*-N3). HR-MS (ESI, acetonitrile), [M+H]: calculated for C₅₁H₄₄BrClN₃O₂P2Pd: 1012.0819 Da, found: 1012.0785 Da, Δm/z = 2.5 ppm. IR (ATR, cm⁻¹): 1701, 1589, 1481, 1435, 1340, 1315, 1291, 1276, 1243, 1200, 1163, 1130, 1097, 1030, 995, 892, 840, 751, 711, 692, 618, 588, 523, 510, 496. Elemental anal. (C₅₁H₄₄BrClN₃O₂P₂Pd): calcd.: C 60.43, H 4.28, Br 7.88, Cl 3.50, N 4.15; found: C 60.62, H 4.35, Br 7.34, Cl 3.62, N 4.35. TGA-DSC (m₀ = 4.8332 mg, 25 °C to 600 °C, 5 K/min): four step degradation, 1. step: -3.09 % (219.3 °C, loss of nitrogen, proceeds exothermic with 94.0 J/g), 2. step: -9.96 % (244.8 °C), 3. step: -9.43 % (300.5 °C), 4. step: -29.67 % (343.8 °C), residue: 45.58 %.

Synthesis of $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (4): Silver 1-(2-bromo-4-ethoxycarbonylphenyl)-3-phenyltriazenide was prepared as described above and 0.24 g of this silver salt (0.53 mmol) was suspended in 10 mL of anhydrous dichloromethane. A suspension of 0.185 g of bis(triphenylphosphane)-dichloro-palladium(II) (0.26 mmol) in 9 mL of toluene was added at once to the silver triazenide. According to the same workup procedures as described for complex **3**, a mixture

of **3** and **4** (ratio of 77:23) was isolated due to an incomplete conversion and very similar solubility properties of these complexes.

Physical data of **4**: The resonances of **3** and **4** are mostly well separated. Only the signals of the complex **4** are recorded here. ¹H NMR (400 MHz, CDCl₃, 297 K): $\delta = 1.45$ (t, J = 7.1 Hz, COOEt <u>CH₃</u>), 4.42 (q, J = 7.1 Hz, COOEt <u>CH₂</u>), 6.50 (d, J = 8.5 Hz, BrArH <u>4-CH</u>), 6.70 (t, J = 7.3 Hz, ArH <u>4-CH</u>), 6.79 (t, J = 7.3 Hz, ArH <u>3,3'-CH</u>), 7.11 (t, J = 7.4 Hz PPh₃ <u>3,3'-CH</u>), 7.48 (m, PPh₃ <u>4-CH</u>, ArH <u>2,2'-CH</u>), 7.69 (m, PPh₃ <u>2,2'-CH</u>), 7.91 (dd, J = 8.6 Hz 1.7 Hz, BrArH <u>5-CH</u>), 8.44 (d, J = 1.9 Hz, BrArH <u>3-CH</u>). ¹³C{¹H} NMR (100 MHz, CDCl₃, 297 K): $\delta = 14.6$ (COOEt <u>CH₃</u>), 61.0 (COOEt <u>CH₂</u>), 117.0 (BrAr <u>2-CBr</u>), 121.5 (BrAr <u>6-CH</u>), 121.6 (Ar <u>2,2'-CH</u>), 122.8 (Ar <u>4-CH</u>), 125.4 (BrAr <u>4-C</u>), 127.7 (t, ²J_{PC} = 5.1 Hz, PPh₃ <u>2,2'-CH</u>), 128.3 (BrAr <u>5-CH</u>), 130.1 (t, ¹J_{PC} = 24.2 Hz, PPh₃ <u>1-C</u>), 130.7 (PPh₃ <u>4-CH</u>), 134.2 (BrAr <u>3-CH</u>), 134.9 (t, ³J_{PC} = 5.2 Hz, PPh₃ <u>3,3'-CH</u>), 148.8 (Ar <u>1-CN</u>), 154.0 (BrAr <u>1-CN</u>), 166.3 (COOEt). ³¹P{¹H} NMR (162 MHz, CDCl₃, 297 K): $\delta = 17.2$.

Synthesis of [(Ph₃P)₂Pd{C₆H₃-2-(N=N-N(Me)Ph)-5-COOEt}Br] (5): Bis(triphenylphosphane)palladium diacetate (315 mg, 0.42 mmol) was suspended in 10 mL of anhydrous tetrahydrofuran. After the suspension was stirred for 10 min, hydrazine monohydrate (11 µL, 11.1 mg, 0.22 mmol) was added. The final clear greenish brown solution was stirred for 30 min at r.t. Then 1-(2-bromo-4ethoxycarbonylphenyl)-3-methyl-3-phenyltriazene (2) (152.5 mg, 0.42 mmol) was dissolved in anhydrous tetrahydrofuran (5 mL) and added via a cannula to the thus prepared palladium(0) solution. The reaction mixture was heated to 60 °C for 4 h. After cooling to r.t. all volatiles were removed in vacuo. The residue was washed three times with n-pentane (3x5 mL). Then the crude product was washed twice with diethyl ether (2x3 mL). Drying in vacuo gave a grey-brown powder. Yield: 225 mg of 5 (75%). Rerystallization was achieved in toluene/*n*-hexane yielding orange rhombohedral crystals. Physical data of **5**: Dec. without melting. ¹H NMR (600 MHz, $[D_8]$ THF, 298 K): δ = 1.21 (t, J = 7.1 Hz, 3H, COOEt CH₃), 3.73 (s, 3H, NCH₃), 4.08 (q, J = 7.1 Hz, 2H, COOEt CH₂), 6.43 (d, J = 8.2 Hz, 1H, subArH 6-<u>CH</u>), 7.01 (d, J = 8.2 Hz, 1H, subArH <u>3-CH</u>), 7.04 (m, 1H, ArH <u>4-CH</u>), 7.17 (t, J = 7.5 Hz, 12H, PPh₃ <u>2,2'-CH</u>), 7.25 (t, J = 7.3 Hz, 6H, PPh₃ <u>4-CH</u>), 7.30 (m, 5H, ArH <u>2,2'-CH, 3,3'-CH</u> sub ArH <u>5-CH</u>), 7.59 (m, 12H, PPh₃ <u>3,3'-CH</u>). ¹³C{¹H} NMR (150 MHz, [D₈]THF, 297 K): δ = 14.7 (COOEt <u>CH₃</u>), 32.9 (<u>NCH₃</u>), 60.0 (COOEt <u>CH₂</u>), 117.2 (subAr <u>6-CH</u>), 117.3 (Ar <u>2,2'-CH</u>), 123.6 (Ar, <u>4-CH</u>), 125.1 (subAr <u>3-CH</u>), 128.0 (subAr <u>CPd</u>), 128.2 (t, ²J_{PC} = 5.1 Hz, PPh₃ <u>2,2'-CH</u>), 129.5 (PPh₃ <u>4-CH</u>), 130.2 (Ar <u>3,3'-CH</u>), 132.7 (t, ¹J_{PC} = 22.9 Hz, PPh₃ <u>1-C</u>), 135.6 (t, ${}^{3}J_{PC}$ = 6.3 Hz, PPh₃ <u>3,3'-CH</u>), 139.3 (t, ${}^{5}J_{PC}$ = 4.6 Hz, subAr <u>5-CH</u>), 146.0 (Ar <u>1-CN</u>), 156.9 (t ${}^{4}J_{PC}$ = 2.5 Hz, subAr <u>4-C</u>), 158.4 (t, ³J_{PC} = 3.7 Hz, subAr <u>1-CN</u>), 166.1 (COOEt). ³¹P{¹H} NMR (243 MHz, [D₈]THF, 297 K): δ = 23.56. HR-MS (ESI, acetonitrile), $[(M-PPh_3-Br)]^+$: calculated for C₃₄H₃₂N₃O₂PPd: 650.1196 Da, found: 650.1219 Da, Δm/z = 5.5 ppm. IR (ATR, cm⁻¹): 3052, 1707, 1597, 1503, 1479, 1433, 1363, 1333, 1271, 1228, 1204, 1101, 1026, 994, 825, 742, 726, 687, 608, 520, 509, 492, 453, 438, 414. Elemental anal. (C₅₂H₄₆BrN₃O₂P₂Pd): calcd.: C 62.88, H 4.67, Br 8.05, N 4.23; found: C 61.88, H 4.60, Br 7.43, N 3.75. TGA-DSC ($m_0 = 6.0109 \text{ mg}$, 25 °C to 600 °C, 5 K/min): three step degradation, 1. step: -10.31 % (216.9 °C, proceeds exothermic with 25.9 J/g), 2. step: -31.34 % (309.3 °C), 3. step: -31.8 % (356.5 °C), residue: 25.04 %.

Crystal structure determinations: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_{α} radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.²⁸⁻³⁰ The structures were solved by direct methods (SHELXS)³¹ and refined by full-matrix least-squares techniques against F_0^2 (SHELXL-97).³¹ The hydrogen atoms of **HA** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.³¹ The crystals of **3** were extremely thin and of low quality, resulting in a substandard data set; however, the quality of the structure determination is sufficient to show connectivity and geometry despite the high final *R* value. Therefore, we only publish the conformation of the molecule and the crystallographic data as

well as structure solution and refinement details are summarized in Table S1 (ESI). XP³² and POV-Ray³³ were used for structure representations.

Electrochemistry: Electrochemical data were obtained by cyclic voltammetry using a conventional single-compartment three-electrode cell arrangement in combination with a potentiostat "AUTOLABs, eco chemie". As working electrode a 0.196 cm² Pt disk, as auxiliary electrode was used glassy carbon and as reference electrode Ag/AgCl (3 M KCl). The measurements were carried out in anhydrous and nitrogen purged acetonitrile ($3 \cdot 10^{-4}$ M substrate concentration with 0.1 M tert-butylammonium tetrafluoroborate as supporting electrolyte. All potentials are referenced by the ferrocenium/ferrocene couple (*E*(Fc/Fc⁺) = 0.437 V).³⁴

Conflicts of interest

There are no conflicts to declare.

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Electronic Supporting Information (ESI)

NMR spectra, cyclovoltammograms, crystallographic and refinement details of the crystal structure determinations, molecule representation and bonding parameters of hydrazine acetate (pdf format). CCDC-1899309 for **2**, CCDC-1899310 for **4**, CCDC-1899311 for **5**, and CCDC-1899364 for hydrazinium acetate. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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Entry	R	R′	Binding mode	Pd-N	N-N'	N'-N''	N-N'-N''	Ref.
1	pTol	<i>p</i> Tol	Monodentate	203.3(4)	133.6(8)	128.6(7)	113.0(5)	3
2	<i>p</i> Tol	<i>p</i> Tol	Monodentate	203.4(7)	129.4(9)	129.6(9)	116.3(8)	22
3	C_6H_4-4-F	C_6H_4 -4-F	Monodentate	212.0	132.4	128.3	111.6	23
4	C_6H_4 -4-Ac	C ₆ H ₄ -4-Ac	Monodentate	204.0	131.8	128.3	112.9	4
5	C_6H_4 -4-NO ₂	C_6H_4 -4-NO ₂	Monodentate	214.9(3)	131.3(4)	128.7(4)	112.4(2)	24
6	C ₆ H ₄ -3-OMe-4-COOMe	C ₆ H ₄ -3-OMe-4-COOMe	Monodentate	203.6	131.3	130.0	113.0	4
7	Ph ^b	C ₆ H ₃ -2-Br-4-COOEt	Monodentate	201.8(11)	129.6(16)	130.9(16)	112.8(10)	Here
8	Ph ^c	C ₆ H ₃ -2-Br-4-COOEt	Monodentate	204.8(2)	130.8(4)	130.3(4)	114.6(2)	Here
9	C_6H_4 -4-NO ₂	C ₆ H ₄ -2-F	Monodentate	204.7(5)	133.4(6)	128.2(6)	111.0(4)	24
10	C_6H_4 -4-NO ₂	C ₆ H ₄ -2-F	Monodentate	202.1(3)	132.5(5)	128.3(5)	111.0(3)	25
11	Ph	Ph	Bidentate	209.5(4), 211.7(4)	130.6(7)	130.8(7)	106.2(4)	5
12	Ph	Ph	Bridging ^d	206.8(4), 209.8(4);	130.2(4);	130.8(4);	117.0(4);	5
				207.3(4), 209.0(4)	130.2(5)	131.4(6)	117.2(4)	
13	Ph	Ph	Bridging ^d	210.0(4), 216.1(4);	129.5(5);	130.0(6);	117.2(4);	7
				210.0(4), 217.6(4)	129.4(5)	130.6(5)	117.7(4)	
14	<i>p</i> Tol	<i>p</i> Tol	Bridging ^d	202.5(5), 214.5(5);	130.8(9);	130.0(9);	116.1(5);	22
				203.6(5), 214.5(4)	128.0(8)	130.4(9)	116.1(5)	
15	<i>p</i> Tol	<i>p</i> Tol	Bridging ^d	212.1(7), 214.2(7);	131.4(9);	129.3(10);	116.3(7);	7
	-			211.8(8), 214.4(8)	129.3(10)	130.4(11)	116.5(8)	
16	<i>o</i> Tol	<i>o</i> Tol	Bridging ^d	211.5(6), 217.6(6);	128.8(8);	128.2(8);	117.7(6);	7
				213.8(5), 213.6(5)	130.3(8)	128.5(8)	116.0(5)	
17	C_6H_4 -4-Br	C ₆ H₄-4-Br	Bridging ^d	211.6(5), 213.7(5);	129.8(7);	130.4(7);	116.7(5);	7
				213.1(5), 216.0(5)	131.0(7)	130.6(7)	116.8(5)	
18	C ₆ H ₄ -2-Br	C ₆ H ₄ -2-Br	Bridging ^d	212.5(4), 215.8(4)	129.8(6)	130.1(6)	118.2(4)	7
19	C ₆ H ₄ -4-OMe	C ₆ H ₄ -4-OMe	Bridging ^d	211.5(6), 213.0(6);	130.0(8);	131.0(8);	116.9(6);	7
				211.2(5), 214.5(5)	130.2(7)	129.9(8)	118.1(5)	
20	<i>p</i> Tol	C ₆ H ₄ -2-SMe	Bridging ^d	201.0(2), 208.7(2)	131.3(3)	129.3(3)	114.3(2)	26
21	pTol	pTol	Bridging ^e	201.8, 202.3;	129.5;	127.4;	119.7;	6
				201.5, 203.8;	129.1;	127.9;	120.7;	
				202.3, 202.3;	128.9;	129.9;	119.4;	
				202.5, 201.0	129.0	128.5	119.9	

Table 2: Comparison of binding modes (see Scheme 1) and selected structural parameters (bond lengths (pm) and angles (deg.), values without e.s.d. values were taken from the CSD database) of palladium(II)-bound triazenide ligands with the substructure Pd(R-N-N'=N''-R').^a

^a Abbreviations: Ac acetyl, Et ethyl, Me methyl, Ph phenyl, Tol tolyl (methylphenyl). ^b Complex $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (**3**). ^c Complex $[(Ph_3P)_2Pd(Ph-N_3-C_6H_3-2-Br-4-COOEt)_2]$ (**4**). ^d Dinuclear palladium(II) complex. ^e Tetranuclear palladium(II) complex.



Palladium triazenides are accessible by metathetical approaches tolerating halogeno- and ester functionalized aryl groups, whereas insertion of Pd into an aryl C-Br bond succeeds after protection of the triazene substructure via *N*-methylation.

Highlights:

- The metathetical approach is a suitable pathway for the synthesis of palladium(II) triazenides.
- Palladium-bound triazenide ligands show perfect delocalization of the negative charge.
- The Pd-triazenide interactions are mainly of ionic nature.
- Triazenide anions prefer a mondentate coordination behavior toward palladium(II).
- Oxidative addition of an aryl C-Br bond onto Pd(0) is tolerated by the triazene substructure.