Cationic Dinuclear Pd−Allyl−Halide Complexes with N-Heterocyclic Carbenes

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Reaction of the mononuclear N-heterocyclic carbene complexes (η^3-C_3H_5)Pd{C(N(R)CH)$_2$}X (R = ^{t}Bu, X = Cl, I (**1a,b**); R = C_6H_3-2,6-^{i}Pr$_2$, X = Cl, I (**2a,b**)) with $TlPF_6$ and TlOTf in CH_2Cl_2 or THF results in partial halide substitution to afford the ionic dinuclear complexes [{(η^3-C_3H_5)Pd(C(N(R)CH)$_2$)}$_2$(μ-X)]Y (R = ^{t}Bu, X = Cl, Y = PF_6 (**3a**), OTf (**3b**) and X = I, Y = OTf (**3c**); R = C_6H_3-2,6-^{i}Pr$_2$, X = Cl, Y = PF_6 (**4a**), OTf (**4b**) and X = I, Y = OTf (**4c**)). According to solution NMR the dinuclear complexes are present as mixtures of diastereomers. The crystal structure of **3a**·0.5($C_4H_{10}O$)·0.5(CH_2Cl_2) has been determined by X-ray crystallography. From the reaction of **2a** with LiMe the PdMe derivative (η^3-C_3H_5)Pd{C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$}Me (**6**) has been obtained. When **1a** was reacted with $B(C_6F_5)_3$, the NHC ligand was transferred to give $(C_6F_5)_3B$−C(N(^{t}Bu)CH)$_2$ and the starting {(η^3-C_3H_5)Pd(μ-Cl)}$_2$.

Introduction

Since the synthesis of the first stable N-heterocyclic carbenes (NHCs) by Arduengo more than a decade ago,[1] NHCs have emerged as an important class of ligands, which are superior to phosphines in many aspects.[2] Among these are the high thermal stability of the products, the tight coordination to the metal, which reduces dissociation, the relative inertness toward oxidation, and the reduced toxicity. In a series of papers the coordination of NHCs to Ni, Pd, and Pt in various oxidation states has already been studied.[1f,3]

We have recently been intrigued by the question as to whether NHC ligands can stabilize ionic three-coordinate 14e complexes of the type [(η^3-C_3H_5)Pd(NHC)]Y with a noncoordinating anion Y, either as an in situ generated species (as suggested in ref 3g) or as an isolated compound. Such coordinatively unsaturated complexes should exhibit interesting structural and catalytic properties. Whereas partial stabilization by coordination of a weakly coordinating solvent (CH_2Cl_2) or by agostic hydrogen interaction of the NHC ligand[4] is not expected to affect the potential catalytic properties, π−σ-allyl isomerization opens the possibility of further coordinatively and electronically unsaturated intermediates. We report here that our attempts to synthesize [(η^3-C_3H_5)Pd(NHC)]Y resulted in the formation of ionic dinuclear complexes [{(η^3-C_3H_5)Pd(NHC)}$_2$-(μ-X)]Y with a bridging halide. In a concurrent paper we report on related Ni and Pd complexes with phosphine ligands.[5]

Results and Discussion

Synthesis and Properties of 1a,b and 2a,b. When {(η^3-C_3H_5)Pd(μ-X)}$_2$ (X = Cl, I) is reacted with the NHCs 1,3-di-*N*-*tert*-butylimidazol-2-ylidene, C{N(^{t}Bu)CH}$_2$, and 1,3-di-*N*-(2,6-diisopropylphenyl)imidazol-2-ylidene, C{N-(C_6H_3-2,6-^{i}Pr$_2$)CH}$_2$, in CH_2Cl_2 at ambient temperature, the dimer is cleaved and the monomeric adducts **1a**,**b** and **2a**,**b** are obtained (Scheme 1). The iodides **1b** and **2b** can also be prepared from the chlorides **1a** and **2a** by treating the latter with NaI in THF (eq 1). This indicates that the strength of the Pd−I bond is higher than that of the Pd−Cl bond. While **2a** was known at the beginning of this study[3f] and a detailed report on

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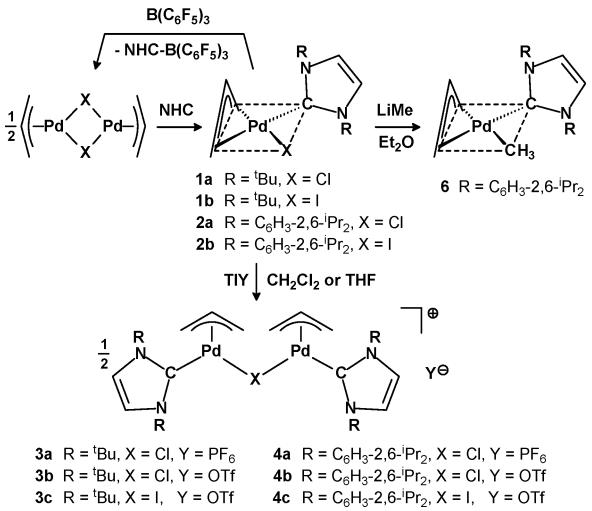
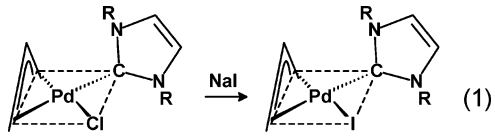
Scheme 1



the synthesis and structures of **1a** and **2a** and other chlorides appeared recently,[3h] the iodides **1b** and **2b** are new.



The complexes are formed almost quantitatively in solution, and the isolated yields are in the range 80−85%. While the chlorides are off-white (**2a**) to pale yellow (**1a**), the color of the iodides **1b** and **2b** is more intense. The complexes decompose (when quickly heated) between 173 and 202 °C, and the iodides decompose about 20 °C below the chlorides. In the EI mass spectra of **1a**,**b** and **2a**,**b** the molecular ions are observed. The molecular ions of the chlorides **1a** and **2a** fragment by cleavage of the allyl group and chlorine to yield $[Pd(NHC)]^+$ as base ions. The molecular ions of the iodides **1b** and **2b** cleave off iodine to afford the base ions $[(C_3H_5)Pd(NHC)]^+$ at 327 and 535, respectively. In the ESIpos mass spectra (CH_2Cl_2) of **1a**,**b** and **2a**,**b** the halide-free ions $[(C_3H_5)Pd(NHC)]^+$ likewise furnish the base peaks. Interestingly, for the iodide **1b** an equally intense ion $[2M - I]^+$ (781, which corresponds to the cation of **3c**, see below, and indicates its high stability) is also found.

In the NMR spectra of **1a**,**b** and **2a**,**b** (Tables 1 and 2) the allyl ligand gives rise to five proton and three carbon resonances, in agreement with asymmetric structures of the complexes.[3d,h] The *tert*-butyl-substituted **1a**,**b** show for the methine and *tert*-butyl groups of the NHC ligand two signals each (^1H and ^{13}C). We conclude from these spectra that (a) the allyl ligand is rigidly bound[3d,h] and does not undergo $\pi-\sigma$-allyl rearrangement and that (b) the coordination of the NHC ligand is also rigid and its rotation about the formal Pd=C bond is slow.[3d] In contrast, for the C_6H_3-2,6-^{i}Pr$_2$-substituted **2a**,**b** there is just one sharp signal for the imidazole ring methine groups, indicating rapid rotation of the NHC ligand about the Pd=C bond that renders the two symmetry-related halves of the NHC ligands equivalent. (Substantial $\pi-\sigma$-allyl rearrangement is still excluded since the syn and anti protons of the allyl ligand are inequivalent.) Since there are three proton and six carbon resonances for the phenyl ring atoms and two sets of $CHMe_aMe_b$ resonances for the inequivalent ortho substituents at each phenyl ring, resulting in a total of 10 proton and 14 carbon resonances for the NHC ligand, rotation about the N−phenyl bonds in **2a**,**b** is, however, restricted. (If it were different, that is, if rotation about the N−phenyl bond occurred but about the Pd=C bond was restricted, 12 proton and 17 carbon resonances would be expected.)

Attempts to activate the chloride **1a** by addition of $B(C_6F_5)_3$ resulted in a transfer of the NHC ligand to the Lewis acid to give $(C_6F_5)_3B-C(N(^tBu)CH)_2$ and the starting $\{(\eta^3-C_3H_5)Pd(\mu-Cl)\}_2$, instead of the desired adduct $(\eta^3-C_3H_5)Pd(NHC)(\mu-Cl)B(C_6F_5)_3$.

Synthesis and Chemical Properties of 3a−c and 4a−c. Nolan et al. have shown that reaction of the neutral halide complexes such as **2a** with $AgBF_4$ or $AgPF_6$ in acetonitrile affords cationic solvent adducts $[(\eta^3-C_3H_5)Pd(NHC)(NCMe)]Y$ (Y = BF_4, PF_6),[3g,6] whereas the products generated in THF were considered unstable.[3g] In a similar approach, we decided to try and activate the starting complexes by exchange of the halide with PF_6 or OTf, and hence reacted the halides **1a**,**b** and **2a**,**b** with $TlPF_6$ and TlOTf in either CH_2Cl_2 or THF as solvent.

When **1a**,**b** (0 °C) and **2a**,**b** (20 °C) are reacted with 0.5 equiv of the Tl reagent, the corresponding amount of TlCl or TlI precipitates and can be removed by filtration. From the resulting solution dinuclear cationic complexes $[\{(\eta^3-C_3H_5)Pd(NHC)\}_2(\mu-X)]Y$ (X = Cl, I; Y = PF_6, OTf; **3a**−**c** and **4a**−**c**) with a halide ion bridging the two Pd centers are isolated (Scheme 1). The μ-I complexes **3c** and **4c** can also be obtained pure when an excess of TlOTf is used; the same holds for the μ-Cl complexes **3a** and **4a** with $TlPF_6$. Thus, for these complexes the bridging halide cannot be removed under the reaction conditions. When the synthesis of the μ-Cl complexes **3b** and **4b** is attempted using an excess of TlOTf, additional signals arise in the ^1H and ^{13}C NMR spectra; these are tentatively attributed to the neutral triflate derivatives $(\eta^3-C_3H_5)Pd(NHC)(OTf)$ (**5a**,**b**) formed as byproducts (up to 50%). The synthesis and isolation of pure **5a**,**b** has not been possible using this route, which is contrasted by the ready formation of the known phosphine complex $(\eta^3-C_3H_5)Pd(P^iPr_3)(OTf)$.[7] It is interesting to note that starting from Pd-halide precursor complexes neither the solvate complexes $[(\eta^3-C_3H_5)Pd(NHC)(S)]Y$ (S = THF, CH_2Cl_2) nor solvent-free three-coordinate complexes $[(\eta^3-C_3H_5)Pd(NHC)]PF_6$ are accessible. Furthermore, the dinuclear triflate complexes **3b**,**c** and **4b**,**c** do not rearrange to form equal amounts of the neutral mononuclear halides and **5a**,**b** (eq 2), as one might expect.

The *N-tert*-butyl-substituted dinuclear **3a**−**c** slowly decompose above 0 °C, both in solution and as a solid,

(6) Although shown by X-ray crystallography to contain acetonitrile as a ligand, these complexes have been repeatedly referred to as (IPr)Pd(allyl)BF_4 and (IPr)Pd(allyl)PF_6 in ref 3g. So far there is no evidence that such species can be formed from halide-containing precursor complexes.

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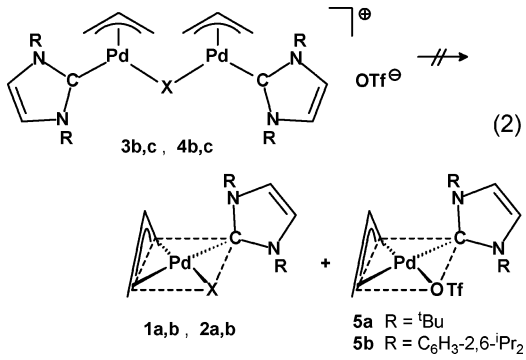
Table 1. ^{1}H and ^{13}C NMR Data of the (η^3-C_3H_5)PdC(N(^{t}Bu)CH)$_2$ Complexes 1a,b and 3a,c[a]

	allyl					C(N(^{t}Bu)CH)$_2$					
	δ(H)			δ(C)		δ(H)		δ(C)			
	H_{meso}	H_{syn}	H_{anti}	C_{meso}	C_{term}	NCH	^{t}Bu	PdC	NCH	CMe_3	Me
1a	5.29	4.03, 3.40	3.23, 2.30	112.8	68.9, 52.3	7.22, 7.20	1.88, 1.71	177.5	118.8, 118.3	58.9, 58.8	32.2, 31.9
1b	5.15	4.17, 3.91	3.03, 2.58	111.8	64.9, 59.9	7.26, 7.24	1.85, 1.69	175.7	119.3, 118.9	58.9, 58.8	32.1, 32.0
3a	5.40	3.83, 3.58	3.30, 2.46	114.1	71.9, 53.1	7.26, 7.25	1.83, 1.67	174.7	119.4, 119.0	58.9	32.3, 31.9
3c	5.26	4.07, 3.88	3.09, 2.76	113.6	67.7, 60.92	7.32, 7.31	1.81, 1.66	173.2	120.0	58.9	32.3, 32.1
3c′	5.26	4.07, 3.92	3.05, 2.76	113.6	67.6, 60.88	7.32, 7.31	1.80, 1.65	173.2	119.6	59.0	32.3, 32.1

[a] **3c** corresponds to the major diastereomer (≈55%) and **3c′** to the minor (≈45%).



and should be handled in the cold. The *N*-aryl-substituted derivatives **4a**–**c** are markedly more stable. When quickly heated, the iodides **3c** and **4c** (dec 160–170 °C) are more stable than the chlorides, and of the latter the *N*-aryl-substituted **4a**,**b** (dec ∼140 °C) decompose less readily than the *N*-*tert*-butyl-substituted **3a**,**b** (dec ∼115 °C). While the chlorides are pale yellow (**3a**, **4a**) or colorless (**3b**, **4b**), depending on the counterion, the color of the iodides is light brown (**3c**, **4c**). All complexes are insoluble in pentane. **3a**–**c** are also insoluble in diethyl ether, but **4a**–**c** dissolve slightly. However, the complexes dissolve well in CH_2Cl_2 and THF. Complex **4a** crystallizes from a THF/Et_2O mixture, forming large yellow crystals, which include solute THF. In the absence of THF we have been able to obtain the complex only in the form of an amorphous powder.

Mass Spectra of 3a–c and 4a–c. The EI mass spectra of **3a**–**c** and **4a**–**c** provided only an indirect indication of the dinuclear structure of the complexes. Even though the EI mass spectra of the PF_6 salts **3a** and **4a** were recorded at high evaporation temperatures (∼200 °C), they displayed solely the molecular ions of the neutral mononuclear chlorides **1a** and **2a**, for which genuine spectra had been observed at 60–80 °C lower temperature. Similarly, the EI mass spectra of the triflate salts **3b**,**c** and **4b**,**c**, recorded at an evaporation temperature of 150–175 °C, agreed with the spectra of the mononuclear halides **1a**,**b** and **2a**,**b**, for which the genuine spectra were established at 25–40 °C lower temperature. No stringent evidence was obtained for the formation of either **5a**,**b** or [(η^3-C_3H_5)Pd(NHC)]PF_6 as a possible second component from the degradation of **3a**–**c** and **4a**–**c**.

In the ESIpos mass spectra (CH_2Cl_2) of the *tert*-butyl-NHC triflate salts **3b**,**c** the base ions are the dinuclear cations (*m*/*e* = 689 and 781). For the PF_6 salt **3a** and for the aryl-NHC complexes **4a**–**c** the base ion is [(C_3H_5)Pd(NHC)]$^+$ (*m*/*e* = 535), as found for the mononuclear halides. However, for **4a**,**b** the dinuclear cation (*m*/*e* = 1105) was also observed in low intensity. In the ESIneg spectra of **3a**–**c** and **4a**–**c** the PF_6 and OTf ions, respectively, furnish the base peaks (no halide ion was detected).

NMR Spectra of 3a–c and 4a–c. In the ambient-temperature NMR spectra of the dinuclear **3a**–**c** and **4a**–**c**, as for the mononuclear **1a**,**b** and **2a**,**b**, five proton and three carbon resonances are found for the allyl ligands, corresponding to an asymmetric coordination at palladium. Likewise, the resonances of the NHC ligands in the *tert*-butyl-substituted **3a**–**c** are in accord with essentially nondynamic coordination, while for the phenyl-substituted **4a**–**c** the resonances indicate rotation about the formal Pd=C bond, but exclude rotation of the phenyl rings about the N–C bonds.

The ^{1}H and ^{13}C NMR spectra of the *N*-alkyl-substituted and chloride-bridged **3a**,**b** are indistinguishable with respect to the cation resonances. Only one set of resonances is observed, which is slightly broadened in the ^{1}H NMR spectra, and in both this seems to be due to an incipient π–σ-allyl rearrangement. For the corresponding *N*-aryl-substituted **4a**,**b** the ^{1}H and ^{13}C NMR spectra of the cation are likewise indistinguishable, but here some of the resonances are doubled. This effect is most clearly seen for the iodide-bridged complexes **3c**, and in particular **4c**, for which two very narrow sets of signals for the allyl and NHC ligands appear at 22 °C. For the chloride-bridged complexes **3a**,**b** and **4a**,**b** the spectra are correspondingly resolved when the temperature is lowered to −30 °C. While for most complexes the intensity ratio of the two sets of signals is close to 1:1 (and thus the resonances cannot be assigned to individual isomers), those of **4c** (major isomer) and **4c′** (minor isomer) appear in an approximate ratio of 3:2 (see Table 2).

Since square-planar (allyl)M(R)X complexes are chiral (clockwise or anti), the dinuclear complexes **3a**–**c** and **4a**–**c** form a mixture of diastereomers. In the meso diastereomer the two (allyl)Pd(R)X moieties have opposite chirality. In view of the bent Pd–μ-X–Pd bond (see molecular structure of **3a**), C_i symmetry of the dinuclear cations is excluded. Thus, for the meso form the rotamer about the Pd–X bonds of highest symmetry has C_s symmetry. In the rac diastereomers the two

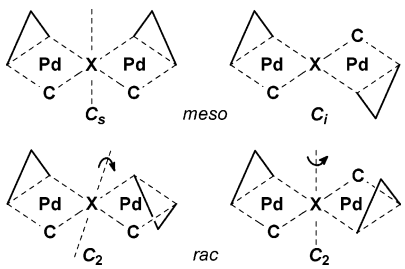


Table 2. ^{1}H and ^{13}C NMR Data of the (η^3-C_3H_5)PdC{N(C_6H_3-2,6-^{i}Pr$_2$)CH}$_2$ Complexes 2a,b, 4a,c, and 6[a]

	Allyl				
	δ(H)			δ(C)	
	H_{meso}	H_{syn}	H_{anti}	C_{meso}	C_{term}
2a	4.84	3.76, 3.08	2.70, 1.57	114.5	71.8, 50.3
2b	4.71	3.88, 3.63	2.47, 1.87	113.1	68.3, 58.9
4a	4.56	3.16, 2.49	2.21, 1.83	115.8	76.9, 51.0
4c	4.44	3.69, ≈2.7	2.03, 1.91	114.5	72.1, 59.9
4c′	4.44	3.67, 2.79	1.98, 1.81	113.7	72.6, 59.8
6	4.52	3.00, 2.56	1.70, 1.40	115.4	58.9, 49.3

	C{N(C_6H_3-2,6-^{i}Pr$_2$)CH}$_2$			
	δ(H)			
	phenyl	NCH	C*H*Me$_2$	CH*Me*$_2$
2a	7.46, 7.31, 7.28	7.19	3.10, 2.83	1.36, 1.31, 1.17, 1.07
2b	7.44, 7.30, 7.27	7.22	3.19, 2.89	1.40, 1.31, 1.17, 1.06
4a	7.45, 7.28, 7.25	7.19	2.73, 2.57	1.24, ..., 1.10, 1.06
4c	7.44, ..., ...	...	≈2.9, ≈2.7	1.24, 1.19, 1.14, 1.04
4c′	7.41, ..., ...	...	≈2.9, ≈2.7	1.25, 1.24, 1.14, 1.05
6	7.41, 7.26, 7.23	7.16	3.13, 2.87	1.32, 1.22, 1.19, 1.06

	δ(C)				
	PdC	phenyl	NCH	*C*HMe$_2$	CH*Me*$_2$
2a	186.2	146.7, 146.5, 136.3, 130.1, 124.2, 124.1	124.7	28.9, 28.8	26.6, 25.8, 23.0, 22.9
2b	185.8	146.6, 146.3, 136.5, 130.2, 124.3, 124.2	125.0	28.9	26.7, 25.9, 23.4, 23.1
4a	183.1	146.4, 146.2, 135.8, 130.7, 124.4, 124.4	125.8	28.9, 28.8	26.6, 25.8, 22.8, 22.6
4c	182.8	146.3, 146.1, 135.8, 130.7, 124.4, 124.3	125.8	28.9	26.8, 25.9, 23.1, 22.8
4c′	182.9	146.2, 146.0, 135.9, 130.7, 124.5, 124.2	125.8	29.1	26.7, 26.0, 23.2, 22.8
6[b]	194.7	146.9, 146.2, 137.1, 129.6, 124.0, 123.9	124.0	28.9, 28.8	26.5, 25.6, 22.9, 22.6

[a] **4c** corresponds to the major diastereomer (≈60%) and **4c′** to the minor (≈40%). Dots mark unresolved resonances. [b] $PdCH_3$: δ(H) −0.37, δ(C) −18.2.

(allyl)Pd(R)X moieties have the same chirality *C,C* or *A,A*. Here, there are two possible prominent rotamers both of C_2 symmetry, and both of them are also possible when the Pd−μ-X−Pd bond is bent such that its bisector corresponds to the 2-fold axis. However, when rotations about the Pd−X bonds allow their interchange, the rotamers will be indistinguishable in the NMR spectra. Thus, the two sets of rather similar NMR spectroscopical data can be attributed to the meso and rac isomers of a diastereomeric mixture with at least some freedom of rotation about the individual Pd−X bonds. Epimerization of these diastereomers is slow for the *N*-aryl-substituted **4a**−**c** at ambient temperature, whereas it is faster for the *N*-alkyl-substituted **3a**,**b** for which the (partly) resolved spectra of the diastereomers first appear at −30 °C.

For **3a**−**c** (Table 1) the ^{1}H and ^{13}C NMR chemical shifts of the NHC ligand almost coincide with those of the mononuclear **1a**,**b**, but the differences in the chemical shifts of the allyl ligand are distinct, and this is especially true for the ^{1}H resonances. For **4a**−**c** (Table 2) only the ^{13}C resonances of the NHC ligand coincide with those of **2a**,**b**, while marked differences are observed for the ^{1}H resonances of the NHC ligand and most of the ^{1}H and ^{13}C allyl resonances.

Structure of 3a. The crystal structure of complex **3a** (Figure 1) was determined by X-ray crystallography. The compound crystallizes with one molecule of diethyl ether and one molecule of dichloromethane for every two ion pairs. Figure 2 shows one of the two independent diastereomeric cations in the unit cell. The space group is acentric ($P2_1$), so the cations are all conformationally chiral. The meso C atoms of all the allyl groups are disordered over two positions, and hence it was not possible to resolve the diastereomers. Although both ends of the cation are chemically identical, the cations exhibit a conformation with C_1 point symmetry, in which the coordination planes of the palladium atoms make different angles to the plane of the central Pd−Cl−Pd unit (plane(Pd1,Cl1,C1,C3,C4)/plane(Pd1,Cl1,-Pd2) 156(2)°, plane(Pd2,Cl1,C15,C17,C18)/plane(Pd1,-Cl1,Pd2) 80(2)°). Interestingly, the two independent cations in the asymmetric unit adopt almost identical conformations (dihedral angles ±4°) despite completely different crystal environments, suggesting that the adopted geometry is the preferred minimum energy conformation. The structure is, however, different from that of the related [{(η^3-C_3H_5)Pd(P^tBu_3)}$_2$(μ-Br)][$B(C_6F_5)_4$], which is described elsewhere.[5]

Complex **3a** is best compared to the mononuclear neutral derivatives **1a**[3h] and (η^3-C_3H_4Me)Pd{C(N(^{t}Bu)-CH)$_2$}Cl (**A**)[3d] or the cationic solvent adducts [(η^3-C_3H_5)-Pd{C(N(C_6H_3-2,6-^{i}Pr$_2$)CH_2)$_2$}(NCMe)]Y (Y = BF_4 (**B**), PF_6 (**C**)).[3g] As for these complexes, the geometry of the palladium atoms in **3a** can be regarded as pseudo-square planar, assuming that only the terminal methylene carbon atoms of the allyl group are coordinated to Pd. It is worth noting that the mean bond lengths of the Pd−Cl half-bridges in **3a** at 2.40 Å (cation 1) and 2.44 Å (cation 2) are only slightly longer than the terminal Pd−Cl bonds in **1a** and **A** (2.39 and 2.38 Å). The mean Pd−C_{NHC} bonds in **3a** are 2.08 Å (cation 1) and 2.06 Å (cation 2) and correspond to those in the parent neutral complexes (2.06 Å for **1a** and **A**) and in the likewise cationic, but mononuclear complexes, **B** (2.07 Å) and **C** (2.05 Å).

As far as the coordination of the allyl group at the Pd center in **3a** is concerned, the Pd−C bonds to the methylene C atoms trans to Cl at 2.10 Å (cation 1) and 2.11 Å (cation 2) are significantly shorter than those to

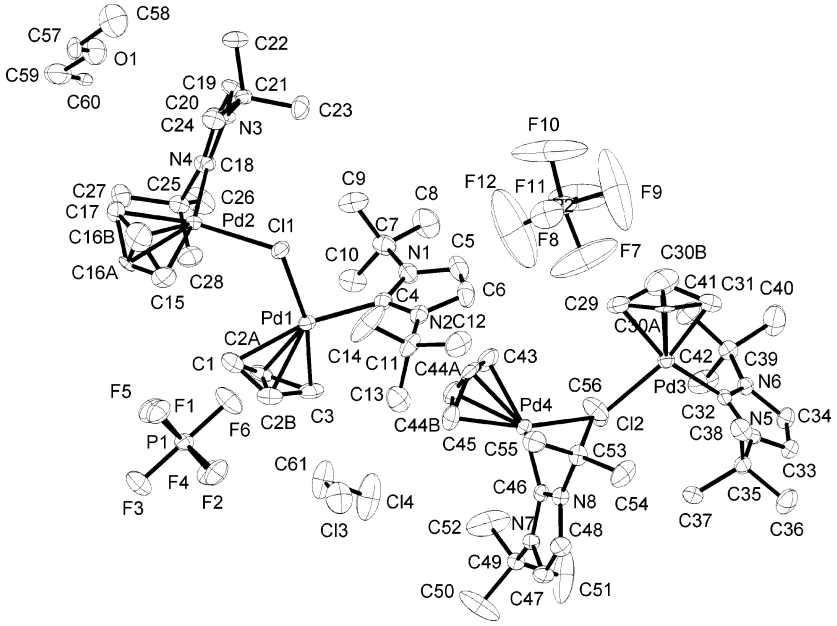


Figure 1. Structure of $[\{(\eta^3\text{-}C_3H_5)Pd(C(N(^tBu)CH)_2)\}_2(\mu\text{-}Cl)][PF_6]\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2Et_2O$ (**3a**) in the crystal.

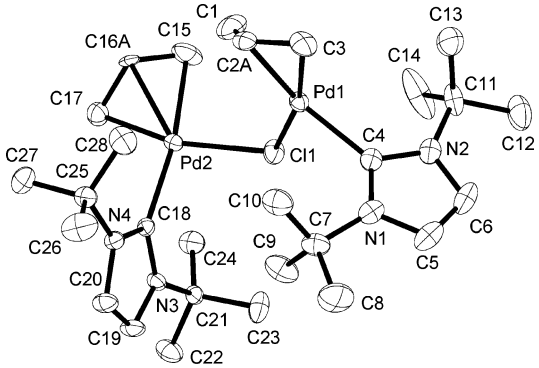


Figure 2. Cation 1 of **3a**. Selected bond distances (Å), angles (deg), and dihedral angles (deg): Pd1−C1 = 2.230(4), Pd1−C3 = 2.095(3), Pd1−C4 = 2.092(3), Pd1−Cl1 = 2.3992(8), Pd2−C15 = 2.190(4), Pd2−C17 = 2.108(3), Pd2−C18 = 2.071(3), Pd2−Cl1 = 2.4020(8), C1−C2A = 1.304(9), C2A−C3 = 1.393(9), C15−C16A = 1.315(7), C16A−C17 = 1.433(6); Pd1−Cl1−Pd2 119.19(3), C1−Pd1−Cl1 = 98.8(1), C3−Pd1−Cl1 = 165.8(1), C1−Pd1−C4 = 166.9(1), C15−Pd2−Cl1 = 96.3(1), C17−Pd2−Cl1 = 163.1(1), C15−Pd2−C18 = 168.4(1); Cl1,Pd1,C4/Cl1,Pd2,C18 112(2).

the methylene C atoms trans to the NHC ligands at 2.21 Å (cation 1) and 2.17 Å (cation 2). A similar bonding situation was encountered for **1a** (2.10 and 2.18 Å, respectively), whereas the difference in bond lengths is less marked for **A** (2.12 and 2.16 Å, respectively). Correspondingly, the C−C bonds of the allyl ligand that are trans to the bridging Cl at 1.41 Å (mean) are longer than those trans to the NHC ligand at 1.31 Å (mean) (**1a**: 1.38 and 1.36 Å). The asymmetric bonding of the allyl group indicates a partial localization of the 4e system.

Synthesis of 6. We have also reacted **2a** with LiMe to afford the methylated **6** (Scheme 1).[8] Colorless **6** is quite stable (dec 130 °C), and it has been characterized by its EI mass and NMR spectra. $(\eta^3\text{-}C_3H_5)Pd(C(N(^tBu)\text{-}CH)_2)CH_3$ has also been prepared very recently; we are presently investigating the protolysis of these complexes by acids of weakly or noncoordinating anions.[9]

Conclusions

We have shown that the reaction of $(\eta^3\text{-}C_3H_5)$Pd(NHC)X complexes (X = halide; **1a**,**b** and **2a**,**b**) with TlY (Y = OTf, PF_6) in a weakly coordinating solvent S (CH_2Cl_2, THF) leads to ionic dinuclear complexes $[\{(\eta^3\text{-}C_3H_5)\text{-}Pd(NHC)\}_2(\mu\text{-}X)]Y$ (**3a**−**c**, **4a**−**c**). The complexes are formed as a mixture of rac and meso diastereomers. The bridging halide ion is tightly coordinated to palladium. The Pd−μ-I−Pd bridges appear stronger than the Pd−μ-Cl−Pd bridges, since whereas the iodide bridges withstand a reaction with excess of TlOTf, the chloride can be partially removed. The halide-free complexes $[(\eta^3\text{-}C_3H_5)Pd(NHC)]PF_6$ or their solvent adducts $[(\eta^3\text{-}C_3H_5)\text{-}Pd(NHC)(S)]PF_6$ are not accessible by this route. These results complement those of ionic dinuclear phosphine derivatives $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ (M = Ni, Pd) with phosphine ligands.[5]

Experimental Part

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$. $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$,[10] $\{(\eta^3\text{-}C_3H_5)PdI\}_2$, and the NHCs[1h,3b,11] were prepared as published. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. EI mass spectra were recorded at 70 eV and refer to ^{35}Cl, ^{106}Pd, and ^{127}I. For the ESI mass spectra an ESQ3000

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instrument was used. ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra at 75.5 MHz (both relative to TMS) on Bruker AMX-300 and DPX-300 instruments. The given NMR data refer to solutions of the compounds in CD_2Cl_2.

(η^3-C_3H_5)Pd{C(N(^{t}Bu)CH)$_2$}Cl (1a). {(η^3-C_3H_5)PdCl}$_2$ (366 mg, 2.00 mmol of Pd) and C(N(^{t}Bu)CH)$_2$ (361 mg, 2.00 mmol) were dissolved in 20 mL of CH_2Cl_2 at 0 °C, and the mixture was stirred for 3 h. The solution was concentrated to about 5 mL, and an equal volume of diethyl ether was added. Cooling to −78 °C gave off-white microcrystals, which were freed from the mother liquor, washed with some cold ether, and dried under vacuum (0 °C): yield 510 mg (70%); dec 191 °C. EI-MS (115 °C): *m/e* (%) 362 ([M]$^+$, 27), 286 ([(NHC)Pd]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 327 ([M − Cl]$^+$, 100). For NMR data, see Table 1. $C_{14}H_{25}ClN_2Pd$ (363.2).

(η^3-C_3H_5)Pd{C(N(^{t}Bu)CH)$_2$}I (1b). Route a. Synthesis was as for **1a**, but starting from {(η^3-C_3H_5)PdI}$_2$ (549 mg, 2.00 mmol of Pd); pale yellow crystals: yield 680 mg (75%). Route b. **1a** (363 mg, 1.00 mmol) was treated with an excess of NaI (ca. 200 mg) in 10 mL of THF at 0 °C for 3 h. After removal of the volatiles under vacuum the residue was extracted with CH_2Cl_2. The extract was concentrated to 5 mL, and an equal volume of diethyl ether was added. Cooling to −78 °C afforded light yellow crystals, which were isolated as described above: yield 340 mg (75%); dec 173 °C. EI-MS (110 °C): *m/e* (%) 454 ([M]$^+$, 7), 327 ([M − I]$^+$, 70), 285 ([M − I − C_3H_6]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 781 ([2M − I]$^+$, 100), 327 ([M − I]$^+$, 100). For NMR data, see Table 1. $C_{14}H_{25}IN_2Pd$ (454.7).

(η^3-C_3H_5)Pd{C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$}Cl (2a). A solution of {(η^3-C_3H_5)PdCl}$_2$ (366 mg, 2.00 mmol of Pd) and C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$ (777 mg, 2.00 mmol) in 30 mL of diethyl ether was stirred at 20 °C for 1 h. Cooling the solution to −60 °C gave light yellow crystals: yield 960 mg (84%); dec 202 °C. EI-MS (145 °C): *m/e* (%) 570 ([M]$^+$, 2), 494 ([(NHC)Pd]$^+$, 31), 387 ([NHC − H]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 535 ([M − Cl]$^+$, 100). For NMR data, see Table 2. $C_{30}H_{41}ClN_2Pd$ (571.5).

(η^3-C_3H_5)Pd{C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$}I (2b). Route a. Synthesis was as for **2a**, but starting from {(η^3-C_3H_5)PdI}$_2$ (549 mg, 2.00 mmol of Pd). Diethyl ether was evaporated under vacuum, and the compound was crystallized from toluene to afford brownish crystals: yield 1.13 g (85%). Route b. **2a** (571 mg, 1.00 mmol) was treated with an excess of NaI (ca. 200 mg) in 10 mL of THF for 3 h. After removal of the volatiles under vacuum the residue was extracted with toluene. Cooling the solution to −78 °C yielded slightly brownish crystals: yield 560 mg (85%); dec 175 °C. EI-MS (155 °C): *m/e* (%) 662 ([M]$^+$, 1), 535 ([M − I]$^+$, 46), 387 ([NHC − H]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 535 ([M − I]$^+$, 100). For NMR data, see Table 2. Anal. Calcd for $C_{30}H_{41}IN_2Pd$ (663.0): C, 54.35; H, 6.23; I, 19.14; N, 4.23; Pd, 16.05. Found: C, 54.30; H, 5.41; I, 18.47; Pd, 15.56.

[{(η^3-C_3H_5)Pd(C(N(^{t}Bu)CH)$_2$)}$_2$(μ-Cl)]PF$_6$·$^1/_2$CH$_2$Cl$_2$·$^1/_2$Et$_2$O (3a). A mixture of **1a** (726 mg, 2.00 mmol) and TlPF$_6$ (350 mg, 1.00 mmol) in 20 mL of CH_2Cl_2 was stirred at 0 °C for 3 h. The precipitated TlCl was removed by filtration. After addition of an about equal volume of diethyl ether (at the end dropwise) the solution was cooled to −40 °C for 3 days to afford pale yellow crystals: yield 690 mg (76%); dec 115 °C. EI-MS (195 °C): *m/e* (%) 362 ([**1a**]$^+$, 13), 286 ([(NHC)Pd]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 327 ([(C_3H_5)Pd(NHC)]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 145 ([PF_6]$^-$, 100). For NMR data, see Table 1. Anal. Calcd for $C_{28}H_{50}ClN_4Pd_2{\cdot}F_6P{\cdot}C_{0.5}HCl{\cdot}C_2H_5O_{0.5}$ (907.5): C, 40.01; H, 6.17; Cl, 7.74; F, 12.45; N, 6.12; O, 0.87; P, 3.38; Pd, 23.25. Found: C, 40.38; H, 5.72; N, 6.61; Pd, 24.85. The elemental analysis is high for C, N, and Pd due to the loss of solvate molecules.

Crystal data for 3a: $[C_{28}H_{50}ClN_4Pd_2]^+[PF_6]^-{\cdot}0.5[C_4H_{10}O]{\cdot}0.5[CH_2Cl_2]$, from diethyl ether/dichloromethane, M_r = 1830.93, crystal size 0.06 × 0.15 × 0.21 mm, a = 11.7790(1) Å, b = 16.7882(1) Å, c = 19.3921(1) Å, β = 90.7460(3)°, V = 3834.43(4) Å^3, T = 100 K, monoclinic, space group $P2_1$ (No. 4), Z = 2, d_{calcd} = 1.586 g cm^{-3}, F(000) = 1864, Nonius KappaCCD diffractometer, λ(Mo Kα) = 0.71073 Å, μ = 1.176 mm^{-1}, 87 312 measured and 23 159 independent reflections (R_{int} = 0.0374), 22 074 with $I > 2\sigma(I)$, θ_{max} = 31.49°, T_{min} = 0.790, T_{max} = 0.937, direct methods (SHELXS-97) and least-squares refinement (SHELXl-97) on F_o^2, both programs from G. Sheldrick, University of Göttingen, 1997; 865 parameters, all the meso C atoms in the η^3-allyl groups disordered over two positions (50:50), Flack parameter −0.01(1), H atoms riding, Chebyshev weights, R_1 = 0.0335 ($I > 2\sigma(I)$), wR_2 = 0.0853 (all data), $\Delta\rho_{max/min}$ = 1.327/−1.143 e Å^{-3} (1.2/0.78 Å from Cl4).

[{(η^3-C_3H_5)Pd(C(N(^{t}Bu)CH)$_2$)}$_2$(μ-Cl)]OTf (3b). A mixture of **1a** (726 mg, 2.00 mmol) and TlOTf (353 mg, 1.00 mmol) in 15 mL of CH_2Cl_2 was stirred at 0 °C for 2 h. The precipitated TlCl was removed by filtration. Diethyl ether (20 mL) was added to the solution, at the end dropwise, to afford a colorless precipitate. The solid was separated by filtration and dried under vacuum (0 °C): yield 714 mg (85%). For NMR data, see **3a** in Table 1. EI-MS (170 °C): *m/e* (%) 362 ([**1a**]$^+$, 6), 327 ([(C_3H_5)Pd(NHC)]$^+$, 5), 285 ([Pd(NHC) − H]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 689 ([M − OTf]$^+$, 100), 327 ([(C_3H_5)Pd(NHC)]$^+$, 30). ESIneg-MS (CH_2Cl_2): *m/e* (%) 149 ([OTf]$^-$, 100). $C_{28}H_{50}ClN_4Pd_2{\cdot}CF_3O_3S$ (840.1).

[{(η^3-C_3H_5)Pd(C(N(^{t}Bu)CH)$_2$)}$_2$(μ-I)]OTf (3c). Synthesis was as for **3b**, but starting from **1b** (910 mg, 2.00 mmol). Light brown crystals were isolated: yield 710 mg (76%); dec 160 °C. EI-MS (150 °C): *m/e* (%) 476 ([(C_3H_5)Pd(NHC)(OTf)]$^+$, 2), 454 ([**1b**]$^+$, 5), 327 ([(C_3H_5)Pd(NHC)]$^+$, 34), 285 ([Pd(NHC) − H]$^+$, 68). ESIpos-MS (CH_2Cl_2): *m/e* (%) 781 ([M − OTf]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 149 ([OTf]$^-$, 100). For NMR data, see Table 1. Anal. Calcd for $C_{28}H_{50}IN_4Pd_2{\cdot}CF_3O_3S$ (931.5): C, 37.39; H, 5.41; F, 6.12; I, 13.62; N, 6.01; O, 5.15; Pd, 22.85; S, 3.44. Found: C, 37.04; H, 5.54; N, 6.01.

[{(η^3-C_3H_5)Pd(C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$)}$_2$(μ-Cl)]PF$_6$·THF (4a). A mixture of **2a** (1144 mg, 2.00 mmol) and TlPF$_6$ (350 mg, 1.00 mmol) in 20 mL of CH_2Cl_2 was stirred for 3 h (20 °C). The precipitated TlCl was removed by filtration, and the solvent was evaporated under vacuum. The residue was redissolved in THF, and twice the amount of diethyl ether was added. Cooling to −40 °C for 3 days afforded pale yellow crystals: yield 1.03 g (78%); dec 138 °C. EI-MS (205 °C): *m/e* (%) 570 ([**2a**]$^+$, 1), 535 ([(C_3H_5)Pd(NHC)]$^+$, 2), 494 ([Pd(NHC)]$^+$, 20), 387 ([NHC − H]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 1105 ([M − PF_6]$^+$, 10), 535 ([(C_3H_5)Pd(NHC)]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 145 ([PF_6]$^-$, 100). For NMR data, see Table 2. Anal. Calcd for $C_{60}H_{82}ClN_4Pd_2{\cdot}F_6P{\cdot}C_4H_8O$ (1324.7): C, 58.03; H, 6.85; Cl, 2.68; F, 8.60; N, 4.23; O, 1.21; P, 2.34; Pd, 16.07. Found: C, 57.83; H, 7.06; N, 4.07; Pd, 15.80.

[{(η^3-C_3H_5)Pd(C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$)}$_2$(μ-Cl)]OTf (4b). A mixture of **2a** (1144 mg, 2.00 mmol) and TlOTf (353 mg, 1.00 mmol) in 20 mL of CH_2Cl_2 was stirred for 1 h (20 °C). The precipitated TlCl was removed by filtration, the solution was concentrated under vacuum to 10 mL, and about 10 mL of diethyl ether was added dropwise. Keeping the solution at 0 °C for 2 days afforded colorless microcrystals: yield 820 mg (65%); dec 144 °C. EI-MS (170 °C): *m/e* (%) 684 ([(C_3H_5)Pd(NHC)(OTf)]$^+$, 1), 570 ([**2a**]$^+$, <1), 535 ([(C_3H_5)Pd(NHC)]$^+$, 4), 494 ([Pd(NHC)]$^+$, 21), 387 ([NHC − H]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 1105 ([M − OTf]$^+$, 1), 535 ([(C_3H_5)Pd(NHC)]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 149 ([OTf]$^-$, 100). For NMR data, see **4a** in Table 2. $C_{60}H_{82}ClN_4Pd_2{\cdot}CF_3O_3S$ (1256.7).

[{(η^3-C_3H_5)Pd(C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$)}$_2$(μ-I)]OTf (4c). Synthesis was as for **4b**, but starting from **2b** (1326 mg, 2.00 mmol). Light brown crystals were obtained: yield 930 mg (69%); dec 170 °C. EI-MS (175 °C): *m/e* (%) 684 ([(C_3H_5)Pd(NHC)(OTf)]$^+$, 1), 662 ([**2b**]$^+$, <1), 535 ([(C_3H_5)Pd(NHC)]$^+$, 27), 494 ([(NHC)Pd]$^+$, 10), 389 ([NHC + H]$^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 535 ([(C_3H_5)Pd(NHC)]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 149 ([OTf]$^-$, 100). For NMR data, see Table 2. Anal. Calcd for $C_{60}H_{82}IN_4Pd_2{\cdot}CF_3O_3S$ (1348.2): C, 54.35; H,

6.13; F, 4.23; I, 9.41; N, 4.16; O, 3.56; Pd, 15.79; S, 2.38. Found: C, 54.23; H, 6.25; I, 9.36; N, 4.13; Pd, 15.55.

(η^3-C_3H_5)Pd{C(N(C_6H_3-2,6-^{i}Pr$_2$)CH)$_2$}CH_3 (6). To a solution of **2a** (572 mg, 1.00 mmol) in 20 mL of diethyl ether was added a 1.6 M ethereal solution of LiMe (0.7 mL, 1.1 mmol) at −40 °C. The mixture was allowed to warm to ambient temperature and was stirred for 2 h. After removal of the volatiles under vacuum the residue was extracted twice with 10 mL of pentane, and the solution was concentrated to about 10 mL. Cooling to −40 °C for 2 days afforded colorless crystals: yield 425 mg (77%); dec 130 °C. EI-MS (105 °C): *m/e* (%) 550 ([M]$^+$, 1), 535 ([M − Me]$^+$, 35), 389 ([NHC + H]$^+$, 100). For NMR data, see Table 2. Anal. Calcd for $C_{31}H_{44}N_2Pd$ (551.1): C, 67.56; H, 8.05; N, 5.08; Pd, 19.31. Found: C, 67.83; H, 7.75; N, 5.08; Pd, 19.24.

Supporting Information Available: Tables of X-ray data collection information, atom coordinates and thermal parameters, and bond lengths and angles, together with CIF data, for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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