

First silver complexes of tetrahydropyrimid-2-ylidenes ^{☆,☆☆}

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Received 15 March 2004; accepted 25 April 2004

Abstract

The syntheses and characterizations of homoleptic silver(I) carbene complexes of the type $LAgCl$ (**3**) and $[L_2Ag]_2^+ [Pd_2Cl_6]^{2-}$ (**4**) (L = dimesityltetrahydropyrimid-2-ylidene) are described. **3** was obtained by reaction of the corresponding tetrahydropyrimidinium salt with silver(I) oxide. Subsequent reaction of **3** with $Pd(CH_3CN)_2Cl_2$ afforded complex **4**. The crystal structure of **3** has been determined to be a monomer in the solid state. The ^{13}C NMR spectra of both **3** and **4** exhibit ^{13}C – $^{107,109}Ag$ coupling in solution. Furthermore, both compounds show a downfield shift of the carbene carbon of about 20 ppm to about 205 ppm in the ^{13}C NMR compared to five-membered ring silver(I) carbene complexes. Unlike other silver–carbene complexes, **3** does not undergo ligand exchange and can thus not be used for carbene transfer to other metals.

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Keywords: Silver; Palladium; Tetrahydropyrimid-2-ylidenes

1. Introduction

N-Heterocyclic carbenes have become universal ligands in organometallic and inorganic coordination chemistry [1,2]. There is current interest in novel, stronger donating *N*-heterocyclic carbene ligands. The acyclic bis(dialkylamino)carbenes published by Alder et al. [3] turned out to be the strongest σ -donating carbene ligands so far [4]. Due to their six-membered ring geometry tetrahydropyrimid-2-ylidenes are supposed to be comparable to those systems [4].

Recently our group has shown, that Grubbs type ruthenium complexes with isopropyl and mesityl

substituted tetrahydropyrimid-2-ylidene ligands can be successfully employed as catalysts in olefin metathesis reactions [5].

A very efficient way to obtain NHC metal complexes has been published by Wang and Lin [6]. They described the use of silver(I) complexes which are formed easily by treatment of imidazolium salts with Ag_2O . These compounds are able to transfer their NHC ligand to other metals for e.g. gold or palladium [7].

Silver(I) carbene complexes display a wide variety of structural motives depending on the size of the coordinated carbene [8]. These species tend to oligomerize via silver–silver interactions, bridging halide ligands, or even $Ag-(\mu_2-C_{carbene})-Ag$ interactions [9]. Monomeric examples of such complexes are rare. In fact, only two monomeric carbene complexes of $AgCl$ have been characterized to date [10].

In recent publications, Buchmeiser and co-workers [11] address the synthesis and catalytic properties of tetrahydropyrimid-2-ylidene complexes of palladium. Significant differences between their report and our ongoing studies prompted us to publish our results at this time.

[☆] Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2004.04.032](https://doi.org/10.1016/j.jorganchem.2004.04.032).

^{☆☆} *N*-heterocyclische carbene, Part 37. – Part 36, see [7b].

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2. Results and discussion

2.1. Synthesis and characterization of the ligand and its silver complexes

The synthesis of the tetrahydropyrimidinium salt **2** is achieved in two steps (Scheme 1). Starting from mesityl bromide and 1,3-diaminopropane, the corresponding mesityl substituted diamine **1** is prepared by a palladium catalyzed arylation. Subsequent reaction of the diamine **1** with triethyl orthoformate and ammonium tetrafluoroborate according to Saba and Kaloustian [12] yielded the tetrahydropyrimidinium salt **2**. The silver(I) carbene complex **3** was obtained after stirring tetrahydropyrimidinium salt **2** in CH_2Cl_2 with Ag_2O for 4 h and workup of the filtered solution in 78% yield. This compound was expected to serve as a carbene transfer agent to obtain the corresponding Pd(II) compounds. Therefore **3** was treated with $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ according to a literature procedure for comparable imidazol-2-ylidene compounds [7c] to obtain a biscarbene Pd(II) compound according to Scheme 2. Yet, we obtained the biscarbene Ag(I) compound **4** (Scheme 2) which was identified unambiguously by thorough analysis (see below). Thus the Ag(I) carbene **3** did not transfer its carbene ligand to Pd but its chloride ligand and a second equivalent of **3** then obviously transferred its carbene ligand to the silver monocarbene unit to build a biscarbene Ag(I) cation. The reactivity is therefore reversed to known examples with imidazol-2-ylidene compounds. In contrast to our results, Buchmeiser and co-workers [11a], who carried out the same reaction, claimed to obtain the biscarbene palladium(II) complex $[\text{L}_2\text{Pd}]_2^{2+}[\text{Ag}_2\text{Br}_2\text{Cl}_6]^{4-}$ (L = dimesityltetrahydropyrimid-2-ylidene) **8**. We will demonstrate below, that this claim is unsound.

2, **3** and **4** can be obtained after recrystallization from acetone/toluene (**2**) or DCM/pentane (**3**, **4**) as colorless

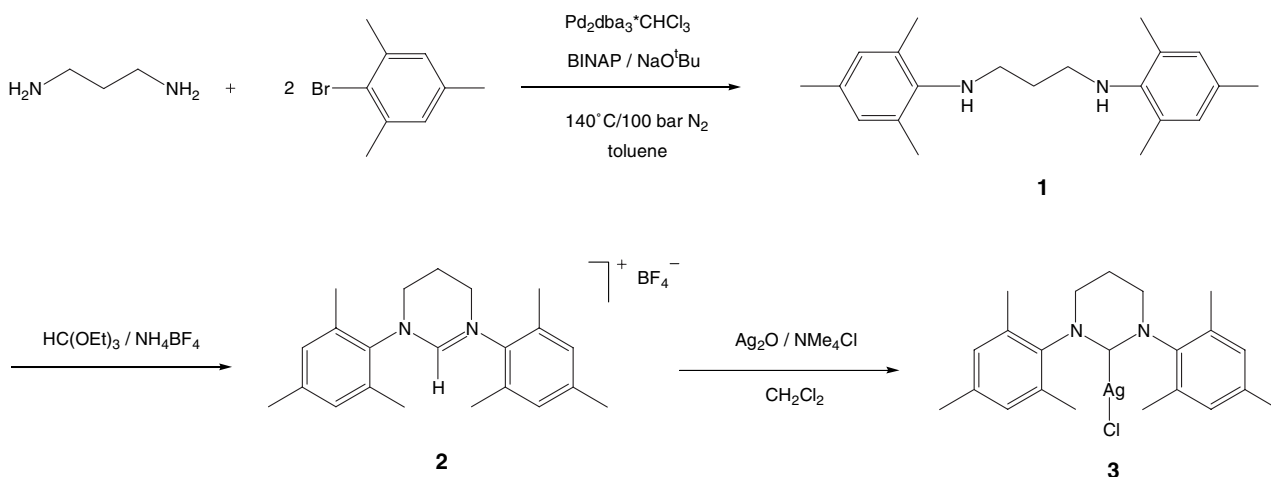
(**2**, **3**) or reddish brown (**4**), crystalline materials, which are readily soluble in most common polar organic solvents (DCM, THF), but insoluble in hexane or diethyl ether. The carbene compounds **3** and **4** are stable against daylight and thermally stable at room temperature. The molecular structures of **2**, **3** and **4** were determined by X-ray diffraction.

Additionally, the compounds were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis and FAB-MS. The spectroscopic data obtained for **2**, **3** and **4** are in accord with the crystallographically determined structures.

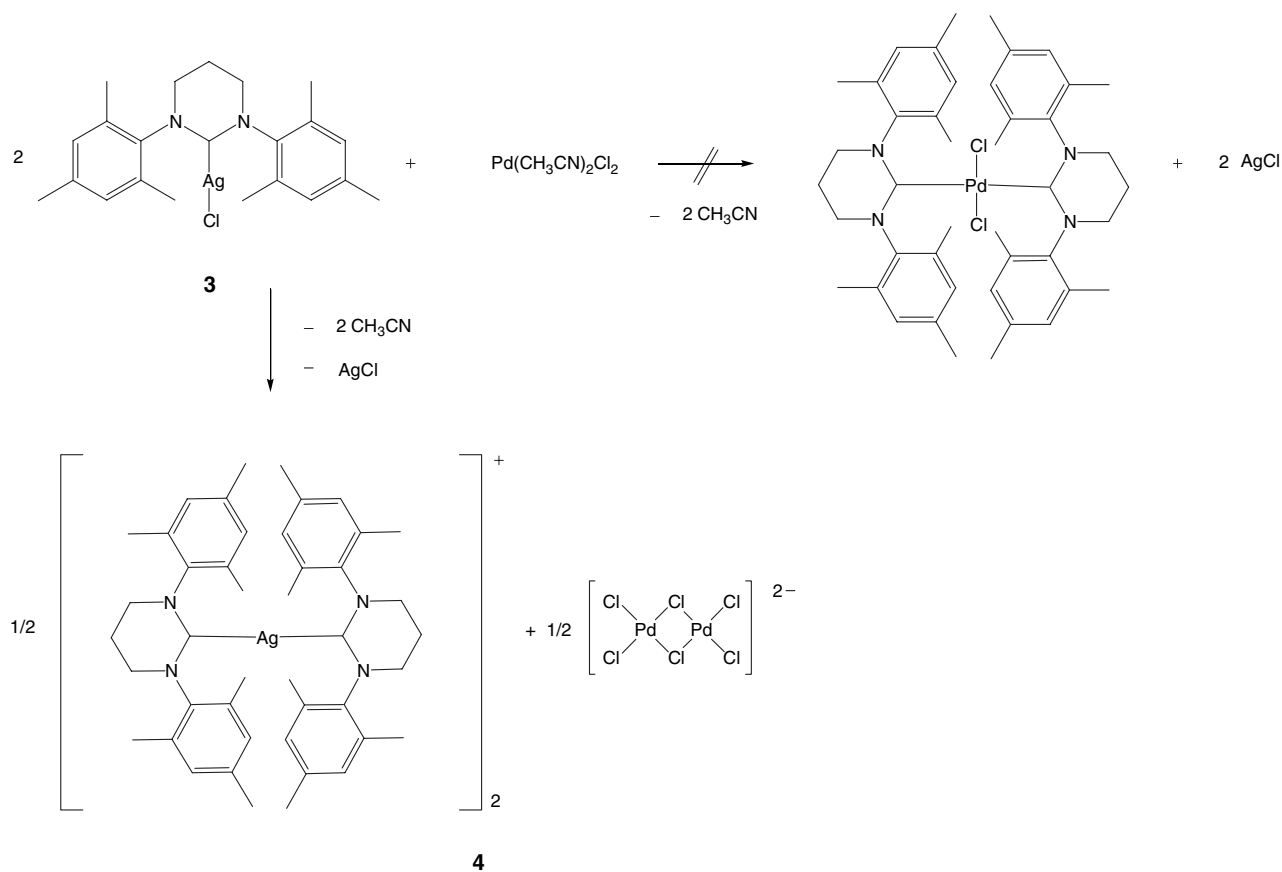
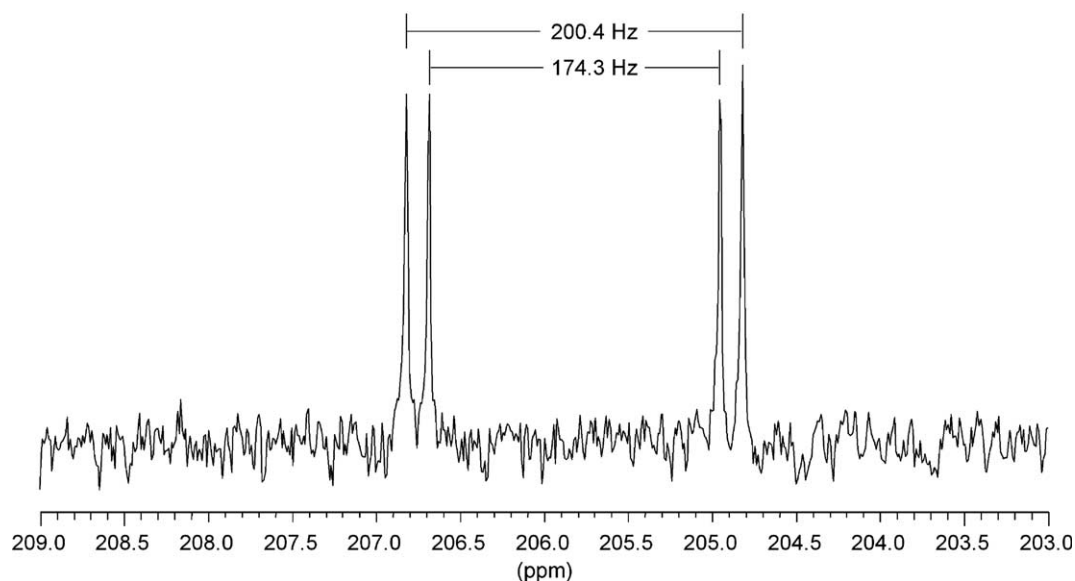
In the case of **3** and **4**, direct information concerning the Ag–C interaction were obtained from the ^{13}C NMR spectra, since ^{107}Ag and ^{13}C – ^{109}Ag coupling is observed for the carbene carbon atom (**3**: 228.4 and 260.4 Hz, **4**: of 174.3 and 201.3 Hz) (Fig. 1).

This information directly confirms that neither **3** nor **4** show a lability of the Ag–carbene bond. This is unexpected, as most of the up to now published compounds of the kind (carbene)AgX show a fluxional behaviour described by Wang and Lin [6], that results in a lack of C–Ag coupling. This aspect and the downfield shift of the carbene carbon atom in the ^{13}C NMR spectra of about 20 ppm from 180 to 200 ppm (205.9 ppm (**3**), 205.8 ppm (**4**)) with respect to literature data [6–10] is probably a result of the stronger metal–carbene bond in tetrahydropyrimid-2-ylidene complexes compared to imidazol-2-ylidene complexes. Therefore the transfer of the carbene ligand to other metals has failed. The work of Buchmeiser and co-workers [11a] misses the ^{13}C NMR signal for the carbon atom in **8**, making it impossible to distinguish between an Ag–carbene and a Pd–carbene bond.

As expected, the mass spectrum of compound **2** contains only one peak, the tetrahydropyrimidinium cation. For the Ag(I) carbene complexes **3** and **4**, the most prominent peak in the mass spectra is a [(car-



Scheme 1. Synthesis of **1**, **2** and **3**.

Scheme 2. Synthesis of the homoleptic tetrahydropyrimid-2-ylidene silver(I) complex **4**.Fig. 1. ¹³C–^{107,109}Ag coupling observed for **4** (solvent: CD₂Cl₂).

bene)₂Ag]⁺ fragment, which in the case of **3** is obviously formed under FAB-MS conditions. A second peak that belongs to the [(carbene)Ag]⁺ cation, indicates the molecular structure of the type (carbene)AgX already determined by X-ray diffraction analysis for **3**. This peak is

also part in the FAB-MS of **4**. In both spectra (for **3** and **4**) the isotope patterns are in accordance with silver carbene fragments (Fig. 2). In contrast, palladium carbene fragments as derived from compound **8** would exhibit a quite different isotope pattern.

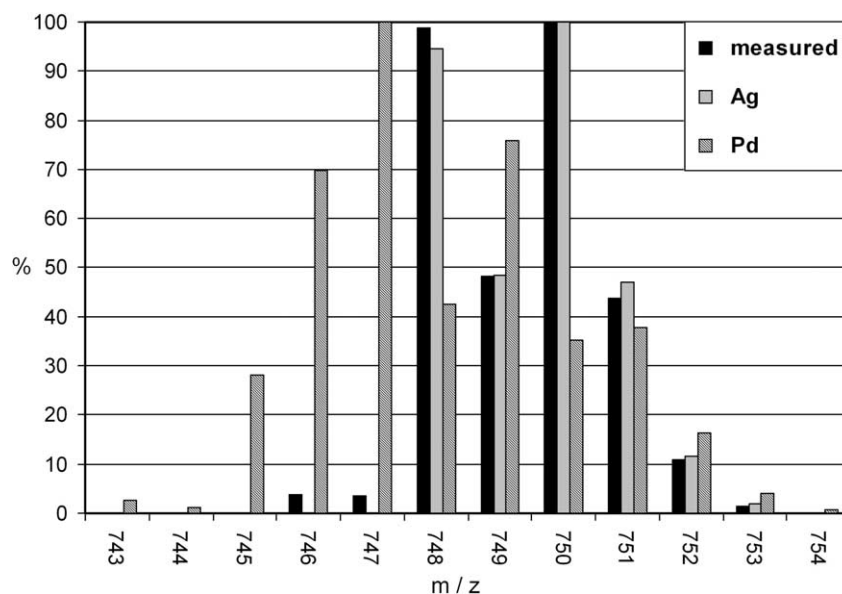


Fig. 2. Details of the FAB-MS spectrum of **4**. Measured and calculated isotope patterns for the $[(\text{carbene})_2\text{Ag}]^+$ fragment in **4** versus $[(\text{carbene})_2\text{Pd}]^+$.

2.2. Molecular structures of **2**, **3** and **4**

The related compounds **5**, **6** and **7** have been previously reported from different synthetic routes and serve as interesting comparisons [13,10b,14].

The molecular structure of the tetrahydropyrimidinium salt **2** in the solid state is depicted in Fig. 4 being the first structure of a tetrahydropyrimidinium salt with aromatic substituents on both nitrogen atoms. It is very similar to that of the corresponding diisopropyltetrahydropyrimidinium salt reported by Alder et al. (Table 1) [13]. The detected $\text{N}-\text{C}_{\text{carbene}}-\text{N}$ angles and $\text{C}_{\text{carbene}}-\text{N}$ distances of **2** are nearly identical to the one published by Alder [13].

The molecular structure of **3** in the solid state is shown in Fig. 5. It is up to now the first structure of a silver(I) tetrahydropyrimid-2-ylidene complex. Most

examples of such silver(I) carbene complexes are similar to $[\text{Ag}(\text{Et}_2\text{-bimy})_2][\text{AgBr}_2]$ (bimy = 1,3-diethylbenzimidazol-2-ylidene), the first Ag(I) carbene complex synthesized via the Ag_2O way [6]. As mentioned above, monomeric examples of such complexes are rare. One of them is the corresponding 1,3-bismesityl-imidazol-2-ylidene silver(I) chloride **6** reported by Abernethy and co-workers [10b] (Fig. 3) which is compared with **3** in Table 1.

The complexes **3** and **6** (Fig. 6) enable us to compare the structural differences between imidazolin-2-ylidene complexes and tetrahydropyrimid-2-ylidene complexes. The transition from the five-membered to the six-membered ring geometry causes a widening of the $\text{N}-\text{C}_{\text{carbene}}-\text{N}$ bond angle from about 105° in imidazole complexes to $124.72(15)^\circ$ in **3**. This results in a compression of the α -angle $\text{C}_{\text{mesityl}}-\text{N}-\text{C}_{\text{carbene}}$ from $121.8(3)^\circ$

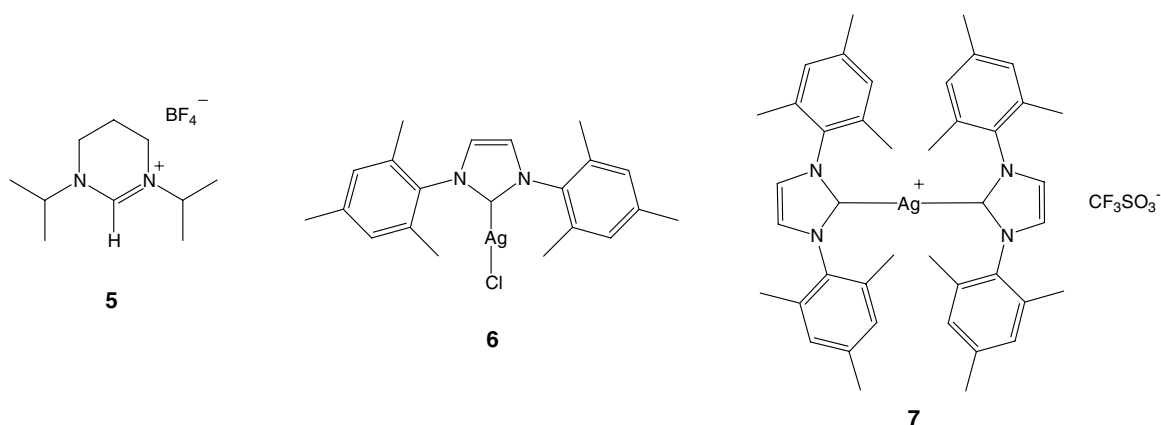


Fig. 3. Related compounds for comparison.

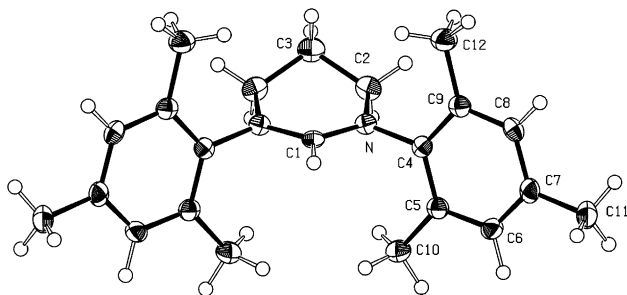


Fig. 4. ORTEP representation of the mono-cationic part of compound **2** in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

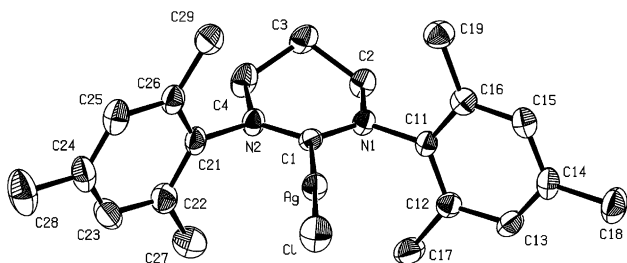


Fig. 5. ORTEP representation of compound **3** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

in the imidazole complex from Abernethy and co-workers [10b] to $119.4(2)^\circ$ and $118.5(2)^\circ$ in **3** (Table 1, Fig. 6). The $C_{\text{carbene}}\text{-Ag}$ distance of $2.095(3)$ Å in **3** is slightly longer than the one reported for the corresponding imidazol-2-ylidene compound ($2.056(7)$ Å) (Table 1) [10b]. This reflects the steric congestion around the metal center for the six-membered ring ligand.

The molecular structure of **4** in the solid state is depicted in Fig. 7. The comparison between compound **4** and the corresponding imidazolin-2-ylidene complex **7** previously reported by Arduengo et al. [14] also reveals the differences, caused by the transition from five-membered to six-membered ring geometry. The $\text{N-C}_{\text{carbene}}\text{-N}$ bond angle is widened from $103.6(4)^\circ$ and $104.8(4)^\circ$ [14] to $118.7(2)^\circ$ and $118.0(2)^\circ$ (Table 1). Therefore again the α -angles $C_{\text{mesityl}}\text{-N-C}_{\text{carbene}}$ are

compressed from average $125.4(4)^\circ$ [14] to average $118.4(2)^\circ$ (Table 1). Like in the monomeric Ag(I) carbene complex **3** discussed above, the $C_{\text{carbene}}\text{-Ag}$ distances of $2.101(3)$ and $2.097(3)$ Å are longer than those reported for the corresponding imidazol-2-ylidene compound $2.067(4)$ and $2.078(4)$ Å [14] (Table 1), indicating once more the higher steric bulk of the six-membered ligand.

The silver atom essentially is linear coordinated ($178.33(10)^\circ$) as it is known from the previously reported compound **7** ($176.3(2)^\circ$) [14]. The planes of the two tetrahydropyrimid-2-ylidene rings are twisted by $86.1(4)^\circ$ from coplanarity ($39.5(7)^\circ$ in **7**). This orientation of the two tetrahydropyrimid-2-ylidene rings is likely the result of steric repulsion between the mesityl substituents on the nitrogens.

In summary, our analytical data prove that the reaction of the tetrahydropyrimid-2-ylidene silver(I) complex **3** with $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ yields the biscarbene silver(I) complex **4** as depicted in Scheme 2 and not the palladium(II) complex **8** published by Buchmeiser and co-workers [11a]. Our assignment is based on the following facts:

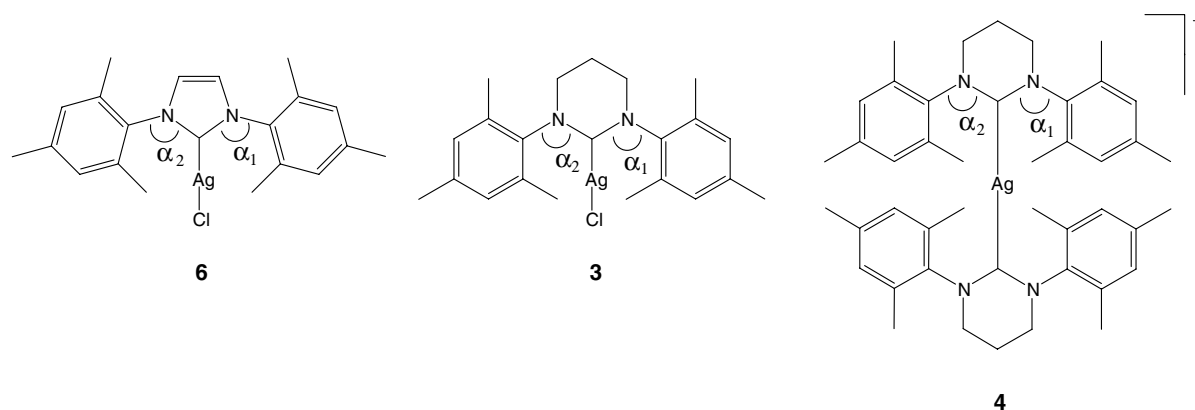
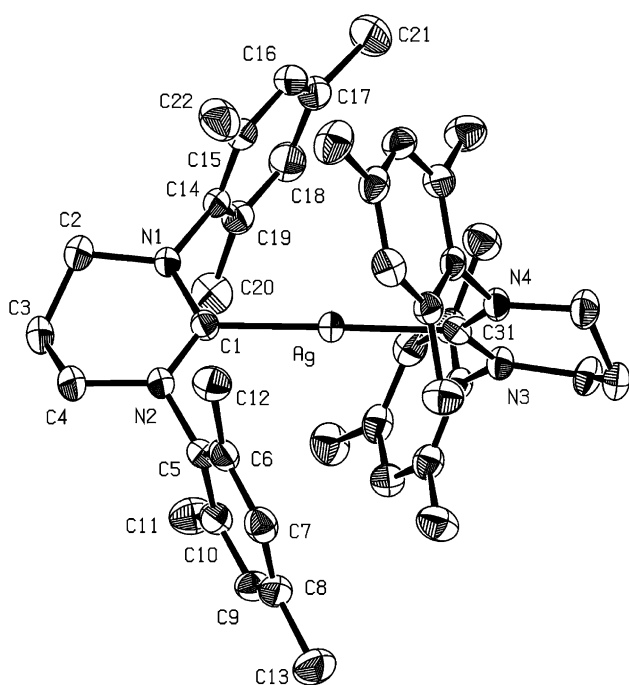
- The structural data of compound **8** are very similar to the data for the silver complex **4**. It is difficult to assign silver and palladium atoms positions only based upon X-ray data without confirmation by further analytical methods. However, calculations with silver in the cationic and palladium in the anionic part of structure **4** result in significantly better R -values compared to the inverse option proposed by Buchmeiser et al.
- The carbene carbon atom in the ^{13}C NMR spectrum of complex **4** exhibits $^{13}\text{C}\text{-}^{107}\text{Ag}$ and $^{13}\text{C}\text{-}^{109}\text{Ag}$ coupling. This coupling weakens the signal of the carbene carbon atom compared to a palladium compound of type **8**. Because of this reason Buchmeiser and co-workers may not have detected a carbene signal in the ^{13}C NMR.
- In the FAB-MS of **4**, all fragments that include the metal center, show an isotope pattern which is consistent with a Ag containing moiety. The isotope pattern of the postulated complex **8** is not represented in the

Table 1

Selected bond angles ($^\circ$) and bond lengths (Å) in **2**, **3**, **4** and related structures (for α_1 and α_2 , see Fig. 6)

	2	5 [13]	3	6 [10b]	4 ^a	7 ^a [14]
$\text{N-C}_{\text{carbene}}\text{-N}$	124.72(15)	125.0(2)	118.3(3)	104.4(5)	118.7(2) 118.0(2)	103.6(4) 104.8(4)
$C_{\text{ipr/mes}}\text{-N-C}_{\text{carbene}}$ (α_1)	120.38(11)	119.6(2)	119.4(2)	121.8(3)	117.3(2) 117.9(2)	125.4(4) 124.3(4)
$C_{\text{ipr/mes}}\text{-N-C}_{\text{carbene}}$ (α_2)	120.38(11)	119.6(2)	118.5(2)	121.8(3)	118.6(2) 119.7(2)	126.3(4) 124.6(4)
$C_{\text{carbene}}\text{-Ag-C}_{\text{carbene}}$	–	–	–	–	178.33(10)	176.3(2)
$C_{\text{carbene}}\text{-N}$ (α_1 -site)	1.3147(14)	1.311(3)	1.338(4)	1.357(5)	1.337(4) 1.343(4)	1.356(6) 1.360(6)
$C_{\text{carbene}}\text{-N}$ (α_2 -site)	1.3147(14)	1.311(3)	1.329(4)	1.357(5)	1.332(3) 1.332(4)	1.352(6) 1.3556(6)
$C_{\text{carbene}}\text{-Ag}$	–	–	2.095(3)	2.056(7)	2.101(3) 2.097(3)	2.067(4) 2.078(4)
Ag-Cl	–	–	2.3213(10)	2.314(2)	–	–

^a In italic the corresponding values for the second carbene coordinated to the metal center.

Fig. 6. α -Angle in **3**, **4** and **6**.Fig. 7. ORTEP representation of the mono-cationic part of compound **4**·**5**(CH₂Cl₂) in the solid state. Thermal ellipsoids are at the 50% probability level. The hydrogen atoms are omitted for clarity.

publication of Buchmeiser and co-workers [11a]. Nevertheless, as a mono charged cation it would show a very different isotope pattern. A double charged [(carbene)₂Pd]²⁺ should be found at $m/z \approx 374$.

- The structural elements in compound **8**, both the [Ag₂X₆]⁴⁻ anion and the linear coordinated ligand Pd(II) dication are without precedence in literature.
- The brownish colour of complex **8** indicates rather a [Pd₂X₆]²⁻ anion instead of a [Ag₂X₆]⁴⁻ anion. Biscarbene palladium(II) compounds are colourless (cf. compound **16** in [11a]).
- The Heck coupling results obtained using **8** as a catalyst don't necessarily indicate a palladium carbene

complex as the active catalyst species. Heck coupling reactions have been reported to be catalyzed by simple palladium(II) salts [15].

3. Conclusion

We have synthesized and characterized first homoleptic tetrahydropyrimidine ylidene silver(I) complexes. The X-ray crystallographic structures of **3** and **4** show a nearly linear geometry for the silver center. The crystal structure of **3** has been determined to be a monomer in the solid state. The NMR spectra of this carbene complexes exhibit coupling of the silver nucleus with the carbene carbon atoms. Unlike many silver complexes of this type, the silver(I) compound **3** does not undergo a rapid ligand exchange. The signals of the carbene carbon atoms of **3** and **4** in the ¹³C NMR spectra are downfield shifted of about 20 ppm to about 205 ppm compared to silver(I) carbene complexes of five-membered ring systems (about 180 ppm). This aspect and the observation that the transfer of a carbene ligand to palladium(II) failed, indicate that the Ag–carbene bond is much stronger than in comparable five-membered ring systems. Therefore this new class of carbene ligands provide stronger σ -donating ligands compared to imidazol-2-ylidene systems. Correspondingly, the reported results of Buchmeiser and co-workers concerning the palladium biscarbene **8** are wrong as we have mentioned above. Further utilization of these compounds for the preparation of transition metal carbene complexes and their use in catalytic reactions is under investigation.

4. Experimental

4.1. General comments

NMR spectra (¹H, ¹³C) were recorded either on a Jeol JMX-GX 400, on a Jeol JMX-GX 270 or on a Bruker

DPX 400 instrument. Chemical shifts are given in ppm. The spectra are calibrated to the residual protons of the solvent (^1H) or to the 13-carbon signals of the solvent (^{13}C). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, q = quintet, m = multiplet. Coupling constants J are given in Hz. FAB-MS spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer (xenon/*p*-nitrobenzyl alcohol). Elemental analyses were carried out by the Microanalytical Laboratory at the TU München.

Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques. All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. Other chemicals were obtained from commercial sources and used without further purification.

4.2. *N,N'*-Dimesitylpropanediamine (**1**)

A 100 ml round-bottom flask was charged $\text{Pd}_2(\text{dba})_3$ (91.6 mg, 0.10 mmol) and (rac)-BINAP (124.6 mg, 0.30 mmol). The mixture was dissolved in toluene (60 ml) at room temperature. Mesityl bromide (15.93 g, 80.0 mmol) and 1,3-diaminopropane (2.56 g, 40.0 mmol) were added to the solution and stirred for 10 min. The solution was transferred into a glass tube containing NaOt-Bu (8.96 g, 93.2 mmol) in an autoclave and was stirred under nitrogen pressure for 70 h at 140 °C in a 250 ml autoclave. After the reaction finished, the solution was washed with toluene. After thorough washing, the water layer containing the salt was treated with NaOH to give *N,N'*-dimesitylpropanediamine as a yellowish brown oil, which was separated and dried in vacuo (yield, 9.68 g, 80%).

^1H (400 MHz, CDCl_3): δ [ppm] = 6.81 (s, 4H, MesH), 3.51 (br, 4H, NCH_2), 2.95 (br, 2H, NH), 2.25 (s, 12H, MesCH₃), 2.22 (s, 6H, MesCH₃), 1.87 (q, J = 7.2 Hz, 2H, CH₂). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3): δ [ppm] = 143.5, 131.4, 129.7, 129.4 (MesC), 47.1 (NCH_2), 32.6 (CH₂), 20.5 (MesCH₃), 18.3 (MesCH₃).

4.3. *N,N'*-Dimesityl-tetrahydropyrimidinium tetrafluoroborate (**2**)

A mixture of dimesitylpropanediamine **1** (3.22 g, 10.4 mmol, 1.0 eq.), NH_4BF_4 (1.09 g, 10.4 mmol, 1.0 eq.), and HC(OEt)_3 (1.54 g, 10.4 mmol, 1.0 eq.) was stirred at 135 °C for 17 h. The crude product, after washing with toluene, was extracted with acetone. Removal of the solvent gave a pinkish powder, that was recrystallized from hot toluene/acetone to give colorless crystals **2** (958 mg, 23%).

^1H (400 MHz, CDCl_3): δ [ppm] = 7.46 (s, 1H, NCN), 6.94 (s, 4H, MesH), 3.91 (t, J = 5.9 Hz, 4H, NCH_2),

2.53 (q, J = 5.9 Hz, 2H, CH₂), 2.29 (s, 12H, MesCH₃), 2.27 (s, 6H, MesCH₃).

$^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3): δ [ppm] = 150.0 (NCN), 140.6, 136.5, 134.4, 130.2 (MesC), 46.5 (NCH_2), 21.0 (MesCH₃), 19.4 (CH₂), 17.5 (MesCH₃).

Anal. Found: C, 64.45; H, 7.06; N, 6.91. Calc. for $\text{C}_{22}\text{H}_{29}\text{BF}_4\text{N}_2$ (408.28): C, 64.72; H, 7.16; N, 6.86.

MS (FAB): 322 ($[\text{M}+1-\text{BF}_4]^+$).

4.4. (*Dimesityltetrahydropyrimid-2-ylidene*) silver(I) chloride (**3**)

A mixture of **2** (350 mg, 0.86 mmol), silver(I) oxide (109 mg, 0.47 mmol, 0.55 eq.) and NMe_4Cl (94 mg, 0.86 mol, 1 eq.) in 30 ml of DCM was stirred for 4 h. The solution was filtered through Celite, the filtrate evaporated to a volume of ca. 5 ml; after addition of hexane complex **3** was obtained as a white solid (310 mg, 78%).

^1H (270 MHz, CD_2Cl_2): δ [ppm] = 6.98 (s, 4H, MesH), 3.38 (t, J = 5.9 Hz, 4H, NCH_2), 2.30 (s, 6H, MesCH₃), 2.27 (s, 12H, MesCH₃), (CH₂ not detected).

$^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CD_2Cl_2): δ [ppm] = 205.9 (dd, 1J ($^{107}\text{Ag}, ^{13}\text{C}$) = 228.4 Hz, 1J ($^{109}\text{Ag}, ^{13}\text{C}$) = 260.4 Hz, NCN), 143.1, 138.3, 134.7, 129.7 (MesC), 42.0 (NCH_2), 20.8 (MesCH₃), 17.7 (MesCH₃), 17.5 (CH₂).

Anal. Found: C, 57.23; H, 6.05; N, 6.00. Calc. for $\text{C}_{22}\text{H}_{28}\text{AgClN}_2$ (463.78): C, 56.97; H, 6.08; N, 6.04.

MS(FAB): 750 ($[(\text{carbene})_2\text{Ag}]^+$), 429 ($[(\text{carbene})\text{Ag}]^+$).

4.5. *Di[bis(dimesityltetrahydropyrimid-2-ylidene)silver(I)] hexachlorodipalladate (**4**)*

A solution of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (50 mg, 0.19 mmol) in 20 ml of DCM was added to a solution of **3** (179 mg, 0.39 mmol, 2 eq.) in 10 ml of DCM. After stirring for 2 h, the solution turned from yellow to dark red. The solution was filtered off the precipitated silver chloride and the solvent was removed in vacuo until ca. 5 ml remained, and 20 ml of hexane was added, causing a red precipitate to form (152 mg, 82%).

^1H (270 MHz, CD_2Cl_2): δ [ppm] = 6.90 (s, 4H, MesH), 3.14 (t, J = 5.9 Hz, 4H, NCH_2), 2.14 (q, J = 5.9 Hz, 2H, CH₂), 2.33 (s, 6H, MesCH₃), 1.76 (s, 12H, MesCH₃).

$^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CD_2Cl_2): δ [ppm] = 205.8 (dd, 1J ($^{107}\text{Ag}, ^{13}\text{C}$) = 174.3 Hz, 1J ($^{109}\text{Ag}, ^{13}\text{C}$) = 201.3 Hz, NCN), 142.8, 138.4, 134.8, 129.9 (MesC), 43.9 (NCH_2), 21.2 (MesCH₃), 20.8 (CH₂), 17.8 (MesCH₃).

Anal. Found: C, 54.81; H, 6.08; N, 5.49. Calc. for $\text{C}_{88}\text{H}_{112}\text{Cl}_6\text{Ag}_2\text{N}_8\text{Pd}_2$ (1923.20): C, 54.96; H, 5.87; N, 5.83.

MS(FAB): 750 ($[(\text{carbene})_2\text{Ag}+1]^+$), 429 ($[(\text{carbene})\text{Ag}]^+$).

4.6. Crystallography

4.6.1. General remarks

The preparation of the single crystals is described above. Selected crystals were coated with perfluorinated ether, fixed in a capillary, transferred to the diffractometer, and cooled in a nitrogen stream (Oxford Cryosystems). Preliminary examination and data collection were carried out with a κ -CCD device (NONIUS MACH3) at the window of a rotating anode (Nonius FR591) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). [16] Data were corrected for Lorentz and polarization effects. Potential absorption effects and/or decay of the crystal were corrected during the scaling procedure [17]. All structures were solved by a combination of direct methods and difference Fourier syntheses. Full-matrix, least-squares refinements were carried out by minimization of $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/err > 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography [18]. All calculations were performed with the STRUX-V [19] system including the programs PLATON [20], SIR92 [21], and SHELXL-97 [22].

4.6.2. Crystal data, data collection and refinement for 2

$[(C_{22}H_{29}N_2)^+]$, $[(BF_4)^-]$, $M_r = 408.28$, colorless fragment ($0.30 \times 0.33 \times 0.53 \text{ mm}^3$), orthorhombic, $Pnma$ (No. 62), $a = 9.0427(1)$, $b = 15.5513(2)$, $c = 15.0906(2) \text{ \AA}$, $V = 2122.13(5) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.278 \text{ g cm}^{-3}$, $F_{000} = 864$, $\mu = 0.099 \text{ mm}^{-1}$. Data collection were performed at $T = 133 \text{ K}$ within the θ -range of $1.88^\circ < \theta < 25.34^\circ$. A total of 46,510 reflections were integrated. After merging ($R_{\text{int}} = 0.041$), 2020 [$I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 209 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the final difference-Fourier map and were allowed to refine. The refinements converged with $R_1 = 0.0413$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0991$ [all data], and GOF = 1.064. The final difference-Fourier map showed no striking feature ($\Delta e_{\text{min/max}} = +0.34 / -0.30 \text{ e \AA}^{-3}$). The BF_4 anion appears to be disordered over two positions (50:50).

4.6.3. Crystal data, data collection and refinement for 3

$C_{22}H_{28}AgClN_2$, $M_r = 463.78$, colorless plate ($0.08 \times 0.36 \times 0.66 \text{ mm}^3$), orthorhombic, $Pbcn$ (No. 60), $a = 30.2113(3)$, $b = 8.9217(1)$, $c = 16.0333(2) \text{ \AA}$, $V = 4321.55(8) \text{ \AA}^3$, $Z = 8$, $d_{\text{calc}} = 1.426 \text{ g cm}^{-3}$, $F_{000} = 1904$, $\mu = 1.064 \text{ mm}^{-1}$. Data collection were performed at $T = 173 \text{ K}$ within the θ -range of $2.38^\circ < \theta < 25.37^\circ$. A total of 54,612 reflections were integrated. After merging ($R_{\text{int}} = 0.048$), 3965 [$I_o > 2\sigma(I_o)$] independent reflections remained and all

were used to refine 241 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions (riding model). The refinements converged with $R_1 = 0.0333$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0908$ [all data], and GOF = 1.053. The final difference-Fourier map showed no striking feature ($\Delta e_{\text{min/max}} = +0.56 / -0.58 \text{ e \AA}^{-3}$). One solvent molecule could not be modelled proper. The problem was solved by using the PLATON Calc Squeeze procedure.

4.6.4. Crystal data, data collection and refinement for 4·5(CH₂Cl₂)

$2[(C_{44}H_{56}AgN_4)^+]$, $[(Cl_6Pd_2)^{2-}]$, $10(CH_2Cl_2)$, $M_r = 2772.40$, reddish brown needle ($0.08 \times 0.10 \times 0.38 \text{ mm}^3$), monoclinic, $P2_1/n$ (No. 14), $a = 1232.41(1)$, $b = 27.1528(2)$, $c = 18.0106(1) \text{ \AA}$, $\beta = 97.0294(3)^\circ$, $V = 5981.65(7) \text{ \AA}^3$, $Z = 2$, $d_{\text{calc}} = 1.539 \text{ g cm}^{-3}$, $F_{000} = 2808$, $\mu = 1.245 \text{ mm}^{-1}$. Data collection were performed at $T = 173 \text{ K}$ within the θ -range of $1.36^\circ < \theta < 25.38^\circ$. A total of 139,313 reflections were integrated. After merging ($R_{\text{int}} = 0.061$), 10962 [$I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 857 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms of the cation were found in the final difference-Fourier map and were allowed to refine. All hydrogen atoms of the five solvent molecules were calculated in ideal positions (riding model). A disorder (73:27 for both) observed for two solvent molecules could be resolved well. The refinements converged with $R_1 = 0.0345$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0737$ [all data], and GOF = 1.029. The final difference-Fourier map showed no striking feature ($\Delta e_{\text{min/max}} = +0.61 / -0.59 \text{ e \AA}^{-3}$).

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-234466 (2), No. CCDC-234465 (3) and No. CCDC-234467 (4·5(CH₂Cl₂)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was generously supported by the Fonds der Chemischen Industrie (studentship for S.K.S.). The Karl Wamsler-Foundation is thanked for a travel fellowship. The authors thank Dr. Jörg Eppinger for helpful discussions. E.H. thanks Cornell Hess for helpful inspirations.

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