

## Article

# Facile N9-Alkylation of Xanthine Derivatives and Their Use as Precursors for *N*-Heterocyclic Carbene Complexes

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**Abstract:** The xanthine-derivatives 1,3,7-trimethylxanthine, 1,3-dimethyl-7-benzylxanthine and 1,3-dimethyl-7-(4-chlorobenzyl)xanthine are readily ethylated at N9 using the cheap alkylating agents ethyl tosylate or diethyl sulfate. The resulting xanthinium tosylate or ethyl sulfate salts can be converted into the corresponding PF<sub>6</sub><sup>−</sup> and chloride salts. The reaction of these xanthinium salts with silver(I) oxide results in the formation of different silver(I) carbene-complexes. In the presence of ammonia, ammine complexes [Ag(NHC)(NH<sub>3</sub>)]PF<sub>6</sub> are formed, whilst with Et<sub>2</sub>NH, the bis(carbene) salts [Ag(NHC)<sub>2</sub>]PF<sub>6</sub> were isolated. Using the xanthinium chloride salts neutral silver(I) carbenes [Ag(NHC)Cl] were prepared. These silver complexes were used in a variety of transmetallation reactions to give the corresponding gold(I), ruthenium(II) as well as rhodium(I) and rhodium(III) complexes. The compounds were characterized by various spectroscopic methods as well as X-ray diffraction.

**Keywords:** xanthines; *N*-heterocyclic carbenes; X-ray structures



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## 1. Introduction

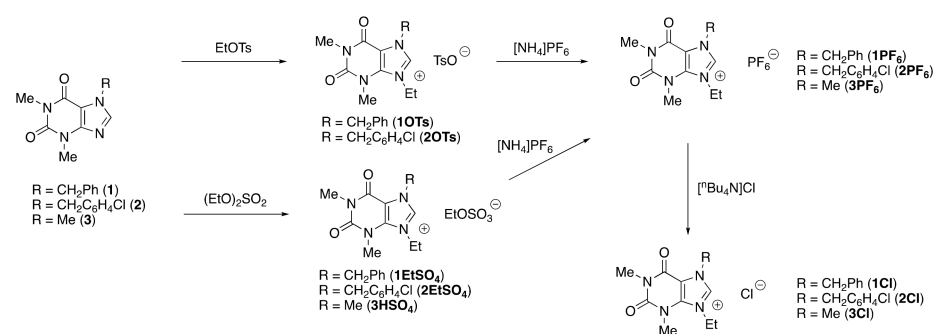
Metal complexes containing *N*-heterocyclic carbenes (NHCs) are today considered a common class of ligands in organometallic chemistry. Their seemingly endless structural variety combined with a very stable metal-carbon-bond makes carbene complexes so important in homogeneous catalysis and also for biomedical applications [1–14]. Typically, most *N*-heterocyclic carbenes are derived from substituted imidazolium, benzimidazolium or triazolium salts. Related to this class of compounds are the xanthinium salts, which may also be used as precursors for *N*-heterocyclic carbenes. Especially xanthinium salts derived from caffeine or theophylline have been studied to some extent. The first reported xanthine-derived NHC complex was the mercury(II) bis(NHC) salt [Hg(NHC)<sub>2</sub>]ClO<sub>4</sub> (NHC = 1,3,7,9-tetramethylxanthin-8-ylidene), prepared by Beck in 1976 [15]. After lying dormant for more than a quarter of a century, the groups of Youngs and Herrmann independently began to reinvestigate NHC-complexes derived from caffeine and its derivatives with rhodium(I), iridium(I) and silver(I) [16–18]. Especially the silver(I) complexes developed and patented by Youngs were found to be highly active against various pathogens [19–24]. Other groups have examined xanthine-derived carbene complexes with metals including Pt(II) [25–27], Pd(II) [28–32], Au(I) [33], Ir(I) [34] and Ag(I) [35,36]. Focus of these studies was their activity against cancer cells (Pt, Pd, Au, Ir and Ag) or homogeneous catalysis (Pd, Rh). There is also a publication on copper complexes containing a caffeine-derived NHC, but the results must be considered doubtful [37]. The compounds are referred to as being blue copper(II) species, but an alleged X-ray structure (data neither shown in the publication nor deposited with the CCDC) and NMR spectroscopic data are clearly consistent with the presence of copper(I). A short review from 2018

summarizes the so far known chemistry of xanthine-based *N*-heterocyclic carbenes [38]. Given our interest in NHC-complexes of various metals and their biological activity and reactivity [39–44], we wished to develop more efficient methods to access a greater variety of xanthinium salts as well as their corresponding metal carbene-complexes.

## 2. Results and Discussion

Quaternization at the 9-position of xanthines including caffeine and its derivatives typically requires forcing conditions (high temperature and pressure), long reaction times and a large excess of alkyl halide. In the case of *N*9-methylation of xanthines, typically, 20 equivalents of methyl iodide are used and reactions are carried out in refluxing DMF or in a closed vessel for up to 20 h [19,28,35,45]. Trimethyloxonium tetrafluoroborate has also been used by some groups for *N*-methylation of xanthines [17,33]. Although reaction conditions are mild and no large excess is required,  $[\text{Me}_3\text{O}]\text{BF}_4$  is considerably more expensive than MeI and requires anhydrous conditions. As an alternative to these reagents, methyl tosylate or dimethyl sulfate have been successfully used for *N*9-methylation in xanthines, affording the respective xanthinium tosylate or methyl sulfate salts in high yields and short reaction times (90 min at 170 °C without additional solvent) [16,46–48]. Based on this procedure, we examined the feasibility of also introducing ethyl groups in position 9 of different xanthine derivatives with ethyl tosylate or diethyl sulfate.

Gratifyingly, heating 1,3-dimethyl-7-benzylxanthine in neat ethyl tosylate at 150 °C cleanly affords the corresponding 1,3-dimethyl-7-benzyl-9-ethylxanthinium tosylate in two hours with an isolated yield of 87% (Scheme 1).



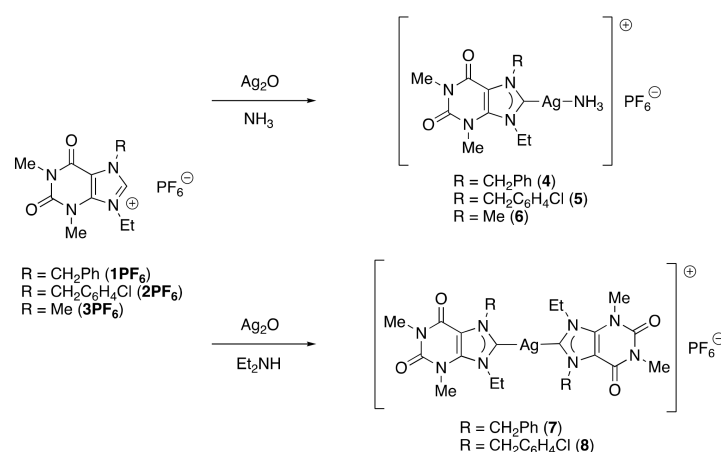
**Scheme 1.** Synthesis of xanthinium salts.

Work-up merely involves washing the product with diethyl ether and drying. This result encouraged us to try the even cheaper diethyl sulfate. Indeed, reacting 1,3-dimethyl-7-benzylxanthine in neat diethyl sulfate at 130 °C for two hours afforded the desired product as the ethyl sulfate salt in 87% yield (Scheme 1). Using the same procedure, the corresponding 4-chlorobenzyl- and caffeine-derivatives were also isolated as colorless solids in high yields (Scheme 1). In the case of caffeine, the ethyl sulfate anion evidently hydrolyzes during the reaction, forming the hydrogen sulfate salt instead. These xanthinium salts were characterized by NMR spectroscopy and electrospray mass spectrometry, the latter (in positive ion mode) shows only one signal corresponding to the respective xanthinium cations and, in negative ion mode, only the signals for the anions ( $\text{EtSO}_4^-$ ,  $\text{TsO}^-$  or  $\text{PF}_6^-$ ). The positive-ion mass spectra of the caffeine derivatives also feature one signal, which can be assigned to the fragment  $[\text{M-Me+H}]^+$ , formed by loss of one methyl group.

The tosylate, ethyl sulfate or hydrogen sulfate anions in these salts could readily be exchanged in water to give the corresponding  $\text{PF}_6^-$  salts **1PF<sub>6</sub>**, **2PF<sub>6</sub>** and **3PF<sub>6</sub>** (Scheme 1). Since halide salts are however the most convenient precursors for *N*-heterocyclic carbene metal complexes, we investigated the possibility of converting the  $\text{PF}_6^-$  salts into the corresponding chlorides. The group of Visentin reported that a xanthinium tetrafluoroborate could be converted into the chloride salt by anion exchange with  $[\text{Ph}_4\text{As}]\text{Cl}$  [31]. Given the toxicity and high cost of  $[\text{Ph}_4\text{As}]\text{Cl}$ , we sought alternative reagents to accomplish this anion exchange. Gratifyingly, we found that mixing THF solutions of the xanthinium  $\text{PF}_6^-$  salts

with  $[^n\text{Bu}_4\text{N}]\text{Cl}$  results in precipitation of the chloride salts **1Cl**, **2Cl** and **3Cl**, which could be isolated almost quantitatively (Scheme 1). Based on mass spectrometry, the samples are free of  $\text{PF}_6^-$  anions and the presence of a chloride anion was confirmed by a sharp singlet in their  $^{35}\text{Cl}$ -NMR spectra. Unfortunately, it was not possible to access the chloride salts directly from the ethyl sulfate of hydrogen sulfate salts.

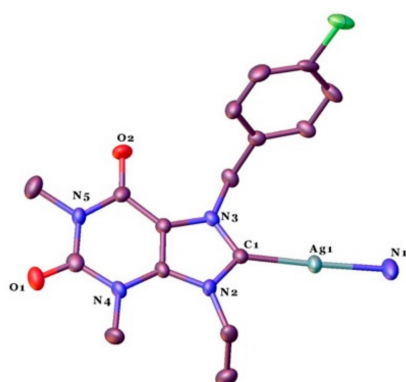
With these xanthinium salts in hand, we examined their use as precursors for *N*-heterocyclic carbene complexes of silver. The reaction of the respective  $\text{PF}_6^-$  salts with  $\text{Ag}_2\text{O}$  in a mixture of ethanol and aqueous ammonia afforded the corresponding cationic silver(I) carbene complexes  $[\text{Ag}(\text{NHC})(\text{NH}_3)]\text{PF}_6$ , (NHC = 1,3-dimethyl-7-benzyl-9-ethylxanthine-8-ylidene (**4**), 1,3-dimethyl-7-(4-chlorobenzyl)-9-ethylxanthine-8-ylidene (**5**) and 1,3,7-trimethyl-9-ethylxanthine-8-ylidene (**6**) containing ammonia as co-ligand (Scheme 2) [49].



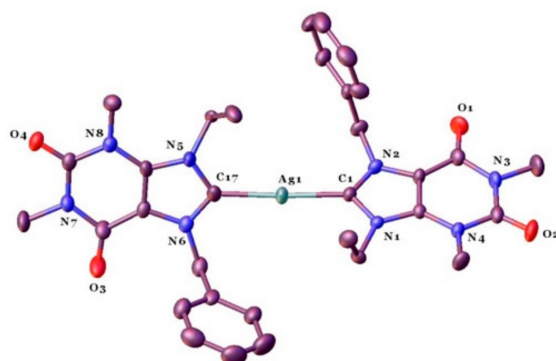
**Scheme 2.** Synthesis of silver-NHC complexes.

When using  $\text{Et}_2\text{NH}$  instead of ammonia, we isolated the bis(carbene) silver(I) salts  $[\text{Ag}(\text{NHC})_2]\text{PF}_6$  (NHC = 1,3-dimethyl-7-benzyl-9-ethylxanthine-8-ylidene (**7**) and 1,3-dimethyl-7-(4-chlorobenzyl)-9-ethylxanthine-8-ylidene (**8**)) (Scheme 2). The silver carbene compounds were characterized by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. The proton spectra of the compounds lack the signal for the proton at position 8, consistent with carbene formation. This is further confirmed by a significant shift of the resonance of the carbon atom at position 8. In the xanthinium salts, these are observed between 138 and 139 ppm, whilst in the silver carbene complexes they fall in the range of 185 to 187 ppm. The chemical shifts of metal-bound carbene-carbon resonances can often vary, depending on the other ligands bound to the metal. In this series of silver compounds, the nature of the second ligand ( $\text{NH}_3$ , carbene or  $\text{Cl}^-$ ) does not appear to have a significant effect on the chemical shift of the carbene-carbon resonance. In the case of the bis(carbene) complexes **7** and **8**, coupling between the  $^{13}\text{C}$  and the  $^{107/109}\text{Ag}$  isotopes with coupling constants of 192 and 217 Hz could be observed. These values are typical for silver(I) NHC-complexes, which have been observed in several other bis(carbene) complexes [50]. In the case of the ammonia complexes **4–6**, broad signals due to the ammine can be observed in their proton NMR spectra at about 3 ppm. Furthermore, bands between 3300 and 3400  $\text{cm}^{-1}$  due to the  $\text{NH}_3$  stretching frequency are seen in their IR spectra. The molecular structures of compounds **5** and **7** are shown in Figures 1 and 2.

In each case, the coordination about the silver is, as expected, linear with angles of 176.28° and 177.29°, respectively. The carbon-silver bond lengths (ca. 2.06 Å) are typical for silver(I)-NHC complexes. Although Ag-carbene complexes with coordinated ammonia were postulated as intermediates and one example was isolated and characterized spectroscopically [49], complex **5** is the only structurally authenticated example of a silver(I) carbene with ammonia co-ligands to date.

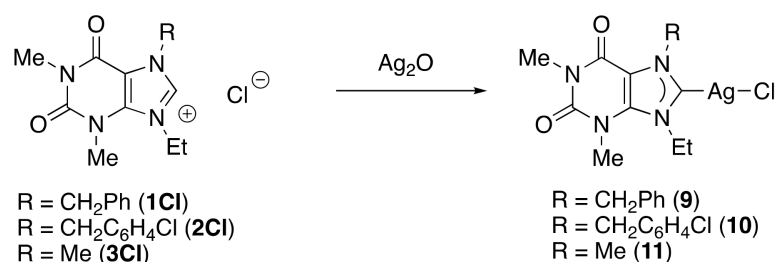


**Figure 1.** Molecular structure of compound 5. Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms and the  $\text{PF}_6^-$  anion have been omitted for clarity.



**Figure 2.** Molecular structure of compound 7. Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms and the  $\text{PF}_6^-$  anion have been omitted for clarity.

The chloride salts **1Cl**, **2Cl** and **3Cl** readily react with  $\text{Ag}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  to form the silver chloride complexes  $[\text{Ag}(\text{NHC})\text{Cl}]$  (NHC = 1,3-dimethyl-7-benzyl-9-ethylxanthine-8-ylidene (**9**), 1,3-dimethyl-7-(4-chlorobenzyl)-9-ethylxanthine-8-ylidene (**10**) and 1,3,7-trimethyl-9-ethylxanthine-8-ylidene (**11**)) as colorless solids in reasonable yields (Scheme 3).



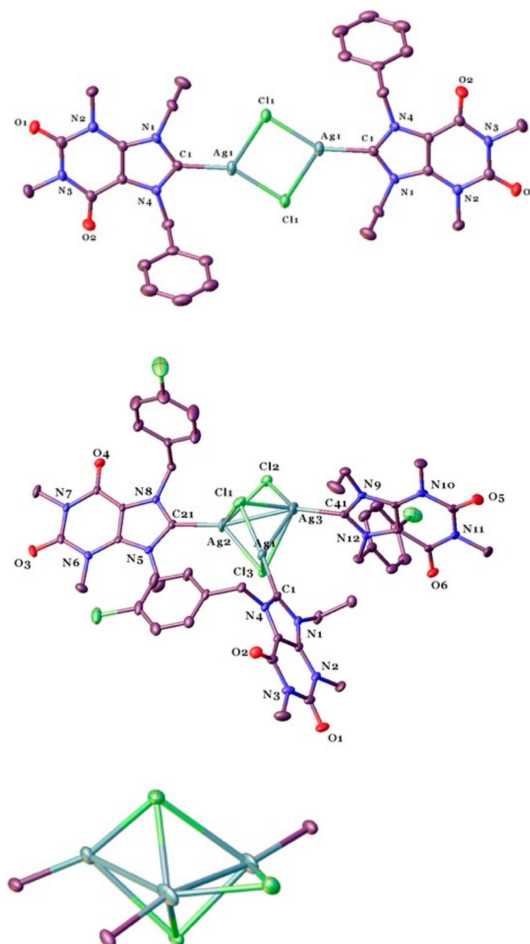
**Scheme 3.** Synthesis of silver-chloride complexes.

The formation of the carbene complex is again evident from the NMR spectroscopic data. In compounds **9** and **10**, the resonance for the carbene-carbon atom is observed at about 187 ppm in their  $^{13}\text{C}$  NMR spectra. In the solid-state, the molecules exist as either a chloro-bridged dimer with tri-coordinated silver atoms (**9**) or a unique trimer (**10**) as depicted in Figure 3.

For compound **9** the two  $\text{Ag}-\text{Cl}$  bond lengths of 2.44 Å and 2.72 Å are unequal, resulting in an  $\text{Ag}_2\text{Cl}_2$  parallelogram. This structural motif is observed in several other silver NHC complexes [51,52]. Crystals of complex **10** were very small and thin, therefore diffraction data was collected at beamline P11 at the PETRA III synchrotron located at DESY in Hamburg, Germany. The trimeric structure of **10** is unique and, so far, has no precedence in the literature. The molecule consists of a planar  $\text{Ag}_3$ -triangle with two shorter (3.11 and



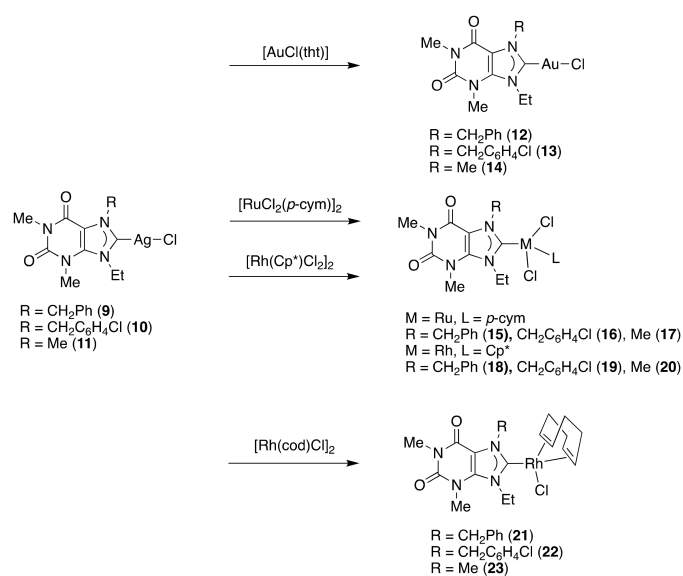
3.21 Å) one much longer (3.89 Å) Ag–Ag distances. Above and below this Ag<sub>3</sub>-plane there is a  $\mu_3$ -bridging chloride ligand. The third chloride acts as  $\mu_2$ -ligand between two silver atoms in the plane of the triangle. Each silver atom is also C-bound to the carbene ligand (Figure 3 bottom). As can be seen, the C–Ag–Cl angles are not linear, resulting in a distorted tetrahedral coordination environment about each silver atom.



**Figure 3.** Molecular structures of compounds **9** (top) and **10** (center and bottom). Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms have been omitted for clarity. Atoms labeled with an asterisk are generated by symmetry. The bottom image shows only the atoms directly attached to Ag in complex **10**.

Silver NHC complexes are commonly used in transmetalation reactions to transfer the NHC ligand to a different metal. We therefore examined the reaction of the silver chloride complexes **9–11** with various other metal salts including [AuCl(tht)] (tht = tetrahydrothiophene), [Ru(*p*-cym)Cl<sub>2</sub>]<sub>2</sub>, [Rh(Cp\*)Cl<sub>2</sub>]<sub>2</sub> and [Rh(cod)Cl]<sub>2</sub>. In each case the corresponding metal xanthine-8-ylidene-derivatives were formed in good yields as air- and moisture-stable solids (Scheme 4).

Complexes **12–23** were characterized by various spectroscopic methods and, in several cases, by X-ray diffraction. In all these compounds, the chemical shifts of the carbene-carbon resonances in the <sup>13</sup>C-NMR spectra are most diagnostic. Compared to the silver-precursors, the resonances are shifted either slightly upfield or downfield, depending on the metal. In case of the Rh-complexes, coupling between the <sup>13</sup>C and <sup>103</sup>Rh nuclei can be observed. Several complexes were characterized by X-ray diffraction, the molecular structures of which are shown in Figures 4–7.



Scheme 4. Transmetalation reactions.

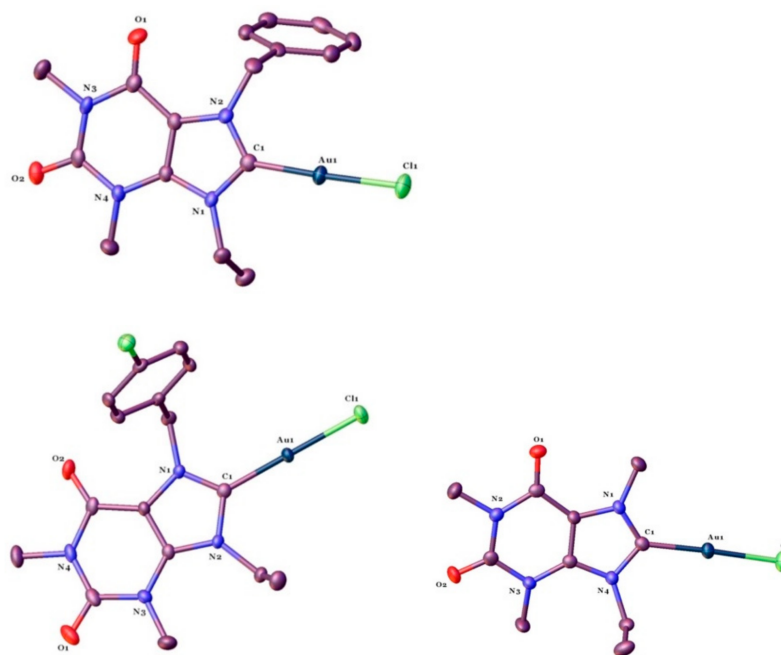


Figure 4. Molecular structures of compounds 12 (top), 13 (middle) and 14 (bottom). Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

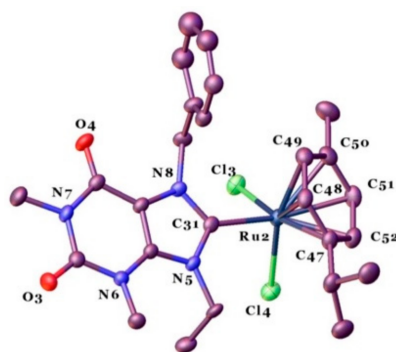
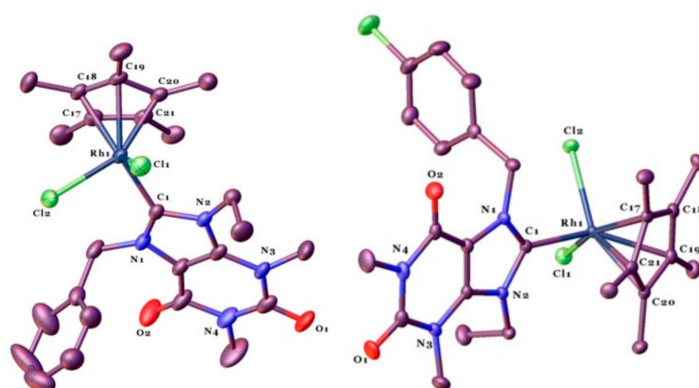
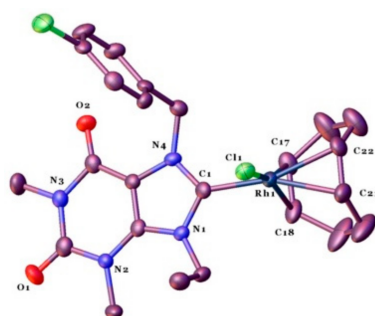


Figure 5. Molecular structure of compound 15. Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms have been omitted for clarity.



**Figure 6.** Molecular structures of compounds **18** (top) and **19** (bottom). Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms have been omitted for clarity.



**Figure 7.** Molecular structure of compound **22**. Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

The gold(I) complexes (Figure 4) feature linear coordination (C–Au–Cl angles of 177–179°) at the gold, as would be expected. There is only one other reported X-ray structure of a xanthine-derived NHC Au(I) halide complex, namely that of the iodo-complex [Au(NHC)I] (NHC = 1,3,7,9-tetramethylxanthine-8-ylidene) [33]. The Au–C bond lengths in **12**–**13** are with around 1.9 Å, similar to those observed in the 1,3,7,9-tetramethylxanthine-8-ylidene derivative.

The structure of the ruthenium(II) complex **15** (Figure 5) features one C-bound carbene and two chloride ligands at the arene–Ru center. This piano-stool type arrangement is typical for this class of compounds. While the preparation and biological properties of the 1,3,7,9-tetramethylxanthine-8-ylidene-analogue of **15** have been published [53], this is the first X-ray structure of an arene ruthenium complex containing a xanthine-derived carbene ligand.

The Rh(III) complexes **18** and **19** (Figure 6) feature a similar piano-stool geometry, with the xanthine-derivative C8-bound to the metal. The only other structurally characterized examples of Cp\*Rh(III) complexes with xanthine-derived carbene ligands are those reported by Hahn containing 7-picolyl- or 7-imidazolyl-substituted theobromine-derivatives [54].

The structure of complex **22** (Figure 7) contains a *cis*-configured, square planar rhodium(I) center with a C8-bound xanthine-derivative. The overall geometry is similar to that reported for the 1,3,7,9-tetramethylxanthine-8-ylidene-analogue [RhI(cod)(NHC)] [18].

### 3. Materials and Methods

Reactions were routinely carried out under ambient conditions without protection from air or moisture. Solvents were HPLC-grade and all other chemicals were procured from commercial suppliers (Merck, Darmstadt, Germany, Alfa Aesar, Kandel, Germany, TCI Chemicals, Eschborn, Germany or Acros Organics, Geel, Belgium) and were used as received. 1,3-Dimethyl-7-benzylxanthine was prepared from theophylline and benzyl bromide as described previously [55,56]. The 4-chlorobenzyl-derivative was prepared

similarly.  $[\text{AuCl}(\text{tbt})]$ ,  $[\text{RuCl}_2(p\text{-cym})]_2$ ,  $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$  and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  were prepared by known methods [57–60]. NMR spectra were recorded on Bruker Avance 400 or Bruker Avance III 600 instruments (Bruker, Berlin, Germany). Spectra were referenced externally to  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ), 1 M aq.  $\text{NaCl}$  ( $^{35}\text{Cl}$ ) or 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). High-resolution electrospray mass spectra were measured on a Bruker Daltonics micrOTOF instrument (Bruker, Bremen, Germany). IR spectra were recorded on a Nicolet iS5 spectrometer (Thermo Fisher Scientific, Erlangen, Germany) fitted with a diamond iD7 ATR unit.

### 1,3-Dimethyl-7-benzyl-9-ethylxanthinium tosylate (1OTs)

A mixture of 1,3-dimethyl-7-benzylxanthine (**1**) (0.100 g, 0.370 mmol) and ethyl tosylate (0.267 g, 1.35 mmol) was heated in an open vial to 150 °C for 2 h. After cooling, excess diethyl ether was added and the resulting solid was isolated by filtration, washed with  $\text{Et}_2\text{O}$  and subsequently dried in air. As a result, 0.151 g (87%) of a colorless solid was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 9.63 (s, 1 H,  $\text{C}^8\text{H}$ ), 7.34–7.49 (m, 7 H, OTs, Ph), 7.10 (d,  $J$  = 8.4 Hz, 2 H, OTs), 5.71 (s, 2 H,  $\text{N}^7\text{CH}_2$ ), 4.59 (q,  $J$  = 7.2 Hz, 2 H,  $\text{N}^9\text{CH}_2$ ), 3.71 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.26 (s, 3 H,  $\text{N}^1\text{Me}$ ), 2.29 (s, 3 H, Me OTs), 1.54 (t,  $J$  = 7.2 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 153.06 ( $\text{C}^6=\text{O}$ ), 150.27 ( $\text{C}^2=\text{O}$ ), 145.68 (OTs), 139.51 ( $\text{C}^4$ ), 138.51 ( $\text{C}^8$ ), 137.55 (OTs), 134.14 (Ph), 128.78, (Ph), 128.67 (Ph), 128.04 (Ph), 127.98 (OTs), 125.40 (OTs), 107.09 ( $\text{C}^5$ ), 51.21 ( $\text{N}^7\text{CH}_2$ ), 45.32 ( $\text{N}^9\text{CH}_2$ ), 31.66 ( $\text{N}^3\text{Me}$ ), 28.39 ( $\text{N}^1\text{Me}$ ), 20.72 (Me OTs), 15.03 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  299.1508; found 299.1511.

### 1,3-Dimethyl-7-(4-chlorobenzyl)-9-ethylxanthinium tosylate (2OTs)

This was prepared as described above using 1,3-dimethyl-7-(4-chlorobenzyl)xanthine (**2**) (0.100 g, 0.330 mmol) and ethyl tosylate (0.238 g, 1.19 mmol). As a result, 0.139 g (84%) of a colorless solid was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 9.60 (s, 1 H,  $\text{C}^8\text{H}$ ), 7.44–7.49 (m, 6 H, OTs, Bn), 7.09–7.12 (m, 2 H, OTs), 5.68 (s, 2 H,  $\text{N}^7\text{CH}_2$ ), 4.58 (q,  $J$  = 7.2 Hz, 2 H,  $\text{N}^9\text{CH}_2$ ), 3.71 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.25 (s, 3 H,  $\text{N}^1\text{Me}$ ), 2.29 (s, 3 H, Me OTs), 1.53 (t,  $J$  = 7.2 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 153.02 ( $\text{C}^6=\text{O}$ ), 150.25 ( $\text{C}^2=\text{O}$ ), 145.68 (OTs), 139.51 ( $\text{C}^4$ ), 138.61 ( $\text{C}^8$ ), 137.54 (OTs), 133.43 (Bn), 133.05 (Bn), 130.09 (Bn), 128.72 (Bn), 127.97 (OTs), 125.39 (OTs), 107.06 ( $\text{C}^5$ ), 50.57 ( $\text{N}^7\text{CH}_2$ ), 45.34 ( $\text{N}^9\text{CH}_2$ ), 31.66 ( $\text{N}^3\text{Me}$ ), 28.39 ( $\text{N}^1\text{Me}$ ), 20.71 (Me OTs), 14.96 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  333.1118; found 333.1118.

### 1,3-Dimethyl-7-benzyl-9-ethylxanthinium ethyl sulfate (1EtSO<sub>4</sub>)

This was prepared as described above by heating a mixture of 1,3-dimethyl-7-benzylxanthine (**1**) (0.20 g, 0.74 mmol) and diethyl sulfate (194  $\mu\text{L}$ , 1.48 mmol) to 130 °C for 2 h. As a result, 0.273 g (87%) of a colorless solid was obtained.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.99 (s, 1 H,  $\text{C}^8\text{H}$ ), 7.34–7.66 (m, 5 H, Ph), 5.80 (s, 2 H,  $\text{N}^7\text{CH}_2$ ), 4.76 (q,  $J$  = 7.2 Hz, 2 H,  $\text{N}^9\text{CH}_2$ ), 3.06 (q,  $J$  = 7.1 Hz, 2 H,  $\text{OCH}_2$ ), 3.85 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.43 (s, 3 H,  $\text{N}^1\text{Me}$ ), 1.68 (t,  $J$  = 7.2 Hz, 3 H, Me), 1.27 (t,  $J$  = 7.1 Hz, 3 H,  $\text{OCH}_2\text{Me}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 153.08 ( $\text{C}^6=\text{O}$ ), 150.29 ( $\text{C}^2=\text{O}$ ), 139.55 ( $\text{C}^4$ ), 138.54 ( $\text{C}^8$ ), 134.15 (Ph), 128.77 (Ph), 128.66 (Ph), 128.03 (Ph), 107.11 ( $\text{C}^5$ ), 61.07 ( $\text{OCH}_2$ ), 51.20 ( $\text{N}^7\text{CH}_2$ ), 45.31 ( $\text{N}^9\text{CH}_2$ ), 31.67 ( $\text{N}^3\text{Me}$ ), 28.39 ( $\text{N}^1\text{Me}$ ), 15.06 (Me,  $\text{OCH}_2\text{Me}$ ). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  299.1508; found 299.1503.

### 1,3-Dimethyl-7-(4-chlorobenzyl)-9-ethylxanthinium ethyl sulfate (2EtSO<sub>4</sub>)

This was prepared as described above using 1,3-dimethyl-7-(4-chlorobenzyl)xanthine (**2**) (0.200 g, 0.650 mmol) and ethyl tosylate (172  $\mu\text{L}$ , 1.31 mmol). As a result, 0.264 g (88%) of a colorless solid was obtained.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.06 (s, 1 H,  $\text{C}^8\text{H}$ ), 7.33–7.62 (m, 4 H, Bn), 5.78 (s, 2 H,  $\text{N}^7\text{CH}_2$ ), 4.74 (q,  $J$  = 7.3 Hz, 2 H,  $\text{N}^9\text{CH}_2$ ), 4.03 (q,  $J$  = 7.1 Hz, 2 H,  $\text{OCH}_2$ ), 3.85 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.43 (s, 3 H,  $\text{N}^1\text{Me}$ ), 1.68 (t,  $J$  = 7.3 Hz, 3 H, Me), 1.27 (t,  $J$  = 7.1 Hz, 3 H,  $\text{OCH}_2\text{Me}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 153.06 ( $\text{C}^6=\text{O}$ ), 150.29 ( $\text{C}^2=\text{O}$ ), 139.56 ( $\text{C}^4$ ), 138.61 ( $\text{C}^8$ ), 133.44 (Bn), 133.05 (Bn), 130.09 (Bn), 128.73 (Bn), 107.10 ( $\text{C}^5$ ), 61.09 ( $\text{OCH}_2$ ), 50.58 ( $\text{N}^7\text{CH}_2$ ), 45.34 ( $\text{N}^9\text{CH}_2$ ), 31.68 ( $\text{N}^3\text{Me}$ ), 28.40 ( $\text{N}^1\text{Me}$ ), 15.07 (Me), 14.99 ( $\text{OCH}_2\text{Me}$ ). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  333.1118; found 333.1122.

### 1,3,7-Trimethyl-9-ethylxanthinium hydrogen sulfate (3HSO<sub>4</sub>)

A mixture of caffeine (3) (0.287 g, 1.480 mmol) and diethyl sulfate (388  $\mu$ L, 2.96 mmol) was heated in an open vial to 130 °C for 2 h. After cooling to room temperature, a 3:7 mixture of acetone and toluene (ca. 10 mL) was added. Upon standing over night, a colorless solid deposited, which was isolated by filtration and was washed with a small amount of acetone. After drying in vacuum, 0.435 g (91%) of the product was obtained. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 9.42 (s, 1 H, C<sup>8</sup>H), 4.58 (q,  $J$  = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 4.07 (s, 3 H, N<sup>7</sup>Me), 3.73 (s, 3 H, N<sup>3</sup>Me), 3.28 (s, 3 H, N<sup>1</sup>Me), 1.53 (t,  $J$  = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 153.31 (C<sup>6</sup>=O), 150.34 (C<sup>2</sup>=O), 138.87 (C<sup>4</sup>), 138.76 (C<sup>8</sup>), 107.87 (C<sup>5</sup>), 44.97 (N<sup>9</sup>CH<sub>2</sub>), 35.61 (N<sup>7</sup>Me), 31.58 (N<sup>3</sup>Me), 28.31 (N<sup>1</sup>Me), 15.06 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for [M-Me+H]<sup>+</sup> 209.1039; found 209.1035.

### 1,3-Dimethyl-7-benzyl-9-ethylxanthinium hexafluorophosphate (1PF<sub>6</sub>)

A solution of 1EtSO<sub>4</sub> (0.100 g, 0.236 mmol) in water (10 mL) was treated with a solution of [NH<sub>4</sub>]PF<sub>6</sub> (0.0403 g, 0.247 mmol) in water (10 mL). After 20 min at room temperature the resulting precipitate was isolated by filtration, washed with water and Et<sub>2</sub>O and was dried in air. A colorless solid was obtained in 74% yield (0.077 g). The compound can also be prepared by the same method from 1OTs in similar yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 9.60 (s, 1 H, C<sup>8</sup>H), 7.32–7.49 (m, 5 H, Ph), 5.71 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.59 (q,  $J$  = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.27 (s, 3 H, N<sup>1</sup>Me), 1.54 (t,  $J$  = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 153.07 (C<sup>6</sup>=O), 150.28 (C<sup>2</sup>=O), 139.51 (C<sup>4</sup>), 138.48 (C<sup>8</sup>), 134.11 (Ph), 128.78 (Ph), 128.68 (Ph), 128.00 (Ph), 107.11 (C<sup>5</sup>), 51.22 (N<sup>7</sup>CH<sub>2</sub>), 45.30 (N<sup>9</sup>CH<sub>2</sub>), 31.66 (N<sup>3</sup>Me), 28.39 (N<sup>1</sup>Me), 15.07 (Me). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>)  $\delta$  = -144.19 (hept.,  $J$  = 711 Hz, PF<sub>6</sub>). High-resolution positive-ion ESMS ( $m/z$ ): calculated for [M]<sup>+</sup> 299.1508; found 299.1511.

### 1,3-Dimethyl-7-(4-chlorobenzyl)-9-ethylxanthinium hexafluorophosphate (2PF<sub>6</sub>)

This was prepared as described above using 2EtSO<sub>4</sub> (0.100 g, 0.218 mmol) and [NH<sub>4</sub>]PF<sub>6</sub> (0.0373 g, 0.229 mmol). As a result, 0.077 g (74%) of a colorless solid was obtained. The compound can also be prepared by the same method from 2OTs in similar yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 9.57 (s, 1 H, C<sup>8</sup>H), 7.44–7.54 (m, 4 H, Bn), 5.70 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.59 (q,  $J$  = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.26 (s, 3 H, N<sup>1</sup>Me), 1.54 (t,  $J$  = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 153.04 (C<sup>6</sup>=O), 150.27 (C<sup>2</sup>=O), 139.52 (C<sup>4</sup>), 138.58 (C<sup>8</sup>), 133.46 (Bn), 133.01 (Bn), 130.07 (Bn), 128.74 (Bn), 107.09 (C<sup>5</sup>), 50.59 (N<sup>7</sup>CH<sub>2</sub>), 45.32 (N<sup>9</sup>CH<sub>2</sub>), 31.67 (N<sup>3</sup>Me), 28.40 (N<sup>1</sup>Me), 15.00 (Me). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>)  $\delta$  = -144.19 (hept.,  $J$  = 711 Hz, PF<sub>6</sub>). High-resolution positive-ion ESMS ( $m/z$ ): calculated for [M]<sup>+</sup> 333.1118; found 333.1118.

### 1,3,7-Trimethyl-9-ethylxanthinium hexafluorophosphate (3PF<sub>6</sub>)

This was prepared as described above using 3HSO<sub>4</sub> (0.433 g, 1.412 mmol) and [NH<sub>4</sub>]PF<sub>6</sub> (0.440 g, 2.70 mmol). As a result, 0.382 g (77%) of a colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 9.34 (s, 1 H, C<sup>8</sup>H), 4.56 (q,  $J$  = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 4.05 (d,  $J$  = 0.6 Hz, 3 H, N<sup>7</sup>Me), 3.71 (s, 3 H, N<sup>3</sup>Me), 3.27 (s, 3 H, N<sup>1</sup>Me), 1.50 (t,  $J$  = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 153.31 (C<sup>6</sup>=O), 150.33 (C<sup>2</sup>=O), 138.85 (C<sup>4</sup>), 138.69 (C<sup>8</sup>), 107.88 (C<sup>5</sup>), 44.98 (N<sup>9</sup>CH<sub>2</sub>), 35.63 (N<sup>7</sup>Me), 31.56 (N<sup>3</sup>Me), 28.32 (N<sup>1</sup>Me), 15.09 (Me). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>)  $\delta$  = -144.21 (hept.,  $J$  = 711 Hz, PF<sub>6</sub>). High-resolution positive-ion ESMS ( $m/z$ ): calculated for [M-Me+H]<sup>+</sup> 209.1039; found 209.1035.

### 1,3-Dimethyl-7-benzyl-9-ethylxanthinium chloride (1Cl)

A solution of 1PF<sub>6</sub> (0.2416 g, 0.544 mmol) in THF (3 mL) was treated with a solution of [nBu<sub>4</sub>N]Cl (0.304 g, 1.094 mmol) in THF (2.5 mL). After 2 h at room temperature the resulting precipitate was isolated by filtration, washed with Et<sub>2</sub>O and dried. A colorless solid was obtained in 85% yield (0.1548 g). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 10.01 (s, 1 H, C<sup>8</sup>H), 7.32–7.54 (m, 5 H, Ph), 5.74 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.62 (q,  $J$  = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.26 (s, 3 H, N<sup>1</sup>Me), 1.55 (t,  $J$  = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 153.08 (C<sup>6</sup>=O), 150.29 (C<sup>2</sup>=O), 139.53 (C<sup>4</sup>), 138.71 (C<sup>8</sup>), 134.22 (Ph), 128.74 (Ph), 128.64 (Ph), 128.09 (Ph), 107.03 (C<sup>5</sup>), 51.10 (N<sup>7</sup>CH<sub>2</sub>), 45.30 (N<sup>9</sup>CH<sub>2</sub>), 31.69 (N<sup>3</sup>Me),



28.39 (N<sup>1</sup>Me), 15.09 (Me). <sup>35</sup>Cl NMR (54 MHz, DMSO-d<sub>6</sub>) δ = 69.4 (s, Cl<sup>-</sup>). High-resolution positive-ion ESMS (*m/z*): calculated for [M]<sup>+</sup> 299.1508; found 299.1503.

### 1,3-Dimethyl-7-(4-chlorobenzyl)-9-ethylxanthinium chloride (2Cl)

This was prepared as described above using 2PF<sub>6</sub> (0.2604 g, 0.544 mmol) and [<sup>n</sup>Bu<sub>4</sub>N]Cl (0.304 g, 1.094 mmol). As a result, 0.152 g (75%) colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 10.01 (s, 1 H, C<sup>8</sup>H), 7.47–7.55 (m, 4 H, Bn), 5.73 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.61 (q, *J* = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.26 (s, 3 H, N<sup>1</sup>Me), 1.55 (t, *J* = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) δ = 153.05 (C<sup>6</sup>=O), 150.27 (C<sup>2</sup>=O), 139.53 (C<sup>4</sup>), 138.81 (C<sup>8</sup>), 133.42 (Bn), 133.14 (Bn), 130.17 (Bn), 128.69 (Bn), 107.00 (C<sup>5</sup>), 50.44 (N<sup>7</sup>CH<sub>2</sub>), 45.33 (N<sup>9</sup>CH<sub>2</sub>), 31.70 (N<sup>3</sup>Me), 28.39 (N<sup>1</sup>Me), 15.01 (Me). <sup>35</sup>Cl NMR (54 MHz, DMSO-d<sub>6</sub>) δ = 69.4 (s, Cl<sup>-</sup>). High-resolution positive-ion ESMS (*m/z*): calculated for [M]<sup>+</sup> 333.1118; found 333.1122.

### 1,3,7-Trimethyl-9-ethylxanthinium chloride (3Cl)

This was prepared as described above using 3PF<sub>6</sub> (0.200 g, 0.543 mmol) and [<sup>n</sup>Bu<sub>4</sub>N]Cl (0.304 g, 1.094 mmol). As a result, 0.136 g (97%) of a colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 9.58 (s, 1 H, C<sup>8</sup>H), 4.58 (q, *J* = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 4.07 (d, *J* = 0.6 Hz, 3 H, N<sup>7</sup>Me), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.28 (s, 3 H, N<sup>1</sup>Me), 1.51 (t, *J* = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-d<sub>6</sub>) δ = 153.32 (C<sup>6</sup>=O), 150.34 (C<sup>2</sup>=O), 138.92 (C<sup>4</sup>), 138.85 (C<sup>8</sup>), 107.82 (C<sup>5</sup>), 44.97 (N<sup>9</sup>CH<sub>2</sub>), 35.59 (N<sup>7</sup>Me), 31.61 (N<sup>3</sup>Me), 28.31 (N<sup>1</sup>Me), 15.12 (Me). <sup>35</sup>Cl NMR (39 MHz, DMSO-d<sub>6</sub>) δ = 38.50 (s, Cl<sup>-</sup>). High-resolution positive-ion ESMS (*m/z*): calculated for [M]<sup>+</sup> 223.1195; found 223.1191.

### [(NHC)Ag(NH<sub>3</sub>)]PF<sub>6</sub> (4)

A suspension of 1PF<sub>6</sub> (0.111 g, 0.250 mmol) in EtOH (3 mL) was treated with Ag<sub>2</sub>O (0.029 g, 0.125 mmol) and concentrated ammonia solution (170 μL, 2.6 mmol). After stirring at room temperature for 30 min, the colorless solid was isolated by filtration and was washed with cold EtOH and Et<sub>2</sub>O. A colorless solid was obtained in 78% yield (0.110 g). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 7.25–7.40 (m, 5 H, Ph), 5.72 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.59 (m, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.50 (s, 3 H, NH<sub>3</sub>), 3.24 (s, 3 H, N<sup>1</sup>Me), 1.42 (m, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-d<sub>6</sub>) δ = 185.27 (C-Ag), 152.93 (C<sup>6</sup>=O), 150.57 (C<sup>2</sup>=O), 140.26 (C<sup>4</sup>), 136.56 (Ph), 128.58 (Ph), 127.88 (Ph), 127.27 (Ph), 108.28 (C<sup>5</sup>), 52.86 (N<sup>7</sup>CH<sub>2</sub>), 46.32 (N<sup>9</sup>CH<sub>2</sub>), 31.35 (N<sup>3</sup>Me), 28.15 (N<sup>1</sup>Me), 17.21 (Me). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>) δ = -144.19 (hept., *J* = 711 Hz, PF<sub>6</sub>). High-resolution positive-ion ESMS (*m/z*): calculated for [M+H+Na]<sup>+</sup> 446.0722; found 446.0686. IR (ATR): 3300–3400 cm<sup>-1</sup> ν(NH<sub>3</sub>), 833 cm<sup>-1</sup> ν(PF<sub>6</sub>).

### [(NHC)Ag(NH<sub>3</sub>)]PF<sub>6</sub> (5)

This was prepared as described above using 2PF<sub>6</sub> (0.119 g, 0.250 mmol), Ag<sub>2</sub>O (0.029 g, 0.125 mmol) and concentrated ammonia solution (170 μL, 2.6 mmol). As a result, 0.116 g (77%) of a colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 7.28–7.45 (m, 4 H, Bn), 5.71 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.60 (m, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.23 (s, 3 H, N<sup>1</sup>Me), 3.03 (s, 3 H, NH<sub>3</sub>), 1.43 (m, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>) δ = 197.15 (C-Ag), 152.92 (C<sup>6</sup>=O), 150.60 (C<sup>2</sup>=O), 140.34 (C<sup>4</sup>), 135.63 (Bn), 132.60 (Bn), 129.10 (Bn), 128.56 (Bn), 108.22 (C<sup>5</sup>), 52.02 (N<sup>7</sup>CH<sub>2</sub>), 46.35 (N<sup>9</sup>CH<sub>2</sub>), 31.39 (N<sup>3</sup>Me), 28.20 (N<sup>1</sup>Me), 17.26 (Me). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>) δ = -144.19 (hept., *J* = 711 Hz, PF<sub>6</sub>). High-resolution positive-ion ESMS (*m/z*): calculated for [M+H+Na]<sup>+</sup> 480.0332; found 480.0328. IR (ATR): 3300–3400 cm<sup>-1</sup> ν(NH<sub>3</sub>), 833 cm<sup>-1</sup> ν(PF<sub>6</sub>). X-ray quality crystals were obtained by slow diffusion of CHCl<sub>3</sub> into an acetone solution of the compound.

### [(NHC)Ag(NH<sub>3</sub>)]PF<sub>6</sub> (6)

This was prepared as described above using 3PF<sub>6</sub> (0.092 g, 0.250 mmol), Ag<sub>2</sub>O (0.029 g, 0.125 mmol) and concentrated ammonia solution (163 μL, 2.7 mmol). As a result, 0.084 g (68%) of a colorless solid was obtained. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ = 4.60 (q, *J* = 7.0 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 4.08 (s, 3 H, N<sup>7</sup>Me), 3.72 (s, 3 H, N<sup>3</sup>Me), 3.26 (s, 3 H, N<sup>1</sup>Me), 3.06 (br. s, 3 H, NH<sub>3</sub>), 1.46 (t, *J* = 7.0 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-d<sub>6</sub>) δ = 153.21 (C<sup>6</sup>=O), 150.68 (C<sup>2</sup>=O), 139.83 (C<sup>4</sup>), 108.88 (C<sup>5</sup>), 46.04 (N<sup>9</sup>CH<sub>2</sub>), 38.03 (N<sup>7</sup>Me), 31.34 (N<sup>3</sup>Me), 28.17 (N<sup>1</sup>Me), 17.38 (Me). The carbene-carbon signal could not be detected. <sup>31</sup>P NMR (DMSO-d<sub>6</sub>)

$\delta = -144.19$  (hept.,  $J = 711$  Hz,  $\text{PF}_6$ ). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  347.0511; found 347.0505. IR (ATR):  $3300\text{--}3400$   $\text{cm}^{-1}$   $\nu(\text{NH}_3)$ ,  $833$   $\text{cm}^{-1}$   $\nu(\text{PF}_6)$ .

#### [Ag(NHC)<sub>2</sub>]PF<sub>6</sub> (7)

A suspension of **1PF<sub>6</sub>** (0.0555 g, 0.125 mmol) in absolute EtOH (2 mL) was treated with Ag<sub>2</sub>O (0.0145 g, 0.0626 mmol) and Et<sub>2</sub>NH (65  $\mu\text{L}$ , 0.627 mmol). After stirring at room temperature for 4 h, the colorless solid was isolated by filtration and was washed with cold EtOH and Et<sub>2</sub>O. A colorless solid was obtained in 80% yield (0.0425 g). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta = 7.25\text{--}7.33$  (m, 10 H, Ph), 5.74 (s, 4 H, N<sup>7</sup>CH<sub>2</sub>), 4.56 (q,  $J = 7.2$  Hz, 4 H, N<sup>9</sup>CH<sub>2</sub>), 3.73 (s, 6 H, N<sup>3</sup>Me), 3.25 (s, 6 H, N<sup>1</sup>Me), 1.39 (t,  $J = 7.2$  Hz, 6 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta = 186.24$  (d,  $J = 217$  Hz, C<sup>109</sup>Ag), 186.22 (d,  $J = 192$  Hz, C<sup>107</sup>Ag), 152.98 (C<sup>6</sup>=O), 150.61 (C<sup>2</sup>=O), 140.23 (C<sup>8</sup>), 136.59 (Ph), 128.61 (Ph), 127.88 (Ph), 127.00 (Ph), 108.34 (C<sup>5</sup>), 52.69 (N<sup>7</sup>CH<sub>2</sub>), 46.35 (N<sup>9</sup>CH<sub>2</sub>), 31.38 (N<sup>3</sup>Me), 28.19 (N<sup>1</sup>Me), 17.26 (Me). <sup>31</sup>P NMR (acetone-*d*<sub>6</sub>)  $\delta = -144.27$  (hept.,  $J = 707$  Hz,  $\text{PF}_6$ ). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  703.1910; found 703.1906. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O into an acetone solution of the compound.

#### [Ag(NHC)<sub>2</sub>]PF<sub>6</sub> (8)

This was prepared as described above using **2PF<sub>6</sub>** (0.0598 g, 0.125 mmol), Ag<sub>2</sub>O (0.0145 g, 0.0626 mmol) and Et<sub>2</sub>NH (65  $\mu\text{L}$ , 0.627 mmol). As a result, 0.040 g (72%) of a colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)  $\delta = 7.30\text{--}7.43$  (m, 8 H, Bn), 5.83 (s, 4 H, N<sup>7</sup>CH<sub>2</sub>), 4.79 (q,  $J = 7.3$  Hz, 4 H, N<sup>9</sup>CH<sub>2</sub>), 3.88 (s, 6 H, N<sup>3</sup>Me), 3.30 (s, 6 H, N<sup>1</sup>Me), 1.60 (t,  $J = 7.3$  Hz, 6 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, Acetone-*d*<sub>6</sub>)  $\delta = 187.42$  (unres. d, C-Ag), 154.96 (C<sup>6</sup>=O), 152.47 (C<sup>2</sup>=O), 142.06 (C<sup>4</sup>), 137.19 (Bn), 135.15 (Bn), 130.77 (Bn), 130.41 (Bn), 110.44 (C<sup>5</sup>), 54.25 (N<sup>7</sup>CH<sub>2</sub>), 48.63 (N<sup>9</sup>CH<sub>2</sub>), 32.77 (N<sup>3</sup>Me), 29.36 (N<sup>1</sup>Me), 18.76 (Me). <sup>31</sup>P NMR (acetone-*d*<sub>6</sub>)  $\delta = -144.27$  (hept.,  $J = 707$  Hz,  $\text{PF}_6$ ). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}]^+$  771.1131; found 771.1130.

#### [Ag(NHC)Cl] (9)

A solution of **1Cl** (0.05 g, 0.149 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7.5 mL) was treated with Ag<sub>2</sub>O (0.0174 g, 0.0751 mmol). After 4 h at room temperature most of the silver oxide had dissolved. The mixture was passed through Celite, and the filtrate was concentrated in vacuum. Addition of Et<sub>2</sub>O precipitated a colorless solid, which was isolated by filtration and was washed with Et<sub>2</sub>O. A colorless solid was obtained in 67% yield (0.0445 g). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta = 7.26\text{--}7.39$  (m, 5 H, Ph), 5.70 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.58 (q,  $J = 7.2$  Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.71 (s, 3 H, N<sup>3</sup>Me), 3.23 (s, 3 H, N<sup>1</sup>Me), 1.44 (t,  $J = 7.2$  Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta = 186.77$  (C-Ag), 152.97 (C<sup>6</sup>=O), 150.59 (C<sup>2</sup>=O), 140.24 (C<sup>4</sup>), 136.56 (Ph), 128.60 (Ph), 127.93 (Ph), 127.38 (Ph), 108.15 (C<sup>5</sup>), 52.88 (N<sup>7</sup>CH<sub>2</sub>), 46.41 (N<sup>9</sup>CH<sub>2</sub>), 31.38 (N<sup>3</sup>Me), 28.20 (N<sup>1</sup>Me), 17.24 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}+\text{Na}]^+$  463.0067; found 463.077. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

#### [Ag(NHC)Cl] (10)

This was prepared as described above using **2Cl** (0.0554 g, 0.140 mmol) and Ag<sub>2</sub>O (0.0174 g, 0.0751 mmol). As a result, 0.0475 g (66%) of a colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)  $\delta = 7.34\text{--}7.58$  (m, 4 H, Bn), 5.81 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.78 (q,  $J = 7.2$  Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.89 (s, 3 H, N<sup>3</sup>Me), 3.31 (s, 3 H, N<sup>1</sup>Me), 1.59 (t,  $J = 7.2$  Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, Acetone-*d*<sub>6</sub>)  $\delta = 187.60$  (C-Ag), 154.87 (C<sup>6</sup>=O), 152.35 (C<sup>2</sup>=O), 142.24 (C<sup>4</sup>), 137.22 (Bn), 135.10 (Bn), 131.48 (Bn), 130.23 (Bn), 110.12 (C<sup>5</sup>), 54.39 (N<sup>7</sup>CH<sub>2</sub>), 48.48 (N<sup>9</sup>CH<sub>2</sub>), 32.78 (N<sup>3</sup>Me), 29.36 (N<sup>1</sup>Me), 18.61 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}+\text{Na}]^+$  496.9677; found 496.9671. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

#### [Ag(NHC)Cl] (11)

This was prepared as described above using **3Cl** (0.0387 g, 0.150 mmol) and Ag<sub>2</sub>O (0.0174 g, 0.0751 mmol). As a result, 0.0285 g (52%) of a colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta = 4.56$  (q,  $J = 7.2$  Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 4.04 (s, 3 H, N<sup>7</sup>Me), 3.70 (s, 3 H, N<sup>3</sup>Me), 3.24 (s, 3 H, N<sup>1</sup>Me), 1.44 (t,  $J = 7.2$  Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta = 185.25$  (C-Ag), 153.18 (C<sup>6</sup>=O), 150.66 (C<sup>2</sup>=O), 139.80 (C<sup>4</sup>), 108.79 (C<sup>5</sup>),

46.09 (N<sup>9</sup>CH<sub>2</sub>), 37.99 (N<sup>7</sup>Me), 31.33 (N<sup>3</sup>Me), 28.14 (N<sup>1</sup>Me), 17.30 (Me). High-resolution positive-ion ESMS (*m/z*): calculated for [M-AgCl]<sup>+</sup> 223.1195; found 223.1218.

#### [Au(NHC)Cl] (12)

A solution of complex **9** (0.0442 g, 0.100 mmol) and [AuCl(tht)] (0.0320 g, 0.0998 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was left to stir at room temperature for ca. 4 h. The mixture was passed through Celite, and the solvent was removed under reduced pressure. The resulting material was washed with Et<sub>2</sub>O and dried in air. A colorless product was obtained in 64% yield (0.034 g). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.62 (d, *J* = 6.7 Hz, 2 H, *o*-Ph), 7.27–7.36 (m, 3 H, *m*-Ph, *p*-Ph), 5.78 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.70 (q, *J* = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.79 (s, 3 H, N<sup>3</sup>Me), 3.38 (s, 3 H, N<sup>1</sup>Me), 1.58 (t, *J* = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>) δ = 176.79 (C-Au), 152.93 (C<sup>6</sup>=O), 150.63 (C<sup>2</sup>=O), 139.33 (C<sup>4</sup>), 134.87 (*ipso*-Ph), 128.84, 128.73, 128.59 (Ph), 108.16 (C<sup>5</sup>), 53.68 (N<sup>7</sup>CH<sub>2</sub>), 46.71 (N<sup>9</sup>CH<sub>2</sub>), 31.68 (N<sup>3</sup>Me), 28.84 (N<sup>1</sup>Me), 17.33 (Me). High-resolution positive-ion ESMS (*m/z*): calculated for [M+Na]<sup>+</sup> 553.0682; found 553.0792.

#### [Au(NHC)Cl] (13)

This was prepared as described above using **10** (0.0476 g, 0.100 mmol) and [AuCl(tht)] (0.0320 g, 0.0998 mmol). As a result, 0.0420 g (74%) colorless solid was obtained. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.58 (d, *J* = 8.4 Hz, 2 H, *o*-C<sub>6</sub>H<sub>4</sub>), 7.28–7.31 (m, 2 H, *m*-C<sub>6</sub>H<sub>4</sub>), 5.74 (s, 2 H, N<sup>7</sup>CH<sub>2</sub>), 4.69 (q, *J* = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 3.79 (s, 3 H, N<sup>3</sup>Me), 3.38 (s, 3 H, N<sup>1</sup>Me), 1.58 (t, *J* = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>) δ = 176.79 (C-Au), 152.96 (C<sup>6</sup>=O), 150.57 (C<sup>2</sup>=O), 139.40 (C<sup>4</sup>), 134.87 (*ipso*-Bn), 133.29 (Bn), 130.10 (Bn), 129.04 (Bn), 108.04 (C<sup>5</sup>), 52.96 (N<sup>7</sup>CH<sub>2</sub>), 46.77 (N<sup>9</sup>CH<sub>2</sub>), 31.70 (N<sup>3</sup>Me), 28.86 (N<sup>1</sup>Me), 17.33 (Me). High-resolution positive-ion ESMS (*m/z*): calculated for [M+Na]<sup>+</sup> 587.0292; found 587.0291.

#### [Au(NHC)Cl] (14)

This was prepared as described above using **11** (0.0365 g, 0.098 mmol) and [AuCl(tht)] (0.0320 g, 0.0998 mmol). As a result, 0.0295 g (55%) colorless solid was obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 4.71 (q, *J* = 7.2 Hz, 2 H, N<sup>9</sup>CH<sub>2</sub>), 4.17 (s, 3 H, N<sup>7</sup>Me), 3.83 (s, 3 H, N<sup>3</sup>Me), 3.43 (s, 3 H, N<sup>1</sup>Me), 1.60 (t, *J* = 7.2 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ = 177.33 (C-Au), 153.28 (C<sup>6</sup>=O), 150.71 (C<sup>2</sup>=O), 138.10 (C<sup>4</sup>), 113.18 (C<sup>5</sup>), 46.47 (N<sup>9</sup>CH<sub>2</sub>), 37.98 (N<sup>7</sup>Me), 31.65 (N<sup>3</sup>Me), 28.76 (N<sup>1</sup>Me), 17.36 (Me). High-resolution positive-ion ESMS (*m/z*): calculated for [M+Na]<sup>+</sup> 477.0369; found 477.0366. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

#### [RuCl<sub>2</sub>(NHC)(*p*-cym)] (15)

This was prepared as described above using complex **9** (0.0438 g, 0.099 mmol) and [RuCl<sub>2</sub>(*p*-cym)]<sub>2</sub> (0.0294 g, 0.048 mmol). A brown product was obtained in 72% yield (0.0431 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 223 K) δ = 7.30–7.48 (m, 3 H, Ph), 6.89 (m, 2 H, Ph), 6.31 (d, 1 H, *J* = 17.0 Hz, N<sup>7</sup>CH<sub>2</sub>), 5.96 (d, 1H, *J* = 17.0 Hz, N<sup>7</sup>CH<sub>2</sub>), 5.44–5.53 (m, 1 H, *p*-cym), 5.33–5.44 (m, 1 H, N<sup>9</sup>CH<sub>2</sub>), 5.19–5.29 (m, 2 H, *p*-cym), 5.17–5.18 (m, 1 H, *p*-cym), 4.34–4.49 (m, 1 H, N<sup>9</sup>CH<sub>2</sub>), 3.78 (s, 3 H, N<sup>3</sup>Me), 3.29 (s, 3 H, N<sup>1</sup>Me), 2.65–2.78 (m, 1 H, *p*-cym), 2.04 (s, 3 H, *p*-cym), 1.52 (s, 3 H, Me), 1.30 (d, *J* = 6.3 Hz, 3 H, *p*-cym), 1.19 (d, *J* = 6.3 Hz, 3 H, *p*-cym). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 223 K) δ = 189.37 (C-Ru), 151.52 (C<sup>6</sup>=O), 150.87 (C<sup>2</sup>=O), 140.88 (C<sup>4</sup>), 138.58 (*ipso*-Ph), 129.19 (Ph), 127.38 (Ph), 123.50 (Ph), 111.12 (C<sup>5</sup>), 107.77 (*p*-cym), 94.64 (*p*-cym), 86.37 (*p*-cym), 86.12 (*p*-cym), 83.42 (*p*-cym), 82.78 (*p*-cym), 53.69 (N<sup>7</sup>CH<sub>2</sub>), 47.18 (N<sup>9</sup>CH<sub>2</sub>), 32.57 (N<sup>3</sup>Me), 30.48 (*p*-cym), 28.67 (N<sup>1</sup>Me), 22.57 (*p*-cym), 22.32 (*p*-cym), 18.01 (*p*-cym), 17.70 (Me). High-resolution positive-ion ESMS (*m/z*): calculated for [M-Cl]<sup>+</sup> 569.1257; found 569.1257. X-ray quality crystals were obtained by slow diffusion of hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

#### [RuCl<sub>2</sub>(NHC)(*p*-cym)] (16)

This was prepared as described above using complex **10** (0.0471 g, 0.107 mmol) and [RuCl<sub>2</sub>(*p*-cym)]<sub>2</sub> (0.0294 g, 0.048 mmol). A brown product was obtained. As a result, 0.0495 g (76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 223 K) δ = 7.35–7.44 (d, *J* = 7.5 Hz, 2 H, Bn), 6.86 (m, 2 H, Bn), 6.30 (d, 1 H, *J* = 17.2 Hz, N<sup>7</sup>CH<sub>2</sub>), 5.87 (d, *J* = 17.2 Hz, N<sup>7</sup>CH<sub>2</sub>), 5.49–5.52 (m, 1 H, *p*-cym), 5.40–5.42 (m, 1 H, N<sup>9</sup>CH<sub>2</sub>), 5.29–5.31 (m, 1 H, *p*-cym), 5.23–5.25 (m, 2 H, *p*-cym), 4.37–4.50 (m, 1 H, N<sup>9</sup>CH<sub>2</sub>), 3.78 (s, 3 H, N<sup>3</sup>Me), 3.29 (s, 3 H, N<sup>1</sup>Me), 2.65–2.78 (m, 1 H, *p*-cym), 2.05 (s, 3 H, *p*-cym), 1.52 (s, 3 H, Me), 1.30 (d, *J* = 4.3 Hz, 3 H, *p*-cym), 1.22 (d,

$J = 5.7$  Hz, 3 H, *p*-cym).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 223 K)  $\delta = 189.52$  (C-Ru), 151.48 ( $\text{C}^6=\text{O}$ ), 150.78 ( $\text{C}^2=\text{O}$ ), 140.97 ( $\text{C}^4$ ), 137.18 (*ipso*-Bn), 132.82 (Bn), 129.38 (Bn), 125.03 (Bn), 110.90 ( $\text{C}^5$ ), 108.04 (*p*-cym), 94.68 (*p*-cym), 86.37 (*p*-cym), 86.06 (*p*-cym), 83.26 (*p*-cym), 83.04 (*p*-cym), 53.41 ( $\text{N}^7\text{CH}_2$ ), 47.23 ( $\text{N}^9\text{CH}_2$ ), 32.55 ( $\text{N}^3\text{Me}$ ), 30.58 (*p*-cym), 28.69 ( $\text{N}^1\text{Me}$ ), 22.46 (*p*-cym), 18.09 (*p*-cym), 17.76 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  603.0868; found 603.0874.

#### [RuCl<sub>2</sub>(NHC)(*p*-cym)] (17)

This was prepared as described above using complex **11** (0.0362 g, 0.099 mmol) and  $[\text{RuCl}_2(\textit{p}\text{-cym})]_2$  (0.0294 g, 0.048 mmol). A brown product was obtained. As a result, 0.0420 g (80%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 5.47\text{--}5.66$  (m, 2 H, *p*-cym), 6.26 (d,  $J = 6.1$  Hz, 2 H, *p*-cym), 4.50–4.67 (m, 2 H,  $\text{N}^9\text{CH}_2$ ), 4.36 (s, 3 H,  $\text{N}^7\text{Me}$ ), 3.77 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.42 (s, 3 H,  $\text{N}^1\text{Me}$ ), 3.02 (unres. pent, 1 H, *p*-cym), 2.18 (s, 3 H, *p*-cym), 1.41 (t,  $J = 7.3$  Hz, 3 H, Me), 1.35 (d,  $J = 6.9$  Hz, 3 H, *p*-cym).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 186.12$  (C-Ru), 152.80 ( $\text{C}^6=\text{O}$ ), 151.17 ( $\text{C}^2=\text{O}$ ), 140.76 ( $\text{C}^4$ ), 111.85 ( $\text{C}^5$ ), 109.36 (*p*-cym), 99.08 (*p*-cym), 86.22 (*p*-cym), 83.03 (*p*-cym), 81.27 (*p*-cym), 80.52 (*p*-cym), 46.70 ( $\text{N}^9\text{CH}_2$ ), 39.66 ( $\text{N}^7\text{Me}$ ), 32.51 ( $\text{N}^3\text{Me}$ ), 30.89 (*p*-cym), 28.58 ( $\text{N}^1\text{Me}$ ), 23.23 (*p*-cym), 22.11 (*p*-cym), 18.93 (*p*-cym), 17.36 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  493.0944; found 493.0947.

#### [RhCl<sub>2</sub>(NHC)(Cp<sup>\*</sup>)] (18)

This was prepared as described above using complex **9** (0.0177 g, 0.040 mmol) and  $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$  (0.0124 g, 0.020 mmol). A red-brown product was obtained in 53% yield (0.013 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.26\text{--}7.32$  (m, 2 H, *m*-Ph), 7.23 (t,  $J = 7.3$  Hz, 1 H, *p*-Ph), 6.89 (d,  $J = 7.3$  Hz, 2 H, *o*-Ph), 6.39 (d,  $J = 16.5$  Hz, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.98 (d,  $J = 16.5$  Hz, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.18–5.29 (m, 2 H,  $\text{N}^9\text{CH}_2$ ), 4.66–4.79 (m, 2 H,  $\text{N}^9\text{CH}_2$ ), 3.79 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.24 (s, 3 H,  $\text{N}^1\text{Me}$ ), 1.54 (s, 15 H, Cp<sup>\*</sup>), 1.49 (t,  $J = 7.3$  Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 183.71$  (d,  $J = 54.5$  Hz, C-Rh), 151.73 ( $\text{C}^6=\text{O}$ ), 151.27 ( $\text{C}^2=\text{O}$ ), 141.13 ( $\text{C}^4$ ), 138.58 (*ipso*-Ph), 128.56 (Ph), 127.12 (Ph), 124.67 (Ph), 111.72 ( $\text{C}^5$ ), 97.21 (d,  $J = 7.2$  Hz, Cp<sup>\*</sup>), 54.78 ( $\text{N}^7\text{CH}_2$ ), 47.10 ( $\text{N}^9\text{CH}_2$ ), 32.50 ( $\text{N}^3\text{Me}$ ), 28.60 ( $\text{N}^1\text{Me}$ ), 17.66 (Me), 9.49 (Cp<sup>\*</sup>). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}+\text{Na}]^+$  629.0933; found 629.0930. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

#### [RhCl<sub>2</sub>(NHC)(Cp<sup>\*</sup>)] (19)

This was prepared as described above using complex **10** (0.0190 g, 0.040 mmol) and  $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$  (0.0124 g, 0.020 mmol). As a result, 0.0140 g, (55%) of a red-brown solid was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.24\text{--}7.28$  (m, 2 H, B), 6.92 (d,  $J = 7.8$  Hz, 2 H, Bn), 6.14–6.29 (s, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.95–6.10 (s, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.10–5.25 (s, 1 H,  $\text{N}^9\text{CH}_2$ ), 4.70–4.90 (s, 1 H,  $\text{N}^9\text{CH}_2$ ), 3.79 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.25 (s, 3 H,  $\text{N}^1\text{Me}$ ), 1.56 (s, 15 H, Cp<sup>\*</sup>), 1.49 (t,  $J = 7.2$  Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 183.60$  (d,  $J = 53.3$  Hz, C-Rh), 151.76 ( $\text{C}^6=\text{O}$ ), 151.20 ( $\text{C}^2=\text{O}$ ), 141.34 ( $\text{C}^4$ ), 136.90 (*ipso*-Bn), 132.93 (Bn), 128.65 (Bn), 126.64 (Bn), 111.52 ( $\text{C}^5$ ), 97.24 (d,  $J = 7.1$  Hz, Cp<sup>\*</sup>), 54.35 ( $\text{N}^7\text{CH}_2$ ), 47.00 ( $\text{N}^9\text{CH}_2$ ), 32.51 ( $\text{N}^3\text{Me}$ ), 28.64 ( $\text{N}^1\text{Me}$ ), 17.77 (Me), 9.52 (Cp<sup>\*</sup>). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  605.0957; found 605.0957. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

#### [RhCl<sub>2</sub>(NHC)(Cp<sup>\*</sup>)] (20)

This was prepared as described above using complex **11** (0.0322 g, 0.0881 mmol) and  $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$  (0.0248 g, 0.0400 mmol). As a result, 0.0355 g, (76%) of a red-brown solid was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 4.73\text{--}5.09$  (m, 2 H,  $\text{N}^9\text{CH}_2$ ), 4.33 (s, 3 H,  $\text{N}^7\text{Me}$ ), 3.75 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.39 (s, 3 H,  $\text{N}^1\text{Me}$ ), 1.66 (s, 15 H, Cp<sup>\*</sup>), 1.39 (t,  $J = 7.2$  Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 152.94$  ( $\text{C}^6=\text{O}$ ), 151.20 ( $\text{C}^2=\text{O}$ ), 140.92 ( $\text{C}^4$ ), 112.06 ( $\text{C}^5$ ), 96.98 (d,  $J = 7.0$  Hz, Cp<sup>\*</sup>), 46.41 ( $\text{N}^9\text{CH}_2$ ), 39.14 ( $\text{N}^7\text{Me}$ ), 32.54 ( $\text{N}^3\text{Me}$ ), 28.61 ( $\text{N}^1\text{Me}$ ), 17.55 (Me), 9.59 (Cp<sup>\*</sup>). The carbene-carbon signal could not be detected. High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  495.1034; found 495.1030.

#### [RhCl(NHC)(cod)] (21)

This was prepared as described above using complex **9** (0.0352 g, 0.0797 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (0.0196 g, 0.0397 mmol). A yellow product was obtained in 48% yield (0.021 g).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.44 (d,  $J$  = 7.3 Hz, 2 H, *o*-Ph), 7.33 (t,  $J$  = 7.3 Hz, 2 H, *m*-Ph), 7.23–7.29 (m, 1 H, *p*-Ph), 6.25 (d,  $J$  = 14.8 Hz, 1 H,  $\text{N}^7\text{CH}_2$ ), 6.10 (d,  $J$  = 14.8 Hz, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.42–5.53 (m, 1 H,  $\text{N}^9\text{CH}_2$ ), 5.16–5.23 (m, 1 H, cod), 5.07–5.15 (m, 1 H, cod), 4.99–5.07 (m, 1 H,  $\text{N}^9\text{CH}_2$ ), 3.78 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.30 (s, 3 H,  $\text{N}^1\text{Me}$ ), 3.26–3.32 (m, 3 H, cod), 2.99–3.06 (m, 1 H, cod), 2.25–2.52 (m, 3 H, cod), 1.83–2.10 (m, 4 H, cod), 1.71–1.76 (m, 1 H, cod), 1.69 (t,  $J$  = 7.2 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.49 (C-Rh), 152.14 ( $\text{C}^6=\text{O}$ ), 150.81 ( $\text{C}^2=\text{O}$ ), 140.08 ( $\text{C}^4$ ), 136.92 (*ipso*-Ph), 128.50 (*m*-Ph), 127.66 (*p*-Ph), 127.32 (*o*-Ph), 109.00 ( $\text{C}^5$ ), 100.89 (d,  $J$  = 6.8 Hz, cod), 100.12 (d,  $J$  = 6.8 Hz, cod), 69.84 (d,  $J$  = 14.3 Hz, cod), 69.67 (d,  $J$  = 14.3 Hz, cod), 53.71 ( $\text{N}^7\text{CH}_2$ ), 46.33 ( $\text{N}^9\text{CH}_2$ ), 33.53 (cod), 31.89 (cod), 31.59 ( $\text{N}^3\text{Me}$ ), 28.55 (cod), 28.11 ( $\text{N}^1\text{Me}$ ), 29.25 (cod), 17.67 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  509.1424; found 509.1429.

#### [RhCl(NHC)(cod)] (22)

This was prepared as described above using complex **10** (0.0635 g, 0.1334 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (0.0329 g, 0.0604 mmol). As a result, 0.0520 g (72%) of a yellow solid was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.47 (d,  $J$  = 8.4 Hz, 2 H, Bn), 7.29 (m, 2 H, Bn), 6.26 (d,  $J$  = 14.7 Hz, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.99 (d,  $J$  = 14.7 Hz, 1 H,  $\text{N}^7\text{CH}_2$ ), 5.40–5.50 (m, 1 H,  $\text{N}^9\text{CH}_2$ ), 5.10–5.23 (m, 2 H, cod), 4.99–5.10 (m, 1 H,  $\text{N}^9\text{CH}_2$ ), 3.78 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.30 (s, 3 H,  $\text{N}^1\text{Me}$ ), 3.00–3.10 (m, 1 H, cod), 2.28–2.52 (m, 3 H, cod), 2.10–2.20 (m, 1 H, cod), 1.75–2.08 (m, 4 H, cod), 1.69 (t,  $J$  = 7.2 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.28 (C-Rh), 152.12 ( $\text{C}^6=\text{O}$ ), 150.74 ( $\text{C}^2=\text{O}$ ), 140.23 ( $\text{C}^4$ ), 135.15 (*ipso*-Bn), 133.66 (Bn), 129.13 (Bn), 128.65 (Bn), 109.94 ( $\text{C}^5$ ), 101.08 (d,  $J$  = 6.7 Hz, cod), 100.54 (d,  $J$  = 6.7 Hz, cod), 69.98 (d,  $J$  = 13.8 Hz, cod), 69.66 (d,  $J$  = 13.8 Hz, cod), 53.19 ( $\text{N}^7\text{CH}_2$ ), 46.35 ( $\text{N}^9\text{CH}_2$ ), 33.41 (cod), 33.06 (cod), 31.58 ( $\text{N}^3\text{Me}$ ), 29.22 (cod), 28.55 ( $\text{N}^1\text{Me}$ ), 28.19 (cod), 16.89 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  543.1034; found 543.1037. X-ray quality crystals were obtained by slow diffusion of hexane into a  $\text{CH}_2\text{Cl}_2$  solution of the compound.

#### [RhCl(NHC)(cod)] (23)

This was prepared as described above using complex **11** (0.0291 g, 0.0796 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (0.0196 g, 0.0360 mmol). As a result, 0.0370 g (99%) of a yellow solid was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 5.40–5.31 (m, 1 H,  $\text{N}^9\text{CH}_2$ ), 5.09 (dd,  $J$  = 21.0, 5.3 Hz, 2 H, cod), 4.90 (m, 1 H,  $\text{N}^9\text{CH}_2$ ), 4.39 (s, 3 H,  $\text{N}^7\text{Me}$ ), 3.76 (s, 3 H,  $\text{N}^3\text{Me}$ ), 3.48–3.39 (m, 2 H, cod), 3.35 (s, 3 H,  $\text{N}^1\text{Me}$ ), 2.53–2.37 (m, 4 H, cod), 2.01 (d,  $J$  = 9.5 Hz, 4 H, cod), 1.61 (t,  $J$  = 7.2 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.11 (br. m, C-Rh), 152.81 ( $\text{C}^6=\text{O}$ ), 150.79 ( $\text{C}^2=\text{O}$ ), 139.61 ( $\text{C}^4$ ), 110.51 ( $\text{C}^5$ ), 100.59 (d,  $J$  = 6.2 Hz, cod), 100.30 (d,  $J$  = 6.2 Hz, cod), 69.62 (cod), 68.88 (cod), 46.04 ( $\text{N}^9\text{CH}_2$ ), 37.42 ( $\text{N}^7\text{CH}_2$ ), 32.79 (d,  $J$  = 5.6 Hz, cod), 31.48 ( $\text{N}^3\text{Me}$ ), 28.81 ( $\text{N}^1\text{Me}$ ), 28.72 (cod), 28.45 (cod), 28.00 (cod), 16.93 (Me). High-resolution positive-ion ESMS ( $m/z$ ): calculated for  $[\text{M}-\text{Cl}]^+$  433.1111; found 433.1114.

#### X-ray crystallography

Diffraction data for complex **15** was collected at 100 K using a Bruker-AXS Kappa Mach3 APEX-II system located in front of a  $\mu\text{s}$  microfocus source equipped with Incoatec Helios mirrors for Mo radiation. For data integration the APEX3 package was employed. For data scaling and absorption correction SADABS was used [61]. Diffraction data for complexes **5**, **7**, **9**, **12–14** and **18–22** was collected at 150 K using a Rigaku Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package [62]. Data for complex **10** was collected at beamline P11, PETRA III DESY Hamburg. For data integration XDS [63] (version 31 January 2020) and for scaling as well as absorption correction SADABS were used. All structures were solved by direct methods or intrinsic phasing (SHELXT [64]) and refined using SHELXL [65] as implemented in the Olex2 graphical user interface [66]. Crystallographic and refinement details are collected in Table S1 in Supplementary Materials.

#### 4. Conclusions

We present, herein, a simple method to ethylate various xanthine derivatives at position N9 using ethyl tosylate or diethyl sulfate. High yields of the pure xanthinium salts



were obtained in short times with minimal work-up. The anions could be exchanged to give the corresponding  $\text{PF}_6^-$  and  $\text{Cl}^-$  salts. The xanthinium  $\text{PF}_6^-$  salts reacted with  $\text{Ag}_2\text{O}$  in the presence of  $\text{NH}_3$  or  $\text{Et}_2\text{NH}$  to furnish either silver carbene complexes with ammonia co-ligands or bis(carbene) silver compounds, respectively. The xanthinium chloride salts gave the corresponding neutral Ag-carbene complexes. These silver compounds were used successfully to transfer the carbene ligands to a variety of other metals including Au(I), Ru(II), Rh(I) and Rh(III). Work is ongoing to incorporate other groups into the xanthine-backbone by this approach and to examine possible applications of these metal-carbenes.

**Supplementary Materials:** The following are available online, Table S1: Crystallographic and refinement details for all X-ray structures reported herein. Figures S1–S70: NMR spectra of the compounds.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds are available from the authors.

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