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Ru–Ag and Ru–Au dicarbene complexes from an abnormal carbene ruthenium system†

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Reaction of $[Ru(OAc)_2(PPh_3)_2]$ with a P-functionalized imidazolium bromide easily affords a cationic abnormal carbene Ru system. Metalation with Ag_2O yields a Ru–Ag complex containing an anionic dicarbene ligand, while subsequent transmetalation with Au(tht)Cl leads to the corresponding Ru–Au system. The bimetallic complexes were characterized by single crystal X-ray diffraction and are the first examples of complexes bearing anionic dicarbene ligands connecting two different d-block elements.

N-heterocyclic carbenes (NHCs) have been widely employed as practical ligands in organometallic chemistry and in catalysis during the last two decades.[1–12] Imidazol-2-ylidene NHC ligands exhibit unique features with respect to stability, donor strength and steric requirements, leading to several coordination modes (Fig. 1).

While the normal carbene coordination (NHC) still remains predominant in transition metal complexes,[1–12] the abnormal coordination mode (aNHC) was first reported by Crabtree in 2001,[13] and several derivatives were isolated subsequently.[14,15] For Ru only a few aNHC-species have been described,[16–21] and some display high catalytic activity in transfer hydrogenation.[17] Compared to NHCs, the aNHC ligands show stronger σ-donating properties and therefore are complementary ligands of widespread relevance for catalysis. The third type of coordination was first described by Arnold in 2006 for lanthanide–potassium complexes, in which anionic dicarbenes (NHDC) have both a normal and an abnormal carbene center,[22] and other examples have been discovered based on main-group elements.[23–26] NHDC complexes containing one d-block and one main group element have been reported very recently by Goicoechea,[27–29] Stephan[30] and Tamm.[31] In addition, examples with two d-block elements are those based on Pd–Pd, Zn–Zn, Ru–Ru, Ir–Ir and Au–Au systems.[21,32–37] By contrast, no hetero-bimetallic NHDC complexes with two different d-block elements have been reported to date. Interestingly, hetero-bimetallic complexes, based on the related 1,2,4-triazolyl-3,5-diylidene carbenes, have been applied in tandem catalysis, and show superior performance compared to a combination of monometallic species due to cooperative effects.[38,39]

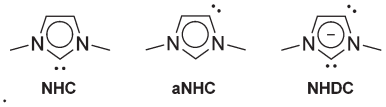

Fig. 1 Possible coordination sites of unsaturated imidazol-2-ylidene ligands: (NHC) normal carbene, (aNHC) abnormal carbene, (NHDC) anionic dicarbene.

Here we report the isolation of the first example of a NHDC complex with two different d-block elements, starting from a cationic aNHC Ru complex and Ag_2O. Transmetalation of the Ru–Ag derivative results in the formation of a Ru–Au complex, enlarging the synthetic scope for NHDC complexes.

The cationic abnormal NHC ruthenium complex **2** can be easily obtained starting from $[Ru(OAc)_2(PPh_3)_2]$ and a functionalized imidazolium bromide (P-NHC·HBr),[40] containing one CH_2 bridged phosphine arm, *via* the normal NHC compound **1** (Scheme 1).

Treatment of $[Ru(OAc)_2(PPh_3)_2]$ with one equivalent of P-NHC·HBr and NaOAc in *t*BuOH at reflux (3 h) affords the NHC complex **1** in 85% yield. A *cis* RuP_2 arrangement has been assigned on the basis of the small $^2J_{PP}$ = 23.6 Hz. The $^{13}C\{^1H\}$ NMR carbene shows signals at δ = 190.3 ppm, as a doublet of doublets with $^2J_{CP}$ = 109.6 and 11.6 Hz, for *trans* and *cis* P atoms, respectively, thus establishing the geometry of **1**.[41] It is worth pointing out that the reaction of $[Ru(OAc)_2(PPh_3)_2]$ with the analogous P-functionalized imid-

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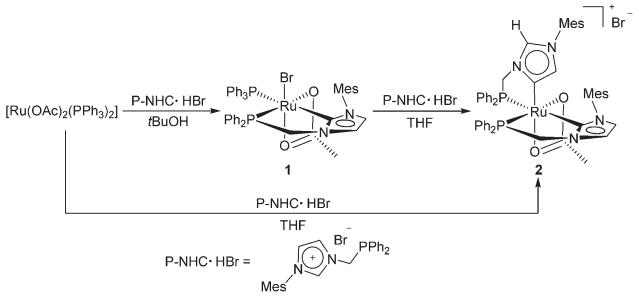


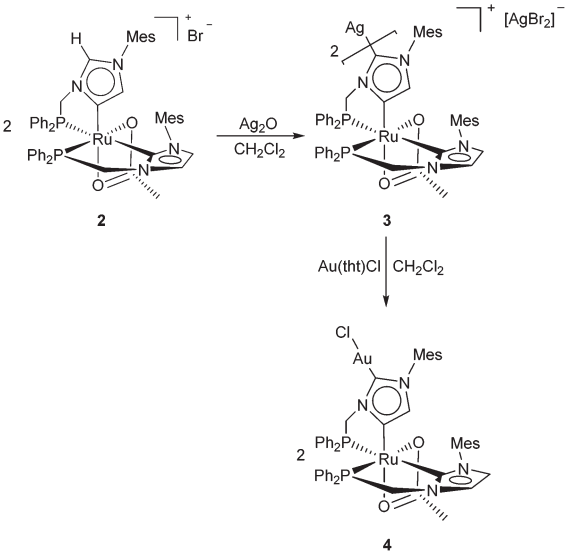
Scheme 1 Syntheses of NHC and aNHC Ru complexes.

azolium bromide with a CH_2CH_2 bridge led to an abnormal NHC Ru complex.[17] Reaction of **1** with one equivalent of P-NHC·HBr in the presence of NaOAc in THF at reflux affords **2** (80% yield) by substitution of PPh_3 and bromide with the chelating aNHC ligand. The two P doublets of **2** at δ = 79.5 and 62.9 ppm ($^2J_{PP}$ = 23.9 Hz) are consistent with the presence of a *cis* RuP_2 geometry. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet of doublets at δ = 191.6 ppm with $^2J_{CP}$ = 102.5 and 11.4 Hz, for a normal carbene with *trans* and *cis* P atoms, and a doublet of doublets at high field δ = 163.0 ppm ($^2J_{CP}$ = 18.4 and 8.5 Hz) for an abnormal carbene with two *cis* P atoms. In the ^1H NMR spectrum, the signal of the NC*H*N proton of the abnormal carbene is exceptionally downfield shifted at δ = 9.75 ppm, close to that of the ligand precursor P-NHC·HBr (10.33 ppm), suggesting a relatively acidic proton.[42–44] Complex **2** can also be prepared directly from $[Ru(OAc)_2(PPh_3)_2]$ and 2 equiv. of P-NHC·HBr in THF in the presence of NaOAc (88% yield). Notably, **2** is a rare example of a Ru-NHC complex bearing both a normal and an abnormal carbene ligand,[16] which may form on account of steric factors involving the bulky mesityl group.

Preliminary results show that **2** (0.1 mol%) displays high catalytic activity in the transfer hydrogenation (TH) of ketones. In the presence of NaO*i*Pr (2 mol%) in 2-propanol at reflux,[40] acetophenone, benzophenone and cyclohexanone are reduced to the corresponding alcohols with 97, 90 and 99% conversion in 20, 80 and 5 min respectively, achieving a TOF up to 49 000 h^{-1}. These results indicate that **2** is among the most active Ru carbene TH catalysts,[17,45–48] even without an amine N–H function which is usually introduced to obtain high activity (bifunctional catalysis).[49,50]

Since the cationic aNHC complex **2**, displaying an NC*H*N proton, can be considered as an "imidazolium salt", we investigated the reaction of **2** with Ag_2O in order to achieve deprotonation and coordination of an Ag atom at the C2 carbon of the abnormal carbene ligand (Scheme 2).

To our delight, the hetero-bimetallic anionic dicarbene **3** was cleanly obtained in 92% yield by stirring a suspension of **2** (2 equiv.) and Ag_2O in CH_2Cl_2 at RT for 7 days, and was characterized by NMR and single crystal X-ray diffraction (Fig. 2).[40] The crystal structure of **3** shows that two Ru units are almost linearly (C1–Ag1–C1′ = 167.8(3)°) linked by the Ag1 atom *via* the anionic dicarbenes. The Ru atoms are coordinated in a



Scheme 2 Synthesis of Ru–Ag and Ru–Au NHDC complexes.

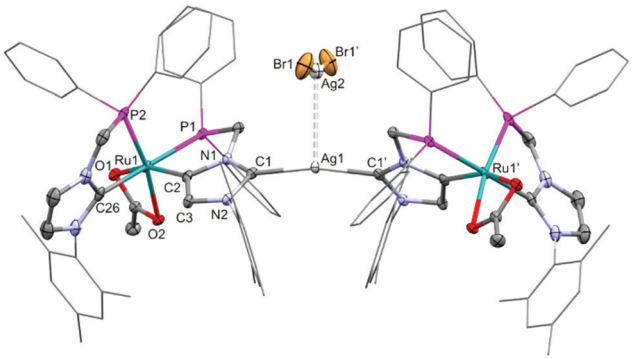


Fig. 2 ORTEP-style molecular structure of **3**. Ellipsoids are shown at 50% probability. For the sake of clarity, hydrogen atoms as well as co-crystallized solvent molecules are omitted and the aromatic substituents are shown as wireframe representation. Selected bond lengths (Å) and angles (°): Ag1–C1 2.112(5), Ag1–Ag2 3.1211(8), Ru1–C2 2.022(5), Ru1–C26 2.089(5), C1–Ag1–C1′ 167.8(3), C1–Ag1–Ag2 96.09(13), C2–Ru1–P1 80.83(14). Symmetry code: 1/2 − *x*, +*y*, −*z*.

pseudo-octahedral geometry, with the same set of ligands as **2**. The Ag1–C1 bond length (2.112(5) Å) is slightly longer compared to other Ag carbenes,[51,52] whereas the Ru1–C2 distance (2.022(5) Å) is similar to that of the related abnormal Ru-aNHC complex[17] and shorter than that of the carbene Ru1–C26 bond (2.089(5) Å). An argentophilic interaction between the $[AgBr_2]^-$ anion and Ag1 is indicated by an Ag1–Ag2 distance of 3.1211(8) Å.[53] Thus, this is the first example of an NHDC complex containing two different d-block elements.

Silver carbene complexes have frequently been employed as transmetalation reagents for the preparation of a large number of NHC complexes.[12,54] Treatment of **3** with 2 equiv. of the gold precursor Au(tht)Cl (tht = tetrahydrothiophene) in CH_2Cl_2 at RT (2 d) afforded the gold NHDC derivative **4** in 93% yield

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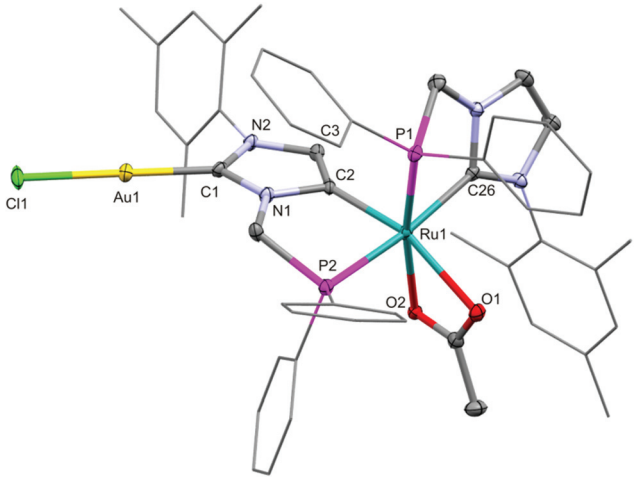

Fig. 3 ORTEP-style molecular structure of **4**. Ellipsoids are shown at 50% probability. For the sake of clarity, hydrogen atoms as well as co-crystallized solvent molecules are omitted and the aromatic substituents are shown as wireframe representation. Selected bond lengths (Å) and angles (°): Au1–C1 1.984(4), Au1–Cl1 2.3026(1), Ru1–C2 2.018(4), C1–Au1–Cl1 178.74(12), C2–Ru1–P1 88.70(11).

(Scheme 2). Upon transmetalation, the Ru–Ag–Ru unit of **3** is split up into two Ru–Au fragments. The gold atom is linearly coordinated by a chloride and the C1-atom of the anionic dicarbene, exhibiting an Au1–C1 distance of 1.984(4) Å and a C1–Au1–Cl1 angle of 178.74(12)°. Almost identical to **3**, the Ru1–C2 distance is 2.018(4) Å (Fig. 3).

The different structures observed for **3** and **4** in the solid state may be associated with subtle effects involving the competition between the neutral [MX(Ru-NHDC)] *versus* the ionic $[M(Ru\text{-}NHDC)_2][MX_2]$ (M = Ag, Au; X = Cl, Br) form.[51] The overall NMR data of **3** and **4** in solution are very similar. However, while for **4** the $^{13}C\{^1H\}$ NMR signal of the C2 carbon bound to Au is at δ = 167.3 ppm with a $^3J_{CP}$ = of 12.7 Hz, no signal was observed for the C2 of **3** even at −90 °C, possibly due to a dynamic process involving the $[AgX_2]^-$ counter ion, a behavior which was reported for other Ag-NHC complexes bearing silver halide anions.[52,55] It is worth pointing out that the syntheses of **3** and **4** occur under mild reaction conditions without modifying the coordination environment of the cationic aNHC Ru complex **2**.

Conclusions

In conclusion, we have reported the first complexes containing an anionic dicarbene ligand connected to two different d-block elements, namely a Ru–Ag and a Ru–Au system. The synthetic pathway entails the use of a cationic abnormal carbene Ru complex, which cleanly undergoes metalation and transmetalation reactions. This Ru derivative was also found to be catalytically active in ketone transfer hydrogenation. Further studies aiming to extend this protocol to the preparation of hetero-bimetallic complexes containing anionic dicarbene ligands *via* cationic aNHC complexes, and examinations of the catalytic utilization of such compounds are currently underway.

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40 The syntheses and characterization of P-NHC·HBr and the complexes **1–4**, as well as the catalytic results, are reported in the ESI.† CCDC 1036993 (compound **3**) and CCDC 1036994 (compound **4**) contain the supplementary crystallographic data for this paper.
41 The $^{31}P\{^1H\}$ NMR spectrum of **1** shows the presence of two closely related species in about 3 : 2 molar ratio, also confirmed by ^1H and $^{13}C\{^1H\}$ NMR measurements, consistent with the presence of two conformers involving the P-NHC five-membered ring. While the $^{31}P\{^1H\}$ NMR spectrum shows a $\Delta\delta < 0.2$ ppm for the two species, in the $^{13}C\{^1H\}$ NMR spectrum the signal which shows the larger difference in chemical shift ($\Delta\delta = 0.9$ ppm) is for the bridged CH_2 group. In addition, a hindered rotation of the Mes group is observed even at 60 °C by ^1H NMR. See ESI† for details.
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