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

Mario J. Bitzer,* Alexander Pöthig, Alexander Jandl, Fritz E. Kühn* and Walter Baratta†

Reaction of [Ru(OAc)2(PPh3)2] with a P-functionalized imidazolium bromide easily affords a cationic abnormal carbene Ru system. Metалation with Ag2O 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 Stephan30 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

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 Ag2O. 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(PPh3)2] and a functionalized imidazolium bromide (P-NHC-HBr),40 containing one CH2 bridged phosphine arm, via the normal NHC compound 1 (Scheme 1).

Treatment of [Ru(OAc)2(PPh3)2] with one equivalent of P-NHC-HBr and NaOAc in iBuOH at reflux (3 h) affords the NHC complex 1 in 85% yield. A cis Ru2P2 arrangement has been assigned on the basis of the small JPP = 23.6 Hz. The 1H NMR carbene shows signals at δ = 190.3 ppm, as a doublet of doublets with JC2P = 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(PPh3)2] with the analogous P-functionalized imid-
azolium bromide with a CH₂CH₂ 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 PPh₃ and bromide with the chelating aNHC ligand. The two P doublets of 2 at δ = 79.5 and 62.9 ppm (²JCP = 23.9 Hz) are consistent with the presence of a cis RuP₂ geometry. The ¹³C{¹H} NMR spectrum shows a doublet of doublets at high field δ = 116.89 ppm (²JCP = 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 proton shifted at δ = 6.14 ppm (trans) and 2.0 Hz (cis) for a normal carbene with trans and cis P atoms, and a doublet of doublets at high field δ = 163.0 ppm (²JCP = 18.4 and 8.5 Hz) for an abnormal carbene with two cis P atoms. Notably, [Ru(OAc)₂(PPh₃)₂] and 2 equiv. of P-NHC·HBr in THF in the presence of NaOAc (88% yield). Notably, [Ru(OAc)₂(PPh₃)₂] and 2 equiv. of P-NHC·HBr in THF at reflux afford 2 (10.33 ppm), suggesting a relatively acidic proton. The δ shift of the NC proton of the abnormal carbene is exceptionally downfield δ = 163.0 ppm (2JCP = 18.4 and 8.5 Hz) for a normal carbene with two cis P atoms, in agreement with the expected lower donating ability of an abnormal carbene. ¹³C{¹H} NMR spectrum shows a doublet of doublets at δ = 191.6 ppm with ²JCP = 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 (²JCP = 18.4 and 8.5 Hz) for an abnormal carbene with two cis P atoms. In the ¹H NMR spectrum, the signal of the NCHN 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(PPh₃)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 NaOAcPr (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 NCHN proton, can be considered as an “imidazolium salt”, we investigated the reaction of 2 with Ag₂O 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 Ag₂O in CH₂Cl₂ at RT for 7 days, and was characterized by NMR and single crystal X-ray diffraction (Fig. 2).⁵⁰ 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 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,¹⁵,⁵³ whereas the Ru₁–C₂ distance (2.022(5) Å) is similar to that of the related abnormal Ru-aNHC complex¹⁷ and shorter than that of the carbene Ru₁–C₂ distance (2.089(5) Å). An argentophilic interaction between the [AgBr₂]⁻ 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 NHDC complexes.¹³,⁵⁴ Treatment of 3 with 2 equiv. of the gold precursor Au(tht)Cl (tht = tetrahydrothiophene) in CH₂Cl₂ at RT (2 d) afforded the gold NHDC derivative 4 in 93% yield.
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.

We thank the Erasmus STA program and the TUM Graduate School for financial support.

Notes and references

1. K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Chem. Rev.*, 2014, **114**, 5215–5272.
2. M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485–496.
3. D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723–6753.
4. Y. Wang and G. H. Robinson, *Dalton Trans.*, 2012, **41**, 337–345.
5. T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940–6952.
6. J. W. Herndon, *Coord. Chem. Rev.*, 2010, **254**, 103–194.
7. G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2009, **110**, 1746–1787.
8. S. Diez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676.
9. F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172.
10. D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655.
11. V. Cesar, S. Bellemín-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619–636.
12. W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309.
13. S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274–2275.
14. R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755–766.
15. P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596–609.
16. G. A. Filonenko, E. Cosimi, L. Lefort, M. P. Conley, C. Copéret, M. Lutz, E. J. M. Hensen and E. A. Pidko, *ACS Catal.*, 2014, **4**, 2667–2671.
17. J. Witt, A. Pöthig, F. E. Kühn and W. Baratta, *Organometallics*, 2013, **32**, 4042–4045.
18. S. Saha, T. Ghatak, B. Saha, H. Doucet and J. K. Bera, *Organometallics*, 2012, **31**, 5500–5505.
19. L. Benhamou, J. Wolf, V. Cesar, A. Labande, R. Poli, N. Lugan and G. Lavigne, *Organometallics*, 2009, **28**, 6981–6993.
20. A. Prades, M. Viciano, M. Sanaú and E. Peris, *Organometallics*, 2008, **27**, 4254–4259.
21. C. E. Ellul, M. F. Mahon, O. Saker and M. K. Whittlesey, *Angew. Chem., Int. Ed.*, 2007, **46**, 6343–6345.
22. P. L. Arnold and S. T. Liddle, *Organometallics*, 2006, **25**, 1485–1491.
23. A. El-Hellani and V. Lavallo, *Angew. Chem., Int. Ed.*, 2014, **53**, 4489–4493.
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 $^1$H 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 $^1$H NMR. See ESI† for details.