Cite this: Chem. Commun., 2012, 48, 3306-3308

COMMUNICATION

Transmetalation of a nucleophilic carbene fragment: from early to late transition metals[†]

Marie Fustier-Boutignon, Hadrien Heuclin, Xavier Frédéric Le Goff and Nicolas Mézailles*

Received 19th December 2011, Accepted 2nd February 2012 DOI: 10.1039/c2cc17934b

Early transition metal nucleophilic carbene complexes have been used as stoichiometric carbene transfer agents in a transmetalation process.

The "Transmetalation" elementary step is at the heart of the extensively studied transition metal complex catalyzed cross coupling reactions.¹ Regardless of some subtleties, the transition state is a heterobimetallic species (eqn (1), Scheme 1), whose energetic accessibility is linked to the ability of the C atom to increase its valency. As a consequence, transmetalation processes involving C sp² or C sp fragments are much more favorable than the corresponding C sp³ which has to go through a "pentavalent-like" transition state.

From another standpoint, electrophilic transition metal carbene complexes, Fischer type carbenes, have been known for nearly 50 years and used extensively as stoichiometric reactants in organic synthesis.² Starting in 1970, successful stoichiometric metal to metal electrophilic carbene transfer has opened the way for the design of a catalytic process in the late 1990s involving transmetalation from group 6 Fischer carbene to a palladium fragment as a key step (eqn (2), Scheme 1).³ DFT calculations carried out in this process have highlighted the energetic accessibility of related heterobimetallic complexes both as a transition state and even as an intermediate in the process.⁴ In the past years, we and others have been developing the use of geminal dianions⁵ (such as A in Scheme 1) as precursors for carbene complexes.⁶ Such highly sensitive and reactive dianionic species are rare because the two lone pairs at the same carbon center need to be efficiently stabilized by strongly electron accepting moieties. It was shown that hypervalent P centers were particularly suitable for this goal.⁵ The underlying strategy was to utilize the dianionic ligand as the sole carrier of the four electrons formally engaged in the M-C interaction in carbene complexes.[‡] So far, this strategy has been very successful and in particular provided simple access to carbene complexes of Ti(IV) and Zr(IV),⁷ of rare earth⁸ or U(IV),⁹ U(V)¹⁰ and U(VI)¹¹

Ecole Polytechnique CNRS, Palaiseau, France.



Scheme 1 Known transmetalation processes and proposed strategy.

with pronounced nucleophilic behavior (reactivity toward carbonyl derivatives, in an alkylidene like fashion). Electron rich metal fragments could also be used (Ru(II) or Pd(II)).¹² However, in some instances, despite efficient stabilization of the dianion A, undesired and uncontrolled redox processes became competitive with coordination, preventing isolation of the desired complexes. We then reasoned that carbene complexes of early transition metals could be used to transfer the carbenic fragment to other metals (middle to late). To our surprise, literature search revealed that only one related process has been reported to date, which involves the alkylidene transfer from Ta(v) to W(vI) (eqn (3)).¹³ In this contribution, we report the first examples of transmetallation reaction involving the stoichiometric transfer of the carbenic fragment from Zr(IV) and Sc(III) complexes to group 8, 9 and 10 metal centers. In particular, this novel strategy has provided the only access to date to a Fe complex using these types of ligands.

In a first series of experiments, the readily available nucleophilic Zr carbene complex 1 was used.^{7b} In order to test the validity of our concept, the transmetalation reaction to form known complexes was attempted. The reactions of dimeric complex 1 with [Ru(PPh₃)₃Cl₂] and [Pd(PPh₃)₂Cl₂] were carried out in THF, and most satisfyingly, led to the formation of the desired

Laboratoire "Hétéroéléments et Coordination",

E-mail: nicolas.mezailles@polytechnique.edu; Fax: 0033 169334440; Tel: 0033 169334402

[†] Electronic supplementary information (ESI) available: Experimental details. CCDC 848404 and 848405. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc17934b



Scheme 2 Transmetalation involving a Zr(IV) carbene complex.

complexes 2 and 3, respectively, as shown by ³¹P NMR spectroscopy (Scheme 2). The kinetics of the reaction appeared slower than with dianion A, and the use of THF as solvent needed to favor the formation of the ZrCl₄ (THF)₂ byproduct (note that the use of THF is precluded when using the dianion A as it readily forms the monoanion).^{5a} The complete formation of complexes 2 and 3 was observed within 15 minutes and several hours, respectively, at room temperature (two sets of triplets at 57.6 ppm and 48.8 ppm, $J_{PP} = 12$ Hz for 2, and a triplet at 21.5 ppm and a doublet at 39.8 ppm, $J_{PP} = 15$ Hz for 3).¹² The transmetalation to Co(II) was then attempted, and appeared to require more forcing conditions (24 h, reflux). The reaction was nevertheless nearly quantitative, and in the ³¹P NMR spectrum, the slow increase of a singlet at 187 ppm corresponding to the previously reported complex 4 was observed,¹⁴ concomitant to the decrease of the signal of complex 1. The desired complex was then isolated in 80% yield. As far as the mechanism is concerned (Scheme 3), the formation of an early intermediate, characterized by a singlet at 22 ppm, was observed in the three cases, which we thus postulated to be the mononuclear Zr complex 5. Complex 5 was independently synthesized and its structure was proven by X-ray diffraction analysis (see ESI[†]). Interestingly, when isolated and dissolved in a non-coordinating solvent (such as CH₂Cl₂) this complex 5 evolved back to complex 1, showing that chloride coordination from a metal-Cl bond is competitive to THF coordination. From this mononuclear Zr complex we then logically propose the formation of a heterobimetallic Zr/M



Scheme 3 Proposed simplified mechanism for the transmetalation.

complex C with bridging Cl as a second intermediate. The overall transfer is rather complex as unlike the above mentioned transfer of an electrophilic carbene fragment, three bonds have to be broken in complex 1 or 5, two Zr-S and the Zr=C bonds to be formed with M in the final complex. Examples of homo or heterobimetallic complexes are known, supporting the intermediacy of complex D in the proposed mechanism.¹⁵ With these encouraging results proving the concept, the synthesis of the more challenging Fe complex was attempted. Indeed, when the dianion A was reacted with several Fe(II) or Fe(III) precursors, only redox to Fe(0) was observed concomitant to the formation of the neutral ligand dppmS₂ most likely by hydrogen abstraction from the solvent. In fact, no Fe complex has been reported to date with these dianionic ligands, although several Ru complexes are known.¹⁶ Interestingly, the reaction of complex 1 with stoichiometric amounts of FeCl₂ did not lead to any decomposition, showing the efficient shutting down of an undesired redox pathway when using a carbene complex in place of the dianion A. However, the reaction appeared very sluggish, even at high temperatures (36 h, toluene reflux) and no Fe(II) complex (expected to be silent by NMR spectroscopy) could be isolated from the reaction mixture. As suggested by the proposed simplified mechanism shown above, a more reactive carbene complex, for which solvent coordination and/or S and/or carbene coordination would be weaker, was therefore needed.

We logically turned our attention to the only known monomeric Sc carbene complex, 6, as it was shown by DFT calculations that the C–Sc π interaction is weaker than in the corresponding Zr complex, \mathbf{B}^{8i} The same first three reactions were carried out (Scheme 4). They all proceeded very smoothly, being complete within 15 minutes at room temperature. The very significant difference in the kinetics of the reaction with CoCl₂ of the two carbene complexes 1 and 6 (24 h, 60 °C vs 15 minutes, RT respectively) proved our hypothesis right. The reaction between complex 6 and a suspension of $[FeCl_2(THF)_{1,5}]$ was followed by ³¹P NMR. The singlet at 10 ppm had totally disappeared within 15 minutes, with a simultaneous deposition of red crystals. After isolation they were dissolved in C_6D_6 and characterized by multinuclear NMR spectroscopy. As expected, the complex is silent by ³¹P NMR, and in the ¹H spectrum, the protons of the phenyl rings are found between 4 and 10 ppm, both indicative of coordination on paramagnetic Fe(II). The crystals were analyzed by X-ray diffraction and proved the formation of a dimer, with the C atom behaving as a bridging dianionic ligand between two Fe centers. A view of the complex



Scheme 4 Reactivity of the Sc(III) carbene complex.



Fig. 1 View of complex 7 (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°). C(1)-P(1) 1.736(4), C(1)-P(2) 1.728(3), P(1)-S(1) 2.028(1), P(2)-S(2) 2.037(1), C(1)-Fe(1) 2.099(3), C(1)-Fe(2) 2.082(3), Fe(1)-Fe(2) 2.5683(8), Fe(1)-S(1) 2.380(1), Fe(2)-S(2) 2.355(1), P(1)-C(1)-P(2) 128.8(2), C(1)-Fe(1)-C(1')-Fe(2) 0.00.

is given in Fig. 1. The structure of complex 7 is similar to the one of the cobalt complex. Complex 7 features a planar C–Fe–C–Fe square core, each central carbon binding two iron atoms, the geometry at the Fe atoms being distorted tetrahedral.

Bond lengths in the ligand in complex 7 are similar to the ones of complex 4 (1.736(4) and 1.728(3) Å vs 1.742 and 1.728 Å for the P-C bonds). The main structural difference is the metalmetal bond. Indeed, the Fe-Fe bond is longer by ca. 0.1 Å in complex 7 than in complex 4 (2.568 Å vs 2.471 Å). The Fe-Fe bond distance is however shorter than the sum of the van der Waals radii (2.64 Å), indicative of a strong interaction. In terms of reactivity, the Fe complex 7 does not react with carbonyl derivatives, such as benzophenone, unlike the Sc and Zr complexes (6 and 1).^{7b,8e} The complex is also stable toward weak acid sources such as CH₃CN or the strongly alkylating agent MeI, in agreement with a strong electron transfer from the formally dianionic ligand to the metal. In line with the apparent paramagnetic nature observed by NMR, the effective moment was measured, using the Evans method, at 3.87 µB (expected 4.0 μ B). This value is in agreement with two Fe(II) centers with S = 1 each.

In conclusion, we show here for the first time that tridentate SCS nucleophilic carbene complexes may be used as stoichiometric carbene transfer agents in a transmetalation process. This novel transformation does allow circumventing redox competitive processes. As such it opens the way for the synthesis of "SCS" carbene complexes of oxidized and oxidizing metal centers. The precise mechanism of this transformation is currently being investigated using molecular modeling.

The authors thank the CNRS and the Ecole Polytechnique for financial support. M. F. B. and H. H. are thankful to the Ecole Polytechnique for fellowships.

Notes and references

[‡] The two substituents at the C are PR₂—X (X = S, O, NR') moieties, and therefore the complexes cannot be called alkylidene complexes which imply alkyl (or H) substituents. They are called here carbene complexes, and can behave as either nucleophilic (alkylidene like behaviour) or electrophilic complexes, depending on the associated metal fragment. See: D. J. Mindiola, J. Scott, *Nat. Chem.*, 2011, **3**, 15.

1 (a) L. Xue and Z. Lin, Chem. Soc. Rev., 2010, **39**, 1692; (b) P. Espinet and A. M. Echavarren, Angew. Chem., Int. Ed., 2004, **43**, 4704; (c) B. Fuentes, M. García-Melchor, A. Lledós, F. Maseras, J. A. Casares, G. Ujaque and P. Espinet, *Chem.-Eur. J.*, 2010, **16**, 8596; (d) A. F. Littke, C. Dai and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 4020.

- 2 K. H. Dötz and J. Stendel Jr, Chem. Rev., 2009, 109, 3227.
- 3 M. Gómez-Gallego, M. J. Mancheño and M. A. Sierra, Acc. Chem. Res., 2005, 38, 44.
- 4 I. Fernández, M. J. Mancheño, R. Vicente, L. A. López and M. A. Sierra, *Chem.-Eur. J.*, 2008, **14**, 11222.
- (a) T. Cantat, L. Ricard, P. Le Floch and N. Mézailles, Organometallics, 2006, 25, 4965; (b) C. M. Ong and D. W. Stephan, J. Am. Chem. Soc., 1999, 121, 1483; (c) A. Kasani, R. P. K. Babu, R. McDonald and R. G. Cavell, Angew. Chem., Int. Ed., 1999, 38, 1483; (d) L. Orzechowski, G. Jansen and S. Harder, Angew. Chem., Int. Ed., 2009, 48, 3825; (e) O. J. Cooper, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, Angew. Chem., Int. Ed., 2010, 49, 5570.
- 6 For recent reviews see: H. Heuclin, M. Fustier, A. Auffrant and N. Mézailles, *Lett. Org. Chem.*, 2010, 7, 596; S. T. Liddle, D. P. Mills and A. J. Wooles, *Chem. Soc. Rev.*, 2011, 40, 2164.
- 7 (a) R. G. Cavell, R. P. K. Babu, A. Kasani and R. McDonald, J. Am. Chem. Soc., 1999, 121, 5805; (b) T. Cantat, L. Ricard, N. Mézailles and P. Le Floch, Organometallics, 2006, 25, 6030.
- 8 (a) T. Cantat, F. Jaroschick, L. Ricard, F. Nief, N. Mézailles and P. Le Floch, Chem. Commun., 2005, 5178; (b) T. Cantat, F. Jaroschick, L. Ricard, P. Le Floch, F. Nief and N. Mézailles, Organometallics, 2006, 25, 1329; (c) S. T. Liddle, J. McMaster, J. C. Green and P. L. Arnold, Chem. Commun., 2008, 1747; (d) A. Buchard, A. Auffrant, L. Ricard, X. F. Le Goff, R. H. Platel, C. K. Williams and P. Le Floch, Dalton Trans., 2009, 10219; (e) S. T. Liddle, D. P. Mills, B. M. Gardner, J. McMaster, C. Jones and W. D. Woodul, Inorg. Chem., 2009, 48, 3520; (f) D. P. Mills, O. J. Cooper, J. McMaster, W. Lewis and S. T. Liddle, *Dalton. Trans.*, 2009, 4547; (g) D. P. Mills, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, Organometallics, 2009, 28, 6771; (h) D. P. Mills, L. Soutar, W. Lewis, A. J. Blake and S. T. Liddle, J. Am. Chem. Soc., 2010, 132, 14379; (i) M. Fustier, X.-F. Le Goff, P. Le Floch and N. Mézailles, J. Am. Chem. Soc., 2010, 132, 13108; (j) A. J. Wooles, D. P. Mills, W. Lewis, A. J. Blake and S. T. Liddle, Dalton Trans., 2010, 39, 500; (k) A. J. Wooles, O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, Organometallics, 2010, 29, 2315.
- 9 (a) T. Cantat, T. Arliguie, A. Noel, P. Thuéry, M. Ephritikhine, P. Le Floch and N. Mézailles, J. Am. Chem. Soc., 2009, **131**, 963; (b) J.-C. Tourneux, J.-C. Berthet, P. Thuéry, N. Mézailles, P. Le Floch and M. Ephritikhine, Dalton Trans., 2010, **39**, 2494; (c) O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, Dalton Trans., 2010, **39**, 5074; (d) D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, Nat. Chem., 2011, **3**, 454; (e) G. Ma, M. J. Ferguson, R. McDonald and R. G. Cavell, Inorg. Chem., 2011, **50**, 6500.
- 10 O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2011, **50**, 2383.
- 11 J.-C. Tourneux, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, P. Le Floch and M. Ephritikine, *Organometallics*, 2011, **30**, 2957.
- 12 (a) T. Cantat, M. Demange, N. Mézailles, L. Ricard, Y. Jean and P. Le Floch, Organometallics, 2005, 24, 4838; (b) T. Cantat, N. Mézailles, L. Ricard, Y. Jean and P. Le Floch, Angew. Chem., Int. Ed., 2004, 43, 6382.
- 13 (a) J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert and W. J. Youngs, J. Am. Chem. Soc., 1980, 102, 4515; (b) R. R. Schrock, S. Rocklage, J. H. Wengrovius, G. Rupprecht and J. Fellmann, J. Mol. Catal., 1980, 8, 73.
- 14 H. Heuclin, T. Cantat, X. F. Le Goff, P. Le Floch and N. Mézailles, *Eur. J. Inorg. Chem.*, 2011, 2540.
- 15 (a) W. P. Leung, C. W. So, J. Z. Wang and T. C. W. Mak, Chem. Commun., 2003, 248; (b) M. Fang, N. D. Jones, K. Friesen, G. Lin, M. J. Ferguson, R. McDonald, R. Lukowski and R. G. Cavell, Organometallics, 2009, 28, 1652.
- 16 (a) V. Cadierno, J. Díez, J. García-Álvarez and J. Gimeno, Organometallics, 2004, 23, 2421; (b) V. Cadierno, J. Díez, J. García-Álvarez and J. Gimeno, J. Organomet. Chem., 2005, 690, 2087.