CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Azoliniums, Adducts, NHCs and Azomethine Ylides: Divergence in Wanzlick Equilibrium and Olefin Metathesis Catalyst Formation

Authors: Phillip Iain Jolly, Anna Marczyk, Paweł Małecki, Osman Ablialimov, Damian Trzybiński, Krzysztof Woźniak, Silvio Osella, Bartosz Trzaskowski, and Karol Grela

To be cited as: *Chem. Eur. J.* 10.1002/chem.201706036

Link to VoR: http://dx.doi.org/10.1002/chem.201706036

Supported by
ACES

WILEY-VCH

10.1002/chem.201706036

WILEY-VCH

COMMUNICATION

Azoliniums, Adducts, NHCs and Azomethine Ylides: Divergence in Wanzlick Equilibrium and Olefin Metathesis Catalyst Formation

Phillip I. Jolly,*[a] Anna Marczyk,[a] Paweł Małecki, [a] Osman Ablialimov,[a] Damian Trzybiński,[a] Krzysztof Woźniak,[a] Silvio Osella,[b] Bartosz Trzaskowski[b] and Karol Grela.*[a]

In memory of Professor Guy Lavigne

Abstract: The dimerization of a saturated *N*-heterocyclic carbene (NHC) to tricyclic piperazine in preference to the commonly observed Wanzlick dimerization is presented. Mechanistic investigations revealed that the *N*-fluorene substituent of the heterocycle is implicated in both ring opening of corresponding carbene dimer and tautomerization of NHC to an azomethine ylide. This has consequences for the fate of the NHC when generated from either an azolinium salt or a pentafluorophenyl-adduct. The insights gained permitted the synthesis of a new indenylidene metathesis precatalyst, which exhibits exceptional selectivity and high TONS in self-metathesis of 1-octene.

Pioneering work by Wanzlick[1] and Öfele[2] independently furnished the first examples of metal coordinated *N*-heterocyclic carbene (NHCs) complexes in 1968. Today NHCs are ubiquitous in organometallic chemistry[3] on account of their excellent *σ*-donor ability[4] and ready modulation of steric properties.[5] The benefits of NHCs as ligands in metal catalysis were not immediately apparent until 1995 when Herrmann *et al*. reported the first catalytic activity of *bis*-NHC palladium complexes in the Heck reaction.[6] However, it is arguably the same groups disclosure of the first active olefin metathesis (OM) precatalyst bearing NHCs,[7] **Ru1** (Figure 2) that really ignited the community's interest, some 30 years after the initial Wanzlick and Ölefe publications. The original homoleptic *bis*-NHC OM precatalyst as well as the subsequent heteroleptic NHC/phosphine ligated **Ru2**[8] where synthesized from stable 'Arduengo carbenes',[9] the very species that eluded Wanzlick and lead him to propose the 'Wanzlick equilibrium': the interconversion of NHCs and their tetraaza-alkene (TAA) dimers.[10] TTAs have interesting chemistry of their own, particularly as strong organic reducing agents, 'super electron donors'[11] but are reputed to be poor reagents for the formation of NHC ruthenium alkylidenes.[12] Thus circumventing their synthesis *via* templating for instance can be advantageous.[3c, 3d, 13]

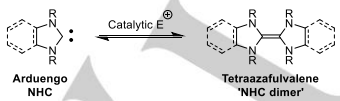


Figure 1. The Wanzlick equilibrium.

[a] Dr P. I. Jolly and Prof. Dr. K. Grela,
Biological and Chemical Research Centre,
University of Warsaw,
Żwirki i Wigury 101,
02-089 Warsaw.
drphilllipjolly@hotmail.com; prof.grela@gmail.com
[b] Centre of New Technologies,
University of Warsaw,
S. Banacha 2c,
02-097 Warsaw.

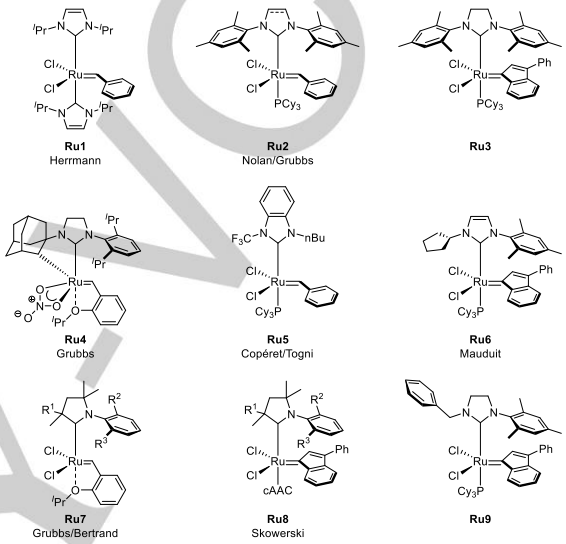


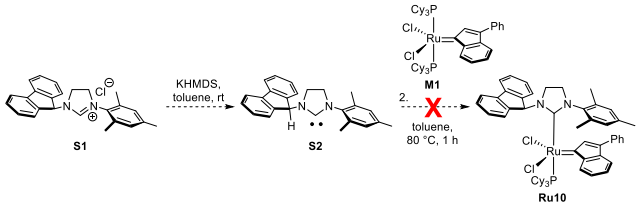
Figure 2. Ru2-3 OM catalysts ligated by symmetrical NHCs; **Ru4-9** specialized OM catalysts coordinated by uNHCs.

OM has now established itself as the preeminent form of catalysis for making new carbon-carbon double bond.[14] The development of well-defined OM precatalysts initiated a revolution in organic chemistry,[15] leading to widespread application in both academia and industry.[16] Heteroleptic Grubbs II precatalysts e.g. **Ru2-3**, ligated by an NHC and another L-type ligand are the most explored due their great stability and reactivity. Indeed, precatalysts bearing symmetrical NHCs (**Ru2-3**) are the work horses of simpler metathetic processes but more specialized application are typically mediated by complexes coordinated by a unsymmetrical *N*-heterocyclic carbene (uNHC), of which **Ru4-9** represents only a fraction of those explored.[17] In spite of the many NHCs explored, 'there are no general rules governing rational ligand design'[18] that might afford a catalyst universally proficient in every form of OM. Thus the development of new specialized catalysts affording high selectivity's and good conversions along with high turnover numbers (TONs) and frequencies (TOF) at low catalyst loadings (in the ppm range) is by no means trivial.

Our own investigations showed **Ru9**[19] exhibited improved stability compared to commercially available **Ru3**, while Hoveyda type analogues also demonstrated improved reactivity.[20] As such, we became interested in complex **Ru10**, an indenylidene complex bearing an *N*-fluorene substituted uNHC. However, all attempts to synthesize **Ru10** from azolinium salts **S1** where thwarted. We now present the successful synthesis of **Ru10** employing pentafluorophenyl NHC-adduct **10**, along with mechanistic observations of corresponding carbene **S2** with insights for Wanzlick equilibrium.

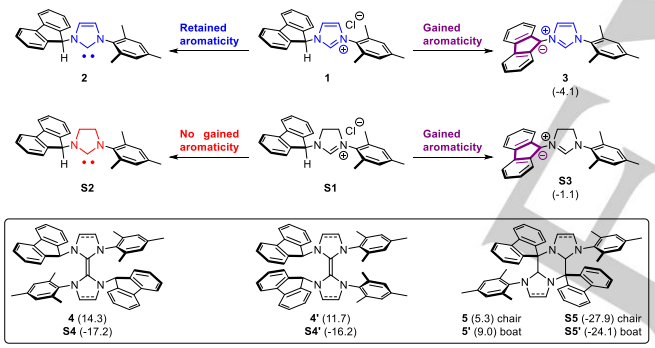
Azolinium salt **S1** was readily prepared based on a standard protocol (see supporting info.). However, deprotonation of **S1**

rapidly formed a red/orange suspension which on reaction with **M1** failed to yield any of the desired precatalyst **Ru10** (scheme 1).



Scheme 1. Attempted synthesis of hybrid complex **Ru10**.

Considering the pK_a values of SIMes 21.3 (in H_2O) and fluorene 22.6 (in DMSO), one might speculate that a deprotonation by a strong base such as KHMDS may not be selective for the C2 proton in azolinium salt **S1**. Indeed, Cesar *et al*. observed the deprotonation of the *N*-fluorene substituent in the analogous unsaturated azolium salt **1**, which cleanly afforded a conjugated mesomeric betaine (CMB) **3** (91% yield).[21] CMBs are a curious class of compounds in equilibrium with NHCs and are also of interest for complex formation.[22] Considering the deprotonation from the vantage point of aromaticity gained in the products, then it would appear energetically favorable to deprotonate the fluorene ring of both **1** and **S1** forming CMBs **3** or **S3** rather than the respective NHCs, **2** and **S2**. In addition, the lack of a stabilizing aromatic NHC or heterocycle in products **S2** and **S3** respectively could lead to further complications *via* dimerization; NHC **S2** affording TAA **S4** or **S4'** while azomethine ylide (AMY) **S3** might yield **S5** in a [3+3] cycloaddition.[23]



Scheme 2. Aromaticity of NHCs **2/S2** Vs CMB **3** and AMY **S3**; hypothetically NHC dimers **4/4´** and **S4/S4´** and ylide dimers **5/5'** and **S5/S5'**. Relative Gibbs free energies shown in brackets, calculated in kcal/mol^{-1} with respect to NHC **2** or **S2** for corresponding systems.

Gibbs free energies calculated using the M06-D3 density functional reveals that the CMB **3** is thermodynamically more stable than the unsaturated NHC **2** by -4.07 kcal/mol^{-1} and consistent with past observations.[21] The saturated NHC, **S2** is marginally less stable than its AMY tautomer, **S3** by only -1.09 kcal/mol^{-1}, suggesting an equilibrium between the tautomer's **S2** and **S3**. Frontier orbital analysis of NHCs **2** and **S2** show almost identical orbitals, the HOMO residing at C2 carbenic center as expected and the LUMO spread over *N*-fluorene system (see supporting info.). While CMB **3** and unsaturated AMY **S3** have almost the same HOMO, their LUMOs differ significantly, residing almost entirely on *N*-mesityl for CMB **3** in contrast to AMY **S3**, with the highest contribution at the imidazoline C2 position (Figure 3). This indicates the reactivity pattern of unsaturated **3** may deviate substantially from saturated **S3,** the latter being more prone to dimerization.

The propensity of NHCs to dimerize is determined by their electronic and steric characteristics, the singlet-triplet energy gap and the π-π stacking or other van der Waals or repulsive interactions between the bulky NHC substituents.[24] When the accumulative effect of these is balanced the preference for either free NHC or dimer is diminished so that both may be isolated[25] or observed simultaneously,[26] adding to the controversy surrounding Wanzlick dimerization.[10d, 24, 27] Fortunately unsaturated imidazol-2-ylidenes e.g. **2** and saturated imidazolin-2-ylidenes e.g. **S2** represent either end of the spectrum. The electronic properties of aromatic imidazolin-2-ylidenes favor monomer to degree that the NHCs must be tethered to induce dimerization,[28] while non-aromatic imidazolin-2-ylidenes dimerize so readily they require steric protection.[25a, 29]

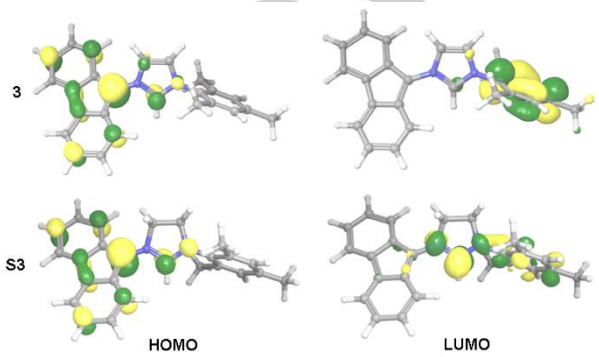


Figure 3. Depiction of HOMOs and LUMOs in CMB **3** and AMY **S3**.

As such, Gibbs free energies for the formation of all possible NHC and AMY dimers **4**, **S4**, **4'**, **S4'**, **5** and **S5** were calculated. Unsurprisingly, unsaturated TAA dimers **4** and **4'** are thermodynamically unstable by 14.3 and 11.7 kcal/mol^{-1} with respect to theoretical NHC **2**, unlike saturated **S4** and **S4'** which are energetically favored by -17.2 and -16.2 kcal/mol^{-1} respectively over the monomer **S2**. Similarly the plausible chair **5** and boat **5'** conformers of piperazine, the theoretical dimer of CMB **3** are unstable relative to the monomer by 9.4 or 13.1 kcal/mol^{-1} respectively. Again, the situation is completely different for saturated AMY **S3**, since piperazines **S5** and **S5'** are favored by -27.9 and -24.1 kcal/mol^{-1} compared to **S3**. Given the accuracy of around 1-2 kcal/mol^{-1} for this DFT method, NHC **2** prefers to exist solely as the monomeric tautomer CMB **3**. In contrast, NHC **S2** is predicted to be in equilibrium with AMY **S3**, with formation of respective dimers, TAAs **S4**,**S4'** or piperazine **S5**,**S5'** both favorable. The results highlight the importance of aromatic stabilization energy in species derived from **1** compared to **S1** and while tautomerism between NHCs and CMBs is known, as is dimerization of AMYs, uniquely **S2** encompasses all possibilities. In effective 'Wanzlick' NHC dimerization is pitted against azomethine ylide dimerization, with the equilibrium between tautomerism, **S2** and **S3** determining the ratio of either TAA **S4** or piperazine **S5** formed.

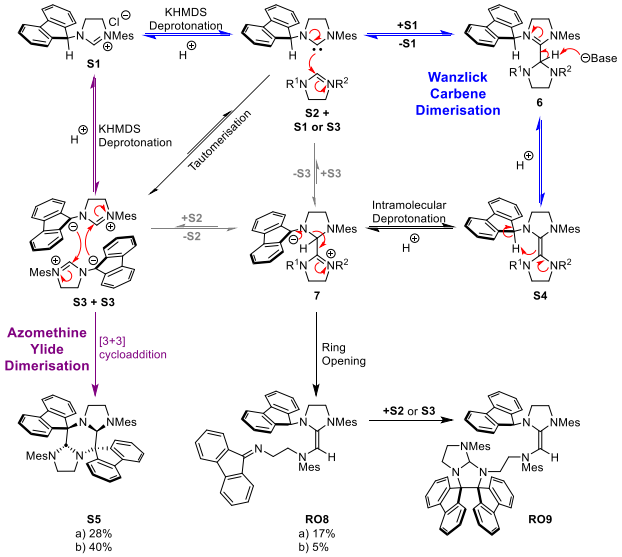
To test our hypothesis **S1** was deprotonated in tetrahydrofuran by KHMDS added in one portion at -30°C then warmed to room temperature. The crude reaction mixture was examined by ^{1}H-NMR exhibiting a veritable forest of signals. However, after a series of crystallizations the ylide dimer **S5** (28%) and two unexpected byproducts **RO8** (17%) and **RO9** where isolated (Scheme 3). All three compounds were unambiguously characterized by single-crystal X-ray diffraction analysis (Figure 4 and Supporting Info.). Numerous possible mechanisms exist, the simplest being deprotonation takes place at *N*-fluorene forming AMY **S3** which then dimerizes to **S5**. A deprotonation generating NHC **S2** followed by: (i) tautomerism to **S3** could then also yield dimer **S5** or (ii) the dimerization of NHC **S2** with an azolinium salt **S1** *via* a Wanzlick mechanism forms TAA **S4**, deprotonation of the *N*-fluorene substituent gives **7** which ring opens to **RO8**. It is conceivable that **7** might disproportionate to NHC **S2** or AMY **S3** then follow respective reaction paths but

10.1002/chem.201706036

WILEY-VCH

COMMUNICATION

we do not believe the reverse is possible as no ring opened products were observed for thermal disproportionation of adduct **10** *vide infra*. Finally, a single crystal of **RO8** was isolated, resulting from attack of either NHC **2** or AMY **S3** at the enamine portion of **RO8** (see supporting info.). Repeating the reaction at -50°C with dropwise addition of KHMDS lead to an improved yield of ylide dimer **S5** (40%) and a reduction in **RO8** (5%)



Scheme 3. Proposed mechanism for the formation of ylide dimer **S5** and ring opened TAA products **RO8** and **RO9**. Reaction conditions (a) single addition of KHMDS (1 equiv.), -30°C to RT, THF; (b) dropwise addition of KHMDS (1 equiv.), -50°C to RT, THF.

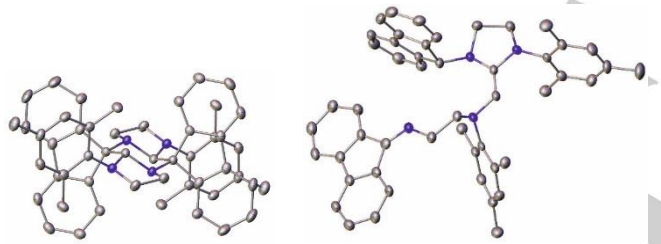
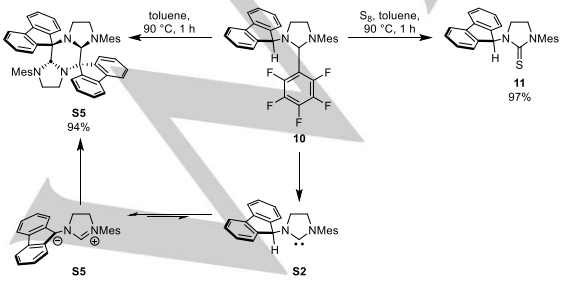


Figure 4. X-ray structures of **S5** (left) and **RO8** (right). Displacement ellipsoids on the molecular diagrams of compounds were drawn at the 50% probability level.

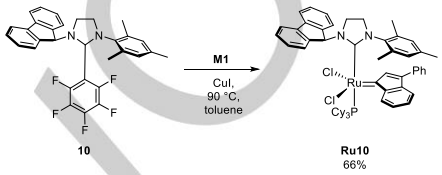
Pentafluorophenyl-adduct **10** was employed to avoid unselective deprotonation and examine the fate of NHC **S2** in the absence electrophilic salt **S1** (Scheme 4). On heating **10** in dry toluene at 90°C a red solution quickly forms, turning green over an hour. Astonishingly, colorless X-ray diffraction quality crystals of **S5** dropped out of solution. While reaction of **10** in the presence of sulfur confirmed the clean generation of transient NHC **2**.



Scheme 4. Azolinium free generation of NHC **S2**, cleanly affording piperazine **S5** or on reaction with sulfur yielding thiourea **11**.

As **RO8** is indicative of TAA **S4**, this suggests Wanzlick dimerization does not occur for **S2** on thermal disproportion of **10**. Thus **S2** must prefer tautomerization to AMY **S3** and subsequent dimerization to **S5**, in preference to the high energy direct NHC dimerization. Overall, the results demonstrate the significant role that the azolinium plays in facilitating dimerization of NHCs with high energy HOMO orbitals, which occurs even at low temperature.

Returning to the desired precatalyst **Ru10**, clearly **S1** is not a good precursor for NHC **S2**. Fortunately, transient NHC **S2** was sufficiently long lived to ligate the ruthenium metal center of **M1** and yield **Ru10** by displacement of phosphine, when **S2** was generated from **10**.



Scheme 5. Successful synthesis of **Ru10** from NHC-adduct **10**.

High selectivity for primary metathesis products (PMPs) from self-metathesis of *α*-olefins at low catalyst loadings requires robust catalysts to minimize isomerization (IP) and secondary metathesis products.[17d] At 50°C and a catalyst loading of 50 ppm both **Ru10** and **Ru3** achieve 76% conversion of neat 1-octene over 3 and 2 hours respectively. However, **Ru10** exhibits significantly superior selectivity in this specialized OM, producing 97% of PMP compared to **Ru3**, 80%.[17d] At the same temperature and 10 ppm loading, **Ru10** affords 62% conversion and 95% selectivity over 8 hours, equivalent to a TON of 29,403 and a TOF of 3,675. Over an extended reaction time of 21 hours, an increase to 77% conversion and a TON of 35,081 is accompanied by a small decrease in selectivity, 91% and a significant decrease of the TOF to 1671. While at 50°C with only a 1 ppm loading of **Ru10**, a 38% conversion, 90% selectivity, a TON of 169,200 and a TOF of 21,150 is achieved over 8 hours. By extending the reaction period to 21 hours the TOF is almost halved to 11083, however selectivity only decreases by 1% to 98% and conversion increases to 52% with a concomitant increase in the TON, up by over a third to 232,735.

Scheme 6. Self-metathesis of 1-octene to 7-tetradecene.

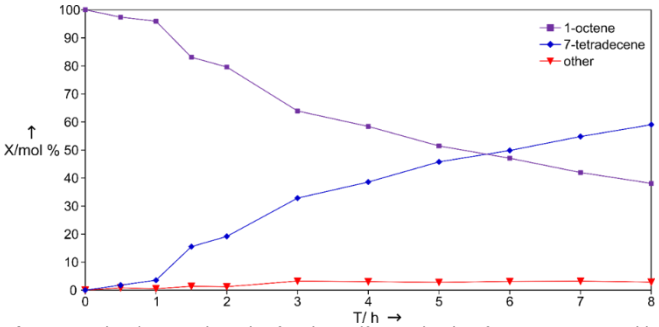


Figure 5. Time/conversion plot for the self-metathesis of neat 1-octene with 10 ppm of **Ru10** at 50°C, decane used as internal standard (lines are visual aids only and not curves of best fit).

In conclusion, *N*-fluorene substituted azolinium **S1** and pentafluorophenyl-adduct **10** have been examined as NHC precursors. The acidity of the *N*-fluorene proton is an Achilles heels in saturated NHC **S2** resulting in the first NHC/AMY tautomerism dimerization sequence or irreversible ring opening of

ChemSusChem
Communications
www.chemsuschem.org

corresponding Wanzlick dimer **S4**, **S4'**. As such, the *N*-fluorene group effectively acts as an indicator for Wanzlick type dimerization and here highlights the significant role that the electrophilic azolinium plays in this mechanism, compared to the neutral adduct. These results demonstrate that there are instances that adducts may serve as better conduits for free NHCs, indeed the new OM precatalyst **Ru10** was only accessible *via* adduct **10**. Initial investigations reveal **Ru10** exhibits exceptional selectivity and high TONS for self-metathesis of 1-octene, further application in other forms of OM and exploration of structure activity relationship are currently underway.

[1] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem. Int. Ed.* **1968**, *7*, 141-142.
[2] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42-P43.
[3] a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342-1363; c) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166-3216; e) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676; f) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485-496.
[4] D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723-6753.
[5] L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705-2733.
[6] a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem. Int. Ed.* **1995**, *34*, 2371-2374; b) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602-2605.
[7] a) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631-2633; b) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2490-2493; c) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1999**, *38*, 2416-2419; d) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem.* **1999**, *111*, 2573-2576.
[8] a) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678; b) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247-2250.
[9] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
[10] a) H. W. Wanzlick, E. Schikora, *Angew. Chem.* **1960**, *72*, 494-494; b) H. W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129-134; c) H. W. Wanzlick, *Angew. Chem. Int. Ed.* **1962**, *1*, 75-80; d) H.-J. Schönherr, H.-W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037-1046.
[11] J. A. Murphy, *J. Org. Chem.* **2014**, *79*, 3731-3746.
[12] T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546-2558.
[13] R. Manzano, F. Rominger, A. S. K. Hashmi, *Organometallics* **2013**, *32*, 2199-2203.
[14] a) A. G. W. R. H. Grubbs, D. J. O'Leary, E. Khosravi, *Handbook of Metathesis*, 2nd ed., Wiley-VCH, Weinheim, **2015**; b) K. Grela, *Olefin Metathesis: Theory and Practice*, John Wiley & Sons, Hoboken, **2014**.
[15] a) R. R. Schrock, *Angew. Chem. Int. Ed.* **2006**, *45*, 3748-3759; b) R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760-3765.
[16] a) S. Chikkali, S. Mecking, *Angew. Chem. Int. Ed.* **2012**, *51*, 5802-5808; b) D. L. Hughes, *Org. Process Res. Dev.* **2016**; c) C. S. Higman, J. A. M. Lummiss, D. E. Fogg, *Angew. Chem. Int. Ed.* **2016**, *55*, 3552-3565.
[17] a) F. B. Hamad, T. Sun, S. Xiao, F. Verpoort, *Coord. Chem. Rev.* **2013**, *257*, 2274-2292; b) M. B. Herbert, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2015**, *54*, 5018-5024; c) B. K. Keitz, K. Endo, P. R. Patel, M. B. Herbert, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 693-699; d) M. Rouen, P. Queval, E. Borré, L. Falivene, A. Poater, M. Berthod, F. Hugues, L. Cavallo, O. Baslé, H. Olivier-Bourbigou, M. Mauduit, *ACS Catalysis* **2016**, *6*, 7970-7976; e) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705-5709; f) V. Lavallo, Y. Canac, A. DeHope, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 7236-7239.
[18] P. S. Engl, C. B. Santiago, C. P. Gordon, W.-C. Liao, A. Fedorov, C. Copéret, M. S. Sigman, A. Togni, *J. Am. Chem. Soc.* **2017**, *139*, 13117-13125.
[19] a) O. Ablialimov, M. Kędziorek, M. Malińska, K. Woźniak, K. Grela, *Organometallics* **2014**, *33*, 2160-2171; b) O. Ablialimov, M. Kędziorek, C. Torborg, M. Malińska, K. Woźniak, K. Grela, *Organometallics* **2012**, *31*, 7316-7319.
[20] P. Małecki, K. Gajda, O. Ablialimov, M. Malińska, R. Gajda, K. Woźniak, A. Kajetanowicz, K. Grela, *Organometallics* **2017**, *36*, 2153-2166.
[21] L. Benhamou, S. Bastin, N. Lugan, G. Lavigne, V. Cesar, *Dalton Trans.* **2014**, *43*, 4474-4482.
[22] a) M. Liu, M. Nieger, E. G. Hübner, A. Schmidt, *Chem. Eur. J.* **2016**, *22*, 5416-5424; b) A. Schmidt, S. Wiechmann, C. F. Otto, in *Adv. Heterocycl. Chem., Vol. 119* (Eds.: E. F. V. Scriven, C. A. Ramsden), Academic Press, **2016**, pp. 143-172.
[23] a) S. Suárez-Pantiga, K. Colas, M. J. Johansson, A. Mendoza, *Angew. Chem. Int. Ed.* **2015**, *54*, 14094-14098; b) S. Suárez-Pantiga, K. Colas, M. J. Johansson, A. Mendoza, *Angew. Chem.* **2015**, *127*, 14300-14304; c) P. Banerjee, A. K. Pandey, *RSC Advances* **2014**, *4*, 33236-33244; d) I. Coldham, R. Hufton, *Chem. Rev.* **2005**, *105*, 2765-2810.
[24] A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan, L. Cavallo, *Organometallics* **2008**, *27*, 2679-2681.
[25] a) R. W. Alder, L. Chaker, F. P. V. Paolini, *Chem. Commun.* **2004**, 2172-2173; b) R. W. Alder, M. E. Blake, *Chem. Commun.* **1997**, 1513-1514; c) A. J. Arduengo, J. R. Goerlich, W. J. Marshall, *Liebigs Annalen* **1997**, *1997*, 365-374; d) J. P. Moerdyk, C. W. Bielawski, *Chem. Commun.* **2014**, *50*, 4551-4553; e) M. Braun, W. Frank, C. Ganter, *Organometallics* **2012**, *31*, 1927-1934.
[26] a) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551-554; b) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem. Int. Ed.* **2000**, *39*, 541-544.
[27] a) D. M. Lemal, R. A. Lovald, K. I. Kawano, *J. Am. Chem. Soc.* **1964**, *86*, 2518-2519; b) H. E. Winberg, J. E. Carnahan, D. D. Coffman, M. Brown, *J. Am. Chem. Soc.* **1965**, *87*, 2055-2056; c) M. K. Denk, K. Hatano, M. Ma, *Tetrahedron Lett.* **1999**, *40*, 2057-2060; d) V. P. W. Böhm, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2000**, *39*, 4036-4038; e) V. P. W. Böhm, W. A. Herrmann, *Angew. Chem.* **2000**, *112*, 4200-4202; f) R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem. Int. Ed.* **2004**, *43*, 5896-5911; g) R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem.* **2004**, *116*, 6020-6036.
[28] a) M.-J. Cheng, C.-L. Lai, C.-H. Hu *, *Mol. Phys.* **2004**, *102*, 2617-2621; b) T. A. Taton, P. Chen, *Angew. Chem. Int. Ed.* **1996**, *35*, 1011-1013; c) T. Andrew Taton, P. Chen, *Angew. Chem.* **1996**, *108*, 1098-1100; d) P. I. Jolly, S. Zhou, D. W. Thomson, J. Garnier, J. A. Parkinson, T. Tuttle, J. A. Murphy, *Chemical Science* **2012**, *3*, 1675-1679; e) S. Haslinger, J. W. Kück, M. R. Anneser, M. Cokoja, A. Pöthig, F. E. Kühn, *Chem. Eur. J.* **2015**, *21*, 17860-17869.
[29] A. J. Arduengo, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027-11028.

Acknowledgements

The CCDC 1590392–1590394 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). The authors are grateful to the National Science Centre (Poland) for the NCN MAESTRO Grant No. DEC-2012/04/ A/ST5/00594. The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project cofinanced by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007−2013. In addition the authors are grateful to Professor Andreas Schmidt for helpful discussions regarding mesomeric-betaines.

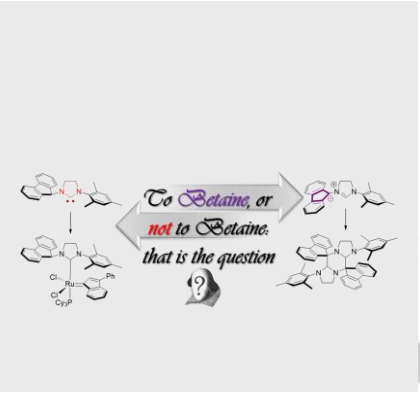
Keywords: Dimerization • Carbene Ligands • Metathesis • Homogeneous Catalysis • Azomethine ylide

10.1002/chem.201706036

WILEY-VCH

COMMUNICATION

Text for Table of Contents



*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title