

# Original Reactivity of $\alpha$ -Diazo- $\beta$ -ketoesters Catalyzed by CpRu Complexes

Cecilia Tortoreto<sup>§</sup>, Thierry Achard, Martina Austeri, Walid Zeghida, and Jérôme Lacour\*

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**Abstract:** Using  $\alpha$ -diazo- $\beta$ -ketoesters as reagents and combinations of CpRu fragments and diimine ligands as catalysts, a series of original transformations have been obtained that can be rationalized by the formation of metal carbenes and metal-bound ylide intermediates. Interesting 1,3-dioxole, enol-acetal and 1,4-dioxene motifs are obtained directly when the reactive mixture is reacted in presence of aldehydes or ketones, THF and epoxides.

**Keywords:** Diazo compounds · Insertions · Metal carbenes · Oxonium ylide

Efficient synthesis and catalysis are in continual demand from academic and industrial laboratories. One effective approach to reach this goal is to use, as reaction intermediates, metal carbenes generated by the decomposition of diazo compounds with catalytic amounts of transition metals.<sup>[1]</sup> The approach is extremely versatile and high levels of selectivity are attained in a large number of transformations (dimerization, metathesis, cyclopropanation, insertion, ylide generation and subsequent rearrangement/macrocyclization reactions).<sup>[1–3]</sup> The reactivity of the metal carbene intermediates depends strongly on both the substituents on the carbon atom and the associated metal, which can control reactivity and selectivity. While most applications use acceptor and donor/acceptor diazo precursors and metals salts/complexes derived from copper<sup>[4]</sup> and rhodium,<sup>[5]</sup> many interesting transformations can be found outside this scheme. Herein, in such a development, the reactivity of metal carbenes obtained by the decomposition of  $\alpha$ -diazo- $\beta$ -ketoesters **1** in the

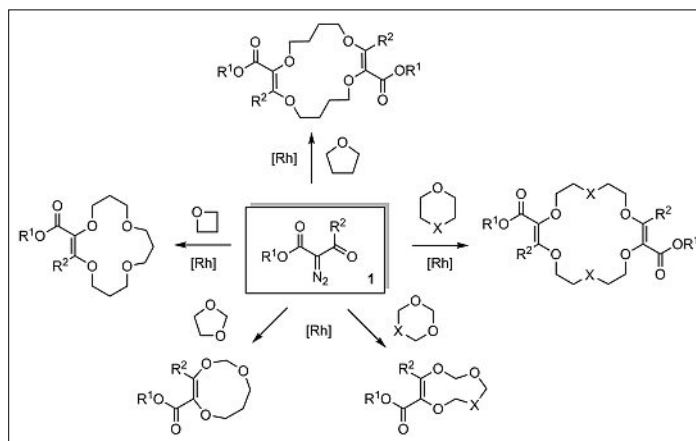
presence of CpRu complexes as catalysts is detailed.

$\alpha$ -Diazo- $\beta$ -ketoesters are readily prepared and easy-to-handle acceptor/acceptor reagents that are characterized by a better chemical stability and a moderate reactivity compared to other diazo derivatives. These compounds react in presence of certain metal sources to form electrophilic carbene intermediates. In this context, our group recently reported their reaction in presence of Lewis basic cyclic ethers and of dirhodium complexes to yield original 16- and 18-membered macrocycles and medium-sized 8- or 9-membered rings in particular (Scheme 1).<sup>[6]</sup> The results were rationalized by invoking the formation of metal-free oxonium ylide intermediates.<sup>[6a,d]</sup> It was then interesting to study if different reactivities could be achieved by using metal catalysts that would form metal-bound ylide intermediates instead, and cyclopentadienyl ruthenium complexes in particular.

In fact, ruthenium complexes,<sup>[7]</sup> including CpRu derivatives<sup>[8]</sup> have become an

interesting alternative to copper and dirhodium salts or complexes for the decomposition of diazo reagents. For instance, Del Zotto and coworkers have shown that complex [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl] reacts with ethyl diazoacetate to promote transformations such as cyclopropanations, N-H and S-H insertions or the reaction of tertiary amines into ammonium ylides that undergo [1,2]-Stevens shifts or sigmatropic rearrangements.<sup>[8]</sup> Having previously shown that combinations of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>]<sup>[9]</sup> and diimine ligands efficiently catalyze enantioselective Carroll rearrangement<sup>[10]</sup> and decarboxylic allylic etherification reactions,<sup>[11]</sup> we decided to examine the influence of this catalytic combination<sup>[12]</sup> on reactions of  $\alpha$ -diazo- $\beta$ -ketoesters with Lewis basic moieties.

First, simple reactions leading to results in line with the common knowledge in the field were tested to establish the viability of the CpRu/diimine combination as catalyst. For instance, insertions into the O–H bond of alcohols,<sup>[1,2d,2e,13]</sup> and condensations with nitriles<sup>[14]</sup> were investi-



Scheme 1. Dirhodium-catalyzed one-pot condensation of  $\alpha$ -diazoacetates and cyclic ethers.

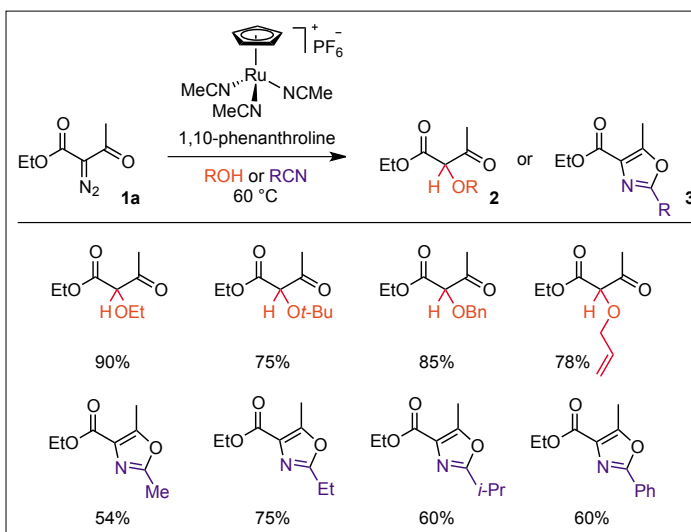
\*Correspondence: Prof. J. Lacour  
University of Geneva  
Department of Chemistry  
Quai Ernest Ansermet 30  
CH-1211 Geneva  
Tel.: +41 22 379 60 62  
E-mail: jerome.lacour@unige.ch

gated. Practically, ethyl diazoacetate **1a** was dissolved in various alcohols and nitriles together with a catalytic amount of  $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$  and 1,10-phenanthroline (phen, 2.5 mol% each). A moderate heating to 60 °C was necessary to induce a gas evolution. To our satisfaction, complete conversions were achieved in all cases (45–60 min) and the corresponding products of insertion **2** or cyclization **3** were isolated in moderate to good yields (Scheme 2).<sup>[15]</sup>

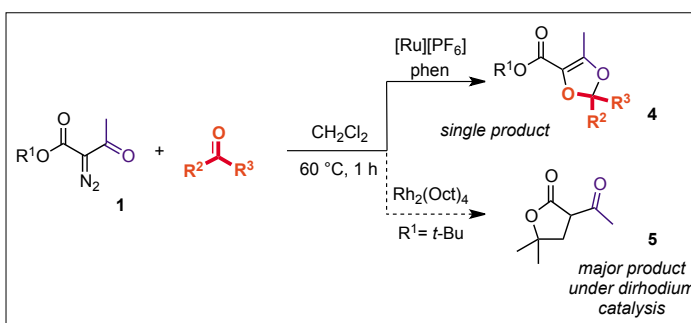
With these results in hand, condensation reactions with carbonyl moieties were examined.<sup>[16]</sup> Diazocarbonyl compounds are in fact known to react with aldehydes and ketones.<sup>[1]</sup> In most cases, the carbonyl group acts as a nucleophile, reacting with the electron-deficient carbene center to form carbonyl ylide intermediates that behave as 1,3-dipoles.<sup>[17]</sup> Several competing pathways are then possible including the formation of epoxides, 1,3-dioxolane and dioxolene moieties through intramolecular rearrangements, intermolecular [3+2]-cycloadditions and condensations.<sup>[18]</sup>

Interestingly, the use of 1 mol% of CpRu complex and phenanthroline in methylene chloride allowed the reaction to proceed using only one equivalent of the corresponding carbonyl compound (Scheme 3).<sup>[15]</sup> Reactions were either more selective or faster than with classical dirhodium and copper catalysts as, in this case, only 1,3-dioxole products **4** were obtained and isolated in good yields. These results contrasted with that of  $\text{Rh}_2(\text{Oct})_4$  catalysis which, under the same conditions using the *tert*-butyl ester as substrate ( $\text{R}^1 = t\text{-Bu}$ , Scheme 3) afforded predominantly lactone **5** in the crude reaction mixture.<sup>[19]</sup> Clearly, competition between intramolecular C-H insertions and intermolecular carbonyl ylide formation is avoided by using the combination of  $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$  and phenanthroline as catalyst. The influence of the diimine ligand was ascertained by using enantiopure pymox (Scheme 4) instead of phen as ligand. Even milder conditions could be used (25 °C, 24 h) to afford an enantioselective condensation forming products **4** with enantiomeric excesses up to 50%.<sup>[15]</sup> These results advocate for the formation of metal-bound carbonyl ylide intermediates **6** (Scheme 5); subsequent ring closure affording products of type **4**.

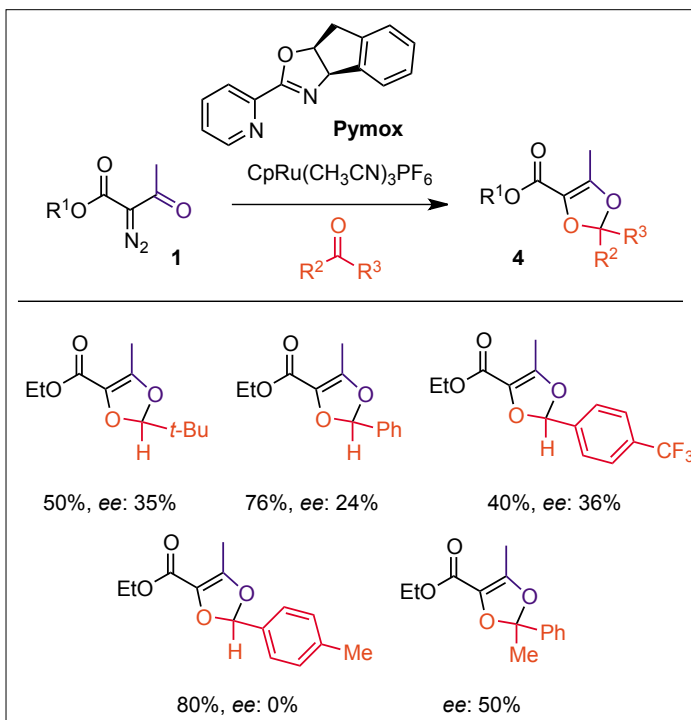
Then, when THF was tested as Lewis basic partner under CpRu/diimine catalysis, an unprecedented 1,3-C-H insertion reaction occurred giving rise to original enol-acetal products of type **7** (Scheme 6).<sup>[20,21]</sup> Interestingly, in the field of intermolecular metal carbene C-H insertions into THF,<sup>[22]</sup> only 'classical' derivatives of type **8** were previously reported with a C-C bond formed by insertion of the carbene into a C-H bond  $\alpha$  to the oxy-



Scheme 2. Insertions and condensation reactions of diazocarbonyls with alcohols and nitriles.



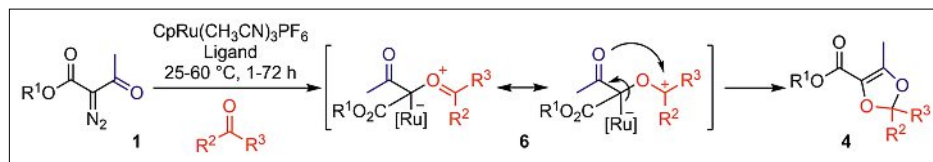
Scheme 3. Preferred condensation over C-H insertion pathway in the CpRu-mediated reactions of diazocarbonyls with aldehydes and ketones. [Ru] indicates complex  $[\text{CpRu}(\text{CH}_3\text{CN})_3]$ .



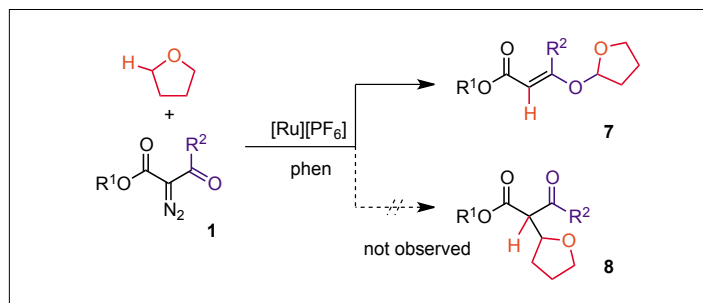
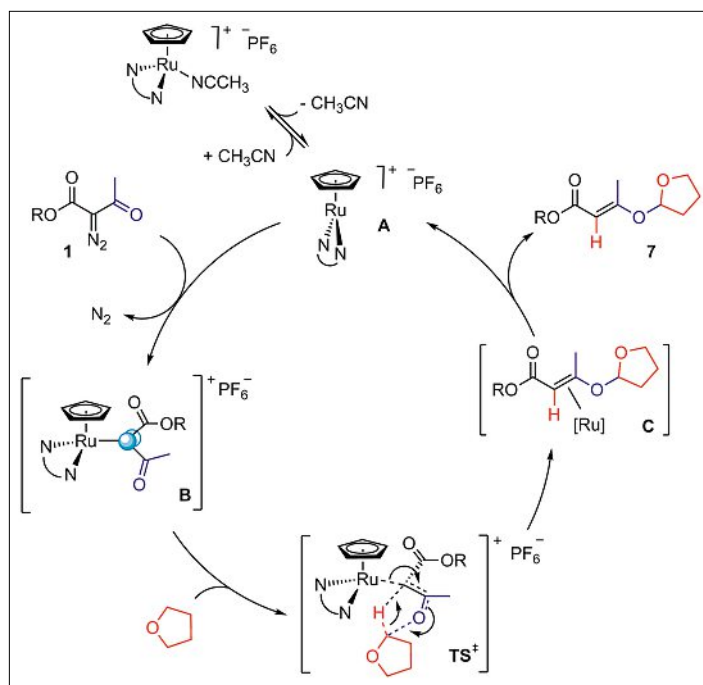
Scheme 4. Enantioselective condensations.

gen ether atom of THF. Evidence for the formation of macrocyclization adducts could not be found (*e.g.* Scheme 1).<sup>[6]</sup> In contrast with what had been observed with donor/acceptor carbenes,<sup>[22b]</sup> the kinetically favored formation of C-O instead of C-C bond adducts is thus attained using the combination of  $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$

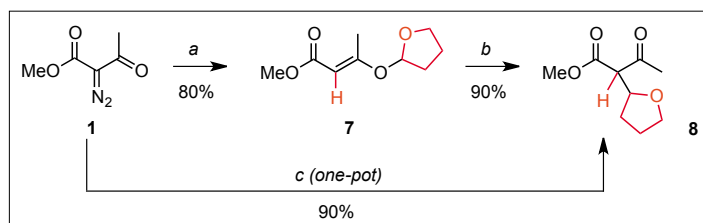
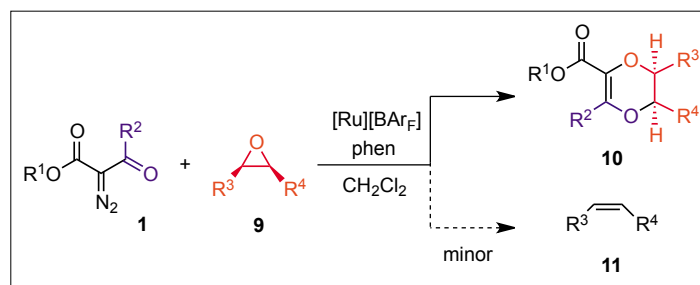
and phen as catalyst. In order to gain some mechanistic insight on the transformation, a series of experiments was performed using a 1:1 mixture of THF and THF- $d_8$ . The absence of cross-over and the occurrence of a primary kinetic isotope effect were noticed. Such experiments suggest a concerted hydrogen transfer as detailed



Scheme 5. Mechanistic rationale.

Scheme 6. Preferred 1,3-C-H insertion pathway. [Ru] indicates complex [CpRu(CH<sub>3</sub>CN)<sub>3</sub>].

Scheme 7. Mechanistic rationale for the 1,3-C-H insertion into THF.

Scheme 8. a) [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>] (2.5 mol%), phen (2.5 mol%), THF, 60 °C, 3 h; b) TMSOTf or Cu(OTf)<sub>2</sub> (5 mol%), CH<sub>2</sub>Cl<sub>2</sub>, 0→25 °C, 1 h; c) [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>] (2.5 mol%), phen (2.5 mol%), THF (1 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, 60 °C, 24 h and then TMSOTf or Cu(OTf)<sub>2</sub> (5 mol%), CH<sub>2</sub>Cl<sub>2</sub>, 0→25 °C, 1 h.Scheme 9. Dioxene formation via three-atom insertion reactions of diazo-carbonyls **1** into epoxides **9**. [Ru] indicates complex [CpRu(CH<sub>3</sub>CN)<sub>3</sub>].

in the mechanistic rationale (Scheme 7). After ligation of the phenanthroline moiety to the CpRu fragment, dissociation of the last acetonitrile leads to the formation of a catalytically active 16-electron species **A**. This electron-deficient entity promotes the decomposition of  $\alpha$ -diazo- $\beta$ -ketoester reagents **1** by a classic addition of the

'enolate' to the Lewis acidic complex and elimination of molecular nitrogen. It affords the metal carbenes intermediates of type **B**. At this stage, it is proposed that a concerted reaction occurs that involves the keto group of the carbene and the less hindered C $_{\alpha}$ -H bond of the ether moiety.<sup>[23]</sup> Concomitant formation of the new C–O

and C–H bonds takes place in a five-membered transition state; this step determines the configuration of enol functional group.

It was further noted that compounds **7** rearrange to the 'classical' products **8** of C–C bond formation when treated with Lewis acids (Scheme 8, step b). For instance, in the presence of Cu(OTf)<sub>2</sub> or TMSOTf (5 mol%), a dissociation occurs to form two reactive enolate and oxycarbenium intermediates that recombine. The C–H insertion and the rearrangement steps can be united in a one-pot sequential process; derivatives **8** are then obtained in a higher yield than for the two-step procedure.

Finally, in a recent study,<sup>[24]</sup> epoxides were used as Lewis basic reactant together with  $\alpha$ -diazo- $\beta$ -ketoesters reagents and the CpRu/diimine catalyst combination. Previously, only few examples of reactions of this type between metal carbenes and epoxides had been reported leading mainly to deoxygenation processes and to the corresponding alkenes by a stereospecific oxygen removal.<sup>[25]</sup> An unexpected result was again obtained as the treatment of epoxides **9** under the conditions optimized for the reaction with THF led to the prevalent formation of dioxene motifs of type **10** (Scheme 9). In practice, the stereoselective ring opening and three-atom insertion reaction was performed by the simple addition of two equivalents of the  $\alpha$ -diazo- $\beta$ -ketoester reagent to a methylene chloride solution of the epoxide (one equivalent) in the presence [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][BAR<sub>F</sub>] and phen (2.5 mol% each). At 60 °C and under relatively high concentration (0.5 M in **1**), conversion of the diazo reagent is complete in usually 24 h. In the crude reaction mixtures, dioxene adducts of type **10** were always the major components over

alkenes **11** derived from the deoxygenation pathway.

Noteworthy, dioxenes **10** were formed as single stereoisomers as indicated by <sup>1</sup>H NMR spectroscopic and X-ray diffraction analyses; *cis*-epoxides giving rise to *cis*-dioxene derivatives in perfectly *syn*-stereoselective ring opening reactions (Scheme

10). Furthermore, when using unsymmetrical *cis*-disubstituted and monosubstituted epoxides, ring-opening products were always obtained as single regioisomers, the substitution reactions occurring at the activated carbon centers (benzylic, allylic or more substituted). To shed some light on the process, both (*R*)- and (*S*)-styrene oxide were tested and the corresponding dioxene product was obtained with a 94% *ee*; X-ray and vibrational circular dichroism analyses clearly indicating the occurrence of a retention of configuration for the ring opening.

A mechanistic rationale coherent with the experimental information is proposed in Scheme 11. It starts with the same species **A** and **B** detailed for the THF functionalization (Scheme 7). Then, a nucleophilic attack of the epoxide occurs on metal carbene **B** and a metal-bound oxonium ylide intermediate **C'** is formed. Promoted by strain and by the electrophilic activation, a C–O bond cleavage occurs in the direction of the carbon that stabilizes better the developing positive charge. This step involving a  $S_N1$ -like pathway explains the observed regioselectivity. Carbocationic intermediate **D'** is then trapped rapidly by the keto group at proximity to form the cyclic 1,4-dioxene skeleton – and this with retention of the original configuration of the reacting carbon center in **E'**. Products **10** are then released and the catalytic cycle continues.

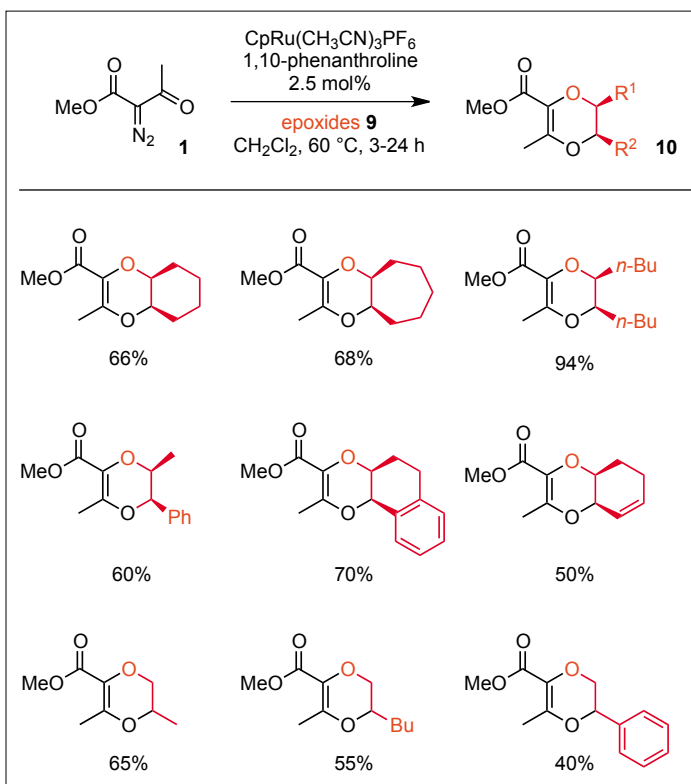
In conclusion, by using  $\alpha$ -diazo- $\beta$ -ketoesters as reagents and combinations of CpRu fragments and diimine ligands as decomposition catalysts, a series of original transformations have been obtained that are best rationalized by the formation of metal carbenes and metal-bound ylide intermediates. Interesting 1,3-dioxole **4**, enol-acetal **7** and 1,4-dioxene **10** motifs were obtained in usually good yields by the use of substrates of common Lewis basic moieties such as aldehydes or ketones, THF and epoxides. The reactions proceeded with usually high levels of stereo (and regio) selectivity. Further applications are looked for.

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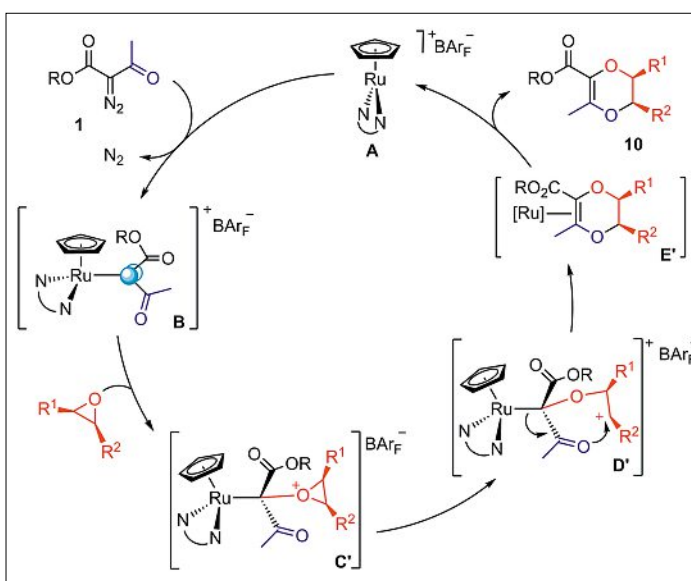
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- [1] M. P. Doyle, M. A. McKervy, T. Ye, 'Modern catalytic methods for organic synthesis with diazo compounds: from cyclopropanes to ylides', Wiley, New York, **1998**.  
 [2] a) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861; b) A. Padwa, M. D.



Scheme 10. Stereo- and regioselective ring openings.



Scheme 11. Mechanistic rationale. N<sub>2</sub> represents ligand phen. R<sup>2</sup>>R<sup>1</sup> in terms of electron-donating ability.

- Weingarten, *Chem. Rev.* **1996**, *96*, 223; c) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911; d) Z. H. Zhang, J. B. Wang, *Tetrahedron* **2008**, *64*, 6577; e) M. M. Diaz-Requejo, P. J. Perez, *J. Organomet. Chem.* **2005**, *690*, 5441; f) C. P. Casey, R. L. Anderson, *J. Organomet. Chem.* **1974**, *73*, C28.  
 [3] R. H. Grubbs, 'Handbook of Metathesis', Wiley-VCH, **2003**.  
 [4] a) W. Kirmse, *Angew. Chem. Int. Ed.* **2003**, *42*, 1088; b) R. G. Salomon, J. K. Kochi, *J. Am. Chem. Soc.* **1973**, *95*, 3300; c) W. R. Moser, *J. Am. Chem. Soc.* **1969**, *91*, 1141; d) H. Nozaki, S. Moriuti, H. Takaya, R. Noyori, *Tetrahedron Lett.* **1966**, 5239; e) H. Nozaki, S. Moriuti, M. Yamabe, R. Noyori, *Tetrahedron Lett.* **1966**, 59 f) M. P. Doyle, C. S. Peterson, D. L. Parker, *Angew. Chem. Int. Ed.* **1996**, *35*, 1334.  
 [5] a) H. M. L. Davies, D. Morton, *Chem. Soc. Rev.* **2011**, *40*, 1857; b) S. Omalley, T. Kodadek, *Tetrahedron Lett.* **1991**, *32*, 2445; c) S. Omalley, T. Kodadek, *Organometallics* **1992**, *11*, 2299; d) J. L. Maxwell, K. C. Brown, D. W. Bartley, T. Kodadek, *Science* **1992**, *256*, 1544; e) R. Paulisse, H. Reimling, E. Hayez, A. J. Hubert, P. Teyssie, *Tetrahedron Lett.* **1973**, 2233; f) H. Brunner, H. Kluschanzoff, K. Wutz, *Bull. Soc. Chim. Belg.* **1989**, *98*, 63; g) M. Kennedy, M. A. McKervy, A. R. Maguire, G. H. P. Roos, *J. Chem. Soc., Chem. Commun.* **1990**, 361; h) S. Hashimoto, N. Watanabe, S. Ikegami, *Tetrahedron Lett.* **1990**, *31*, 5173; i) D. Marcoux, A. B. Charette, *Angew. Chem. Int. Ed.* **2008**, *47*, 10155; j) M. P. Doyle, B. D. Brandes, A. P. Kazala, R. J. Pieters, M. B. Jarstfer, L. M. Watkins, C. T. Eagle, *Tetrahedron Lett.* **1990**, *31*, 6613; k) M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen, R. Ghosh, *J. Am. Chem. Soc.* **1993**, *115*, 9968; l) M. P. Doyle, W. R. Winchester, M. N. Protopenova, A. P. Kazala, L. J. Westrum, *Org. Synth.* **1996**, *73*, 13; m) M. P. Doyle, Q. L. Zhou, C. E. Raab,

- G. H. P. Roos, S. H. Simonsen, V. Lynch, *Inorg. Chem.* **1996**, 35, 6064; n) M. P. Doyle, W. R. Winchester, M. N. Protopopova, P. Muller, G. Bernardinelli, D. Ene, S. Motallebi, *Helv. Chim. Acta* **1993**, 76, 2227; o) M. P. Doyle, W. H. Hu, I. M. Phillips, C. J. Moody, A. G. Pepper, A. M. Z. Slawin, *Adv. Synth. Catal.* **2001**, 343, 112.
- [6] a) W. Zeghida, C. Besnard, J. Lacour, *Angew. Chem. Int. Ed.* **2010**, 49, 7253; b) D. Rix, R. Ballesteros-Garrido, W. Zeghida, C. Besnard, J. Lacour, *Angew. Chem. Int. Ed.* **2011**, 50, 7308; c) R. Ballesteros-Garrido, D. Rix, C. Besnard, J. Lacour, *Chem. Eur. J.* **2012**, 18, 6626; d) M. Vishe, R. Hrdina, L. Guénée, C. Besnard, J. Lacour, *Adv. Synth. Catal.* **2013**, 355, 3161.
- [7] a) G. Maas, T. Werle, M. Alt, D. Mayer, *Tetrahedron* **1993**, 49, 881; b) H. Nishiyama, Y. Itoh, H. Matsumoto, S. B. Park, K. Itoh, *J. Am. Chem. Soc.* **1994**, 116, 2223; c) H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki, K. Itoh, *Bull. Chem. Soc. Jpn.* **1995**, 68, 1247; d) C. M. Che, J. S. Huang, *Coord. Chem. Rev.* **2002**, 231, 151; e) C. Y. Zhou, W. Y. Yu, P. W. H. Chan, C. M. Che, *J. Org. Chem.* **2004**, 69, 7072; f) G. Maas, *Chem. Soc. Rev.* **2004**, 33, 183; g) P. Le Maux, T. Roisnel, I. Nicolas, G. Simonneaux, *Organometallics* **2008**, 27, 3037; h) W. W. Chan, S. H. Yeung, Z. Y. Zhou, A. S. C. Chan, W. Y. Yu, *Org. Lett.* **2010**, 12, 604.
- [8] a) G. Maas, T. Werle, M. Alt, D. Mayer, *Tetrahedron* **1993**, 49, 881; b) H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, K. Itoh, *J. Am. Chem. Soc.* **1994**, 116, 2223; c) H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki, K. Itoh, *B. Chem. Soc. Jpn.* **1995**, 68, 1247; d) W. Baratta, A. DelZotto, P. Rigo, *Chem. Commun.* **1997**, 2163; e) A. Del Zotto, W. Baratta, P. Rigo, *J. Chem. Soc., Perkin Trans. 1* **1999**, 3079; f) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, 101, 2067; g) C.-Y. Zhou, W.-Y. Yu, C.-M. Che, *Org. Lett.* **2002**, 4, 3235; h) C.-M. Che, J.-S. Huang, *Coord. Chem. Rev.* **2002**, 231, 151; i) C.-Y. Zhou, W.-Y. Yu, P. W. H. Chan, C.-M. Che, *J. Org. Chem.* **2004**, 69, 7072; j) G. Maas, *Chem. Soc. Rev.* **2004**, 33, 183; k) P. Le Maux, T. Roisnel, I. N. Nicolas, G. R. Simonneaux, *Organometallics* **2008**, 27, 3037; l) W.-W. Chan, S.-H. Yeung, Z. Zhou, A. S. C. Chan, W.-Y. Yu, *Org. Lett.* **2009**, 12, 604; m) M. Basato, C. Tubaro, A. Biffis, M. Bonato, G. Buscemi, F. Lighezzolo, P. Lunardi, C. Vianini, F. Benetollo, A. Del Zotto, *Chem. Eur. J.* **2009**, 15, 1516; n) L. Xia, Y. R. Lee, *Adv. Synth. Catal.* **2013**, 355, 2361; o) S. Moulin, H. Zhang, S. Raju, C. Bruneau, S. Dérien, *Chem. Eur. J.* **2013**, 19, 3292.
- [9] a) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, 101, 2067; b) E. P. Kündig, F. R. Monnier, *Adv. Synth. Catal.* **2004**, 346, 901; c) A. Mercier, W. C. Yeo, J. Y. Chou, P. D. Chaudhuri, G. Bernardinelli, E. P. Kündig, *Chem. Commun.* **2009**, 5227.
- [10] a) S. Constant, S. Tortoioli, J. Muller, J. Lacour, *Angew. Chem. Int. Ed.* **2007**, 46, 2082; b) S. Constant, S. Tortoioli, J. Muller, D. Linder, F. Buron, J. Lacour, *Angew. Chem. Int. Ed.* **2007**, 46, 8979.
- [11] a) M. Austeri, D. Linder, J. Lacour, *Chem. Eur. J.* **2008**, 14, 5737; b) M. Austeri, D. Linder, J. Lacour, *Adv. Synth. Catal.* **2010**, 352, 3339.
- [12] a) J. L. Renaud, C. Bruneau, B. Demerseman, *Synlett* **2003**, 408; b) M. D. Mbaye, B. Demerseman, J. L. Renaud, L. Toupet, C. Bruneau, *Angew. Chem. Int. Ed.* **2003**, 42, 5066; c) M. D. Mbaye, B. Demerseman, J.-L. Renaud, C. Bruneau, *J. Organomet. Chem.* **2005**, 690, 2149.
- [13] a) E. Aller, D. S. Brown, G. G. Cox, D. J. Miller, C. J. Moody, *J. Org. Chem.* **1995**, 60, 4449; b) P. Bulughapitiya, Y. Landais, L. ParraRapado, D. Planchenault, V. Weber, *J. Org. Chem.* **1997**, 62, 1630; c) J. L. Wood, G. A. Moniz, D. A. Pflum, B. M. Stoltz, A. A. Holubec, H. J. Dietrich, *J. Am. Chem. Soc.* **1999**, 121, 1748; d) T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, 128, 4594; e) S. F. Zhu, C. Chen, Y. Cai, Q. L. Zhou, *Angew. Chem. Int. Ed.* **2008**, 47, 932; f) Y. Liang, H. L. Zhou, Z. X. Yu, *J. Am. Chem. Soc.* **2009**, 131, 17783; g) S. F. Zhu, Q. L. Zhou, *Acc. Chem. Res.* **2012**, 45, 1365; h) D. Gillingham, N. Fei, *Chem. Soc. Rev.* **2013**, 42, 4918.
- [14] Y. Xu, Y. L. Wang, S. Z. Zhu, *Synthesis* **2000**, 513.
- [15] M. Austeri, D. Rix, W. Zeghida, J. Lacour, *Org. Lett.* **2011**, 13, 1394.
- [16] a) M. E. Alonso, P. Jano, *J. Heterocyclic Chem.* **1980**, 17, 721; b) M. E. Alonso, A. W. Chitty, *Tetrahedron Lett.* **1981**, 22, 4181; c) A. E. Russell, J. Brekan, L. Gronenberg, M. P. Doyle, *J. Org. Chem.* **2004**, 69, 5269; d) V. Nikolaev, L. Hennig, H. Heimgartner, B. Schulze, V. Nikolaev, *Tetrahedron Lett.* **2006**, 47, 2643; e) A. Padwa, J. Boonsombat, P. Rashatasakhon, *Tetrahedron Lett.* **2007**, 48, 5938; f) V. V. Nikolaev, H. Heimgartner, A. Linden, I. S. Krylov, V. A. Nikolaev, *Eur. J. Org. Chem.* **2006**, 4737; g) V. V. Nikolaev, B. Schulze, H. Heimgartner, V. A. Nikolaev, *Heterocycles* **2007**, 73, 433.
- [17] D. M. Hodgson, F. Y. T. M. Pierard, P. A. Stuppel, *Chem. Soc. Rev.* **2001**, 30, 50.
- [18] J. Wang, 'Comprehensive Organometallic Chemistry III', Eds. D. M. P. Mingos, R. H. Crabtree, 'Applications II: Transition metal compounds in organic synthesis 2', Elsevier, Oxford, **2007**, Vol. 11 pp. 151–178.
- [19] For related lactone formations, see: a) M. P. Doyle, L. J. Westrum, W. N. E. Wolthuis, M. M. See, W. P. Boone, V. Bagheri, M. M. Pearson, *J. Am. Chem. Soc.* **1993**, 115, 958; b) A. G. H. Wee, Q. Yu, *J. Org. Chem.* **1997**, 62, 3324.
- [20] C. Tortoreto, T. Achard, W. Zeghida, M. Austeri, L. Guénée, J. Lacour, *Angew. Chem. Int. Ed.* **2012**, 51, 5847.
- [21] Adducts **7** are characterized by <sup>1</sup>H NMR signals at 5.66 (d, *J* = 4 Hz, O-CH-O) and 5.32 (s, C=CH) ppm. The *E* configuration of the double bond was unambiguously determined by NOESY experiment and X-ray diffraction studies.
- [22] a) H. M. L. Davies, T. Hansen, *J. Am. Chem. Soc.* **1997**, 119, 9075; b) H. M. L. Davies, T. Hansen, M. R. Churchill, *J. Am. Chem. Soc.* **2000**, 122, 3063; c) M. M. Diaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, P. J. Perez, *J. Am. Chem. Soc.* **2002**, 124, 896; d) J. M. Fraile, J. I. Garcia, J. A. Mayoral, M. Roldan, *Org. Lett.* **2007**, 9, 731; e) H. M. Mbuvi, L. K. Woo, *Organometallics* **2008**, 27, 637; f) H. Suematsu, T. Katsuki, *J. Am. Chem. Soc.* **2009**, 131, 14218; g) C. J. Lovely, J. A. Flores, X. F. Meng, H. V. R. Dias, *Synlett* **2009**, 129; h) J. M. Fraile, J. A. Mayoral, N. Ravasio, M. Roldan, L. Sordelli, F. Zacccheria, *J. Catal.* **2011**, 281, 273.
- [23] C. Özen, N. S. Tüzün, *Organometallics* **2008**, 27, 4600.
- [24] T. Achard, C. Tortoreto, A. I. Poblador-Bahamonde, L. Guénée, T. Bürgi, J. Lacour, *Angew. Chem. Int. Ed.* **2014**, 53, doi: 10.1002/anie.201402994R2.
- [25] A. Padwa, S. F. Hornbuckle, *Chem. Rev.* **1991**, 91, 263.