Tetrahedron Letters 51 (2010) 605–608

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Methylenepyran unsaturated Fischer carbene complexes from γ-methylpyrylium salts and alkynylcarbenes. Evolution to spiro-pyran-cyclopentenone compounds

Fatou Ba, Pascal Le Poul, Françoise Robin-Le Guen, Nolwenn Cabon, Bertrand Caro *

Sciences Chimiques de Rennes UMR CNRS 6226, I.U.T. Lannion, rue Edouard Branly BP 30219, Lannion Cedex, France

ARTICLE INFO

Article history:
Received 16 September 2009
Revised 13 November 2009
Accepted 16 November 2009
Available online 20 November 2009

Keywords:
Push–pull molecules
Methylenepyrans
Fischer alkynylcarbenes complexes
Spiro-fused-pyran-cyclopentenenone

ABSTRACT

Push–pull methylenepyran compounds **3** containing ferrocenyl or aryl groups are synthesized from reaction of condensation between γ-methyl-pyrylium salts **1** as precursors of γ-methylenepyrans and alkynylcarbene complexes **2** as Michaël-type acceptors. The new carbenes **3** evolve in CH_2Cl_2 solution at room temperature to provide spiro-fused-pyran-cyclopentenenone **4** and polysubstituted cyclopentenones **5**.

Due to their exceptional reactivity towards a great variety of nucleophiles, pyrylium salts and their chalcogeno congeners (Scheme 1) are versatile reagents for the synthesis of carbocyclic and heterocyclic compounds.[1] Taking advantage of these properties, we have recently shown that organometallic pyrylium salts act as convenient markers for proteins (Scheme 1A; $R_3 = \eta^5$-$C_5H_4Re(CO)_3$, cymentrenyl, benchrotrenyl, ferrocenyl and ruthenocenyl groups).[2]

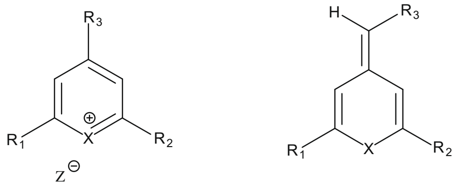
On the other hand, we have recently reported on an efficient access to push–pull methylenepyran Fischer-type carbene complexes. This was achieved by the action of stabilized carbanions of CH_3–C(Y)═M$(CO)_5$ carbenes (Y = OCH_3, SPh) towards 2,6-substituted pyrylium salts, free of substituent or bearing a methoxy leaving group on the 4 (γ) position (Scheme 1A; R_3 = H or OCH_3).[3,4] Methylenechalcogenopyran carboxaldehydes and vinylogues (Scheme 1B; R_3 = –CHO, R_3 = –CH═CH–CHO) provided efficient NLO phores in which the methylenechalcogenopyran groups act as proaromatic donors (Scheme 1B; $R_3 = -(CH{=}CH)_n-C(Y)M(CO)_5$).[5]

Moreover, Pd^0 catalytic self-dimerization of these carbenes allowed the formation of extended bischalcogenopyrans, a class of molecules having interesting redox electrochemical dynamic properties mainly due to the presence of electron-rich π spacers.[6]

Another interest of pyrylium salt lies in the acidity of hydrogen atoms of the methyl or alkyl groups in α or γ position (Scheme 1A). Deprotonation gives α- and γ-methylene or alkylidenepyrans which display nucleophilic properties[1,7] (Scheme 1B for γ-methylenepyran R_3 = H or γ-alkylidenepyran R_3 = CH_3, C_2H_5 group).

While our main aim was to explore redox properties of metallocenyl extended bispyrans, a new class of metallocenyl electron-rich molecules potentially precursor of molecular materials, we suspected that reaction of ferrocenyl alkynyl Fischer-type carbene complexes, acting as Michael acceptors, with γ-methylpyrylium salts in basic media could provide γ-methylenepyran alkenyl carbene complexes containing metallocenyl group. Subsequent Sierra self-dimerization should allow a convenient access to the expected extended electron-rich bispyran molecules.[6]

Indeed, the role of group 6 metal alkynylcarbene complexes as Michael-type acceptor is well documented.[8] They react easily with



1A
Pyrylium salts (X = O)
chalcogenopyrylium salts (X = S, Se, Te)
$R_1 = R_2$ = aryl, tBu, thienyl.
R_3 (see text)

1B
Alkylidene pyrans (X = O)
Chalcogenoalkylidene pyrans (X = S, Se, Te)
$R_1 = R_2$ = aryl, tBu, thienyl.
R_3 (see text)

Scheme 1. Pyrylium salts and methylene pyran compounds.

---

* Corresponding author. Fax: +33 2 9648 1320.
E-mail address: Bertrand.caro@univ-rennes1.fr (B. Caro).

0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.11.072

O, N, P and C nucleophiles including electron-rich C=C double bonds.[9] In particular, it has been reported by Aumann group that α- and γ-methylene dihydroquinoleine and γ-methylidenedihydropyridine undergo a 1,4-addition to phenylethynyl carbene complexes to give unstable heterocyclic metallahexatrienes which evolve, by cyclization, to spiro-fused cyclopentadienes.[9c] On the other hand less sterically γ-methylene dihydropyridines gave a 1,2-addition, leading to a zwitterionic pyridinium carbonyl metallates after a 1,2-migration of the $W(CO)_5$ moiety.[9c] Therefore, it was of interest to test the reactivity of γ-methylenepyrans towards alkynylcarbenes.

The following describes, in contrast with the results obtained in dihydropyridine series, the formation of γ-methylenepyran ferrocenyl or aryl substituted alkenyl carbene complexes. Their conversion to spiro-fused pyran-cyclopentenones is also reported. Such evolution was not previously observed by us for analogous carbene complexes of similar length, but free of ferrocenyl or aryl substituent in the alkene spacer.[5]

First, we chose to study the reaction between 2,6-diphenyl-4-methylpyrylium tetrafluoroborate **1a** and ferrocenylalkynylcarbene complex **2a** (Scheme 2). When a mixture of **1a** and **2a** in THF, cooled to 0 °C, is treated with 3 equiv. of triethylamine, a colour change immediately occurs (red to blue). After five minutes, a careful control of the reaction mixture by TLC analysis (silica plate) reveals a complete transformation (observation of a single blue spot). After hydrolysis on ice, extraction with diethylether, drying on anhydrous $MgSO_4$ and evaporation of the solvent at 20–30 °C, a dark solid is isolated. At this stage, a TLC monitoring shows below and above the initial spot, uncoloured and coloured spots suggesting partial evolution of the initially formed blue compound. A flash chromatography on silica gel and distillation of the solvent in the cold furnished a pure solid for which NMR spectra, recorded at low temperature (−40 °C) are consistent with the formation of the heterocyclic carbene **3a** (Scheme 2, Table 1, carbene **3a**[10]). The reaction has been extended, without any modification to 2,6-ditertiobutyl-4-methyl **1b** or 2,4,6-trimethylpyrylium salt **1c** and ferrocenyl or aryl alkynyl carbenes complexes **2a–c** (Scheme 2, Table 1).

The push–pull γ-methylenepyran alkenyl carbene complexes **3b–f** were obtained in fair yields. Carbenes **3a–f** are moderately stable solids at room temperature but can be stocked for weeks in the cold (−20 °C). As far as we are aware these reactions constitute the first example of methylenepyran addition to electron-deficient alkynes.

The reaction of trimethylpyrylium salt **1c** and the ferrocenyl carbene **2a** gives only one product resulting from γ-condensation. This agrees with the regioselectivity of other condensation reactions involving this salt, which is closely linked with the higher acidity of the hydrogen atoms borne by the γ-methyl group, known to undergo deuteration about 10 times faster than the α-methyl hydrogens.[1] This is also in line with theoretical calculations which indicate lower energies for the symmetrical γ-methylenepyrans.[11]

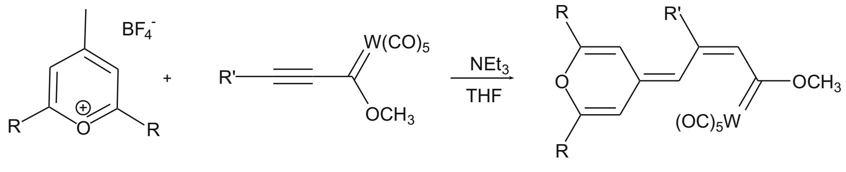
It can be noted that we have not detected the formation of zwitterionic metal compounds corresponding to a 1–2 addition of methylenepyrans to alkynyl carbene, as observed for analogous γ-methylene dihydropyridine.[9c]

Moreover, cross-conjugated carbenes coming from a metathesis of the C–C exocyclic double bond of methylenepyrans were not observed. Similar behaviour was noted for methylene dihydroquinoline series.[9c]

Therefore the given results are well rationalized by Michael-type addition of the pyran electron-rich carbon–carbon exocyclic double bond, stemming from deprotonation of the pyrylium salt, to the alkynyl carbene leading to the zwitterionic intermediate **A** (Scheme 3).

Successive protonation, deprotonation steps gave the expected unsaturated carbene **3**. Intermediates of type **A** were commonly evoked in conjugated nucleophilic addition to alkynyl carbenes,[12] and in some instance were characterized by NMR experiments at low temperature[13] and by X-ray analysis.[14] As exemplified by the ^{1}H and ^{13}C NMR spectra of **3a–f** it seems that protonation of the central carbon of the allenic moiety is stereospecific (one isomer detected) (Table 1).

One of main features of **3a–c** ^{1}H NMR recordings ($CDCl_3$ solution) is the progressive disappearance of the carbene signals and the concomitant appearance of new signals when raising the temperature from −40 °C to room temperature. This suggests a conversion of carbenes **3a–c** to other products in $CDCl_3$ solution. Thus, solution of ferrocenyl carbenes **3a–c** in CH_2Cl_2 was left at room temperature for 24 h under N_2 atmosphere. Successive TLC analysis showed the slow formation of red compounds and $W(CO)_6$, respectively. After complete reaction, the solutions were chromatographed on silica gel to give red solid for which IRFT, ^{1}H and ^{13}C NMR and mass spectrography analyses are consistent with

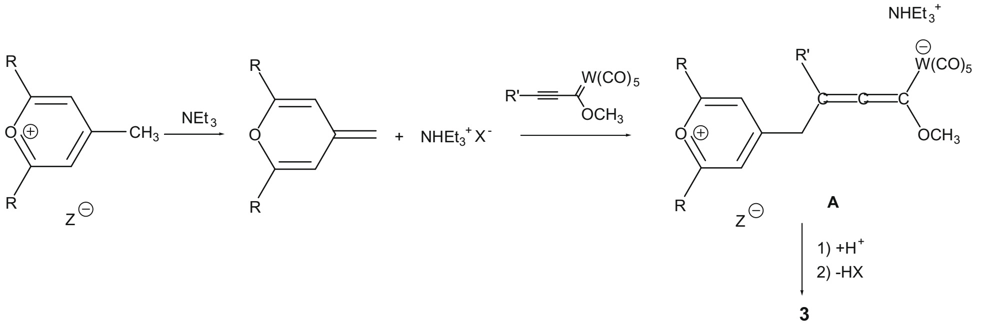


1 **2** **3**

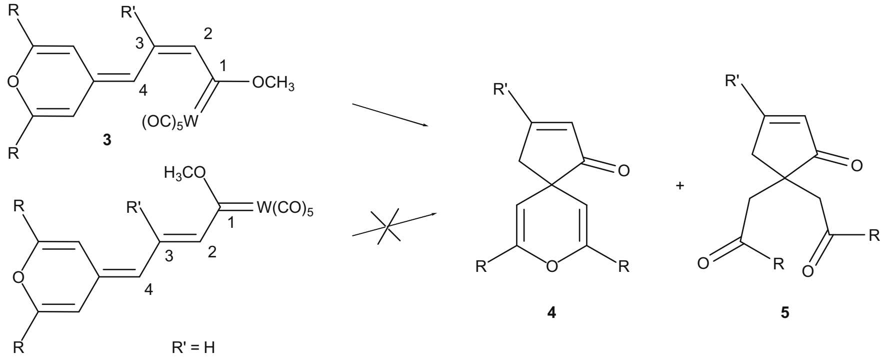
Scheme 2. Formation of aryl and ferrocenyl methylenepyran carbene complexes.

Table 1
Yield of isolated carbene complexes

	Pyrylium salts	Alkynyl carbenes	Alkenyl carbenes	Yield%
1	**1a**: R = Ph, $Z^- = BF_4^-$	**2a**: R′ = Fc	**3a**: R = Ph, R′ = Fc	63
2	**1b**: R = *t*Bu, $Z^- = BF_4^-$	**2a**: R′ = Fc	**3b**: R = *t*Bu, R′ = Fc	46
3	**1c**: R = CH_3, $Z^- = PF_6^-$	**2a**: R′ = Fc	**3c**: R = CH_3, R′ = Fc	64
4	**1d**: R = Ph, $Z^- = BF_4^-$	**2b**: R′ = Ph	**3d**: R = Ph, R′ = Ph	30
5	**1b**: R = *t*Bu, $Z^- = BF_4^-$	**2b**: R′ = Ph	**3e**: R = *t*Bu, R′ = Ph	54
6	**1b**: R = *t*Bu, $Z^- = BF_4^-$	**2c**: R′ = *p*-$OMeC_6H_4$	**3f**: R = *t*Bu, R′ = *p*-$OMeC_6H_4$	40



Scheme 3. Formation of zwitterionic intermediate.



Scheme 4. Cyclopentenone formation.

Table 2
Yield of cyclopentenone formation

Entry	Spiro-pyran cyclopentenone **4**	Yield%	Substituted cyclopentenones **5**	Yield%
1	**4a**: R = Ph, R′ = Fc	83	**5a**: R = Ph, R′ = Fc	No
2	**4b**: R = *t*Bu, R′ = Fc	85	**5b**: R = *t*Bu, R′ = Fc	No
3	**4c**: R = CH_3, R′ = Fc	85	**5c**: R = CH_3, R′ = Fc	No
4	**4d**: R = Ph, R′ = Ph	27	**5d**: R = Ph, R′ = Ph	No
5	**4e**: R = *t*Bu, R′ = Ph	29	**5e**: R = *t*Bu, R′ = Ph	16
6	**4f**: R = *t*Bu, R′ = *p*-$OMeC_6H_4$	No	**5f**: R = *t*Bu, R′ = *p*-$OMeC_6H_4$	89

the spiro-pyran-cyclopentenone skeleton **4a–c** as exemplified in Scheme 4 (Table 2).[15]

Aryl carbenes **3d–f** evolve similarly. Nevertheless a pyran ring opening occurred, leading to the formation of tricetones **5** as the sole and minor compounds from **3f** and **3e** conversion, respectively. For **3d** ester formation resulting from $W(CO)_5$ substitution by O was also observed (18% yield).

The reaction reported here is a new example of cyclization of metallahexatrienes to cyclopentenones, a conversion which rarely provided spiranic structures.[8]

It is noteworthy, that the presence of a pyran ring in **4**, which can act as 1–5 pentadione equivalent[16] could offer further synthetic opportunities in cyclopentenone chemistry.

Finally, given that methylenepyran carbene complexes (Scheme 4) of similar unsaturated chain length, free of ferrocenyl or aryl groups, which display a trans (*E*) configuration for the C_2–C_3 double bond are stable compounds,[5,6] we propose that the conversion of carbene **3** to cyclopentenones is favoured by a *E* configuration. Such a stereochemistry allows the proximity between the exocyclic double bond and the carbene carbon atom, a necessary condition to observe the ring closure[9,17] (Scheme 4).

In summary we have described a simple procedure for the synthesis of push–pull methylenepyran ferrocenyl and aryl substituted alkenyl carbene complexes using pyrylium salts as precursors of γ-methylenepyrans and alkynyl carbenes as Michael-type acceptors. The obtained heterocyclic metallahexatrienes evolve in solution at room temperature to spiro-pyran-cyclopentenone compounds or/and to polysubstituted cyclopentenones substituted by two CH_2COR groups. The reported process constitutes a new approach to cyclopentenone framework[18] and to ferrocenyl cyclopentenone[19] which could have possible medicinal applications.[20] Thus, further developments aimed at the formation of polycyclic skeletons taking advantage of the presence of three ketones functions in **5**. However, the low stability of carbenes **3** makes tricky the formation of extended diferrocenyl bispyrans using the Sierra Pd^0 catalytic self-dimerization methodology.[21]

Acknowledgements

This work is supported by the CNRS and the University of Rennes1. We are grateful to N. Kervarec, S. Cerantola and G. Simon for recording NMR spectra. Sincere gratitude towards N. Kervarec from Service Commun de Recherche de RMN et de RPE, Université de Bretagne Occidentale for NOESY/ROESY experiments.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.072.

References and notes

1. Balaban, A. T.; Dinculescu, A.; Dorofeenko, G. N.; Mezheritskii, V. V.; Koblik, A. V.; Fischer, G. W. In *Pyrylium Salt: Synthesis, Reactions and Physical Properties. Advances in Heterocyclic Chemistry*, Katrizky, A. R., Ed.; Academic New York, 1982.
2. (a) Salmain, M.; Lamisza, K. L.; Jaouen, G.; Senechal-Tocquer, M.-C.; Senechal, D.; Caro, B. *Bioconjugate Chem.* **1994**, *5*, 655–659; (b) Maliska, K. L.; Top, S.; Vaisserman, J.; Caro, B.; Senechal-Tocquer, M.-C.; Senechal, D.; Saillard, J.-Y.; Triki, S.; Kahlal, S.; Britten, J. F.; McGlinchey, M.; Jaouen, G. *Organometallics* **1995**, *14*, 5273–5280; (c) Caro, B.; Robin-Le Guen, F.; Salmain, M.; Jaouen, G. *Tetrahedron* **2000**, *56*, 257–263; (d) Egan, D.; Salmain, M.; Mc Ardle, P.; Jaouen, G.; Caro, B. *Spectrochim. Acta* **2002**, *58*, 941–951; (e) Salmain, M.; Caro, B.; Robin-Le Guen, F.; Blais, J.-C.; Jaouen, G. *Chem. Biochem.* **2004**, *5*, 99–109.
3. Caro, B.; Le Poul, P.; Robin-Le Guen, F.; Saillard, J.-Y.; Kahlal, S.; Moinet, C.; Le Poul, N.; Vaissermann, J. *Tetrahedron* **2002**, *58*, 7519–7530.
4. Le Bihan, J.-Y.; Faux, N.; Caro, B.; Robin-Le Guen, F.; Le Poul, P. *J. Organomet. Chem.* **2007**, *692*, 5517–5522.
5. (a) Faux, N.; Caro, B.; Robin-Le Guen, F.; Le Poul, P.; Nakatani, K.; Ishow, E. *J. Organomet. Chem.* **2005**, *690*, 4982–4988; (b) Faux, N.; Robin-Le Guen, F.; Le Poul, P.; Caro, B.; Nakatani, K.; Ishow, E.; Golhen, S. *Eur. J. Inorg. Chem.* **2006**, *17*, 3489–3497.
6. Faux, N.; Robin-Le Guen, F.; Le Poul, P.; Caro, B.; Le Poul, N.; Le Mest, Y.; Green, S. J.; Le Roux, S.; Kahlal, S.; Saillard, J.-Y. *Tetrahedron* **2007**, *63*, 7142–7153.
7. Mezheritskii, V. V.; Vaisserman, A. L.; Dorofeenko, G. N. *Heterocycles* **1979**, *12*, 51.
8. (a) Herndon, J. W. *Coord. Chem. Rev.* **2009**, *253*, 1517–1595; (b) Herndon, J. W. *Coord. Chem. Rev.* **2006**, *250*, 1889–1964; (c) Barluenga, J.; Fernandez-Rodriguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539–587; (d) Barluenga, J.; Santamaria, J.; Tomas, M. *Chem. Rev.* **2004**, *104*, 2259–2284; (e) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257–1280; (f) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17–31; (g) De Maijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964–4002; (h) Sierra, M. *Chem. Rev.* **2000**, *100*, 3591–3638; (i) Lian, Y.; Wulff, W. D. *J. Am. Chem. Soc.* **2005**, *127*, 17162–17163.
9. (a) Aumann, R.; Meyer, A. G.; Fröhlich, R. *Organometallics* **1996**, *15*, 5018–5027; (b) Göttker-Schnetmann, I.; Aumann, R.; Berganger, K. *Organometallics* **2001**, *20*, 3574–3581; (c) Göttker-Schnetmann, I.; Aumann, R.; Kataeva, O.; Holst, C.; Frölich, R. *Organometallics* **2001**, *20*, 2889–2904.
10. *Formation of* **3a** (Scheme 2, Table 1): A THF solution of pyrylium salt **1a** (0.290 g, $8.68.10^{-4}$ mol) was cooled to 0 °C. $NEt_3$and carbene **2a** (0.500 g, $8.68.10^{-4}$ mol) were then added. The solution turned blue. After 10 min, the THF solution was poured on ice. Extraction with diethylether, drying on $MgSO_4$, and distillation under vacuum led to a blue residue. The solid was dissolved in cold CH_2Cl_2 (−10 °C) and a flash chromatography was performed (silica gel, mixture of cold petroleum ether/diethylether 90/10). Distillation of the solvent under vacuum provides a blue solid (447 mg). TLC analysis shows only a blue spot.
    ^{1}H NMR (500 MHz, $CDCl_3$, −40 °C) δ 4.24 (5H, s, C_5H_5), 4.52 (2H, s, C_5H_4), 4.53 (3H, s, OCH_3), 4.67 (2H, s, C_5H_4), 6.27 (1H, s, H_{pyran}), 6.35 (1H, s, $H_{\mathrm{exocyclic}}$), 6.68 (1H, s, H_{pyran}), 7.40 (2H, m, $H_{\mathrm{Ph}(para)}$), 7.57 (4H, m, $H_{\mathrm{Ph}(meta)}$), 7.80 (4H, m, $H_{\mathrm{Ph}(ortho)}$), 7.88 (1H, s, $HC{=}C(Fc)$). ^{13}C NMR (HMQC, HMBC, $CDCl_3$, −40 °C) δ 68.8 (OCH_3), 71.0 (C_5H_5), 71.2 (C_5H_4), 71.9 (C_5H_4), 88.8 (C_{qFc}), 107.6 (C_{pyran}), 109.5 (C_{pyran}), 116.9 (C_4), 128.8 ($C_{\mathrm{Ph}(meta)}$), 129.0 ($C_{\mathrm{Ph}(para)}$), 131.9 ($C_{\mathrm{Ph}(ortho)}$), 139.7 (C_2), 139.9 (C_{pyran}), 154.8 (C_{pyran}), 155.4 (C_{pyran}), 286.1 (C_1). IR (KBr): ν 2050, 1921, 1900, 1643, 1535, 1429, 1104, 940, 797 cm^{-1}.
11. Zvezdina, E. A.; Zhadanova, M. P.; Bren, A.; Dorofeenko, G. N. *Khim. Geterotsikl. Soeden.* **1976**, 1494.
12. See for example (a) Stein, F.; Duetsch, M.; Pohl, E.; Herbst-Irmer, R.; De Mejeire, A. *Organometallics* **1993**, *12*, 2556–2564; (b) Pipoh, R.; Van Heldick, R.; Henkel, G. *Organometallics* **1993**, *12*, 2236–2242; (c) Dötz, K. H.; Christoffers, C.; Knochel, P. *J. Organomet. Chem.* **1995**, *489*, C84; (d) Aumann, R.; Yu, Z.; Fröhlich, R. *J. Organomet.* **1997**, *459*, 311–318; (e) Aumann, R.; Roths, K.; Fröhlich, R. *Organometallics* **1997**, *16*, 5893–5899; (f) Aumann, R.; Roths, K. B.; Köbmerer, M.; Fröhlich, R. *J. Organomet. Chem.* **1998**, *556*, 119–127; (g) Aumann, R.; Hildmann, B.; Fröhlich, R. *Organometallics* **1998**, *17*, 1197–1201; (h) Aumann, R.; Kömeier, M.; Mück-Lichtenfeld, C.; Zippel, F. *Eur. J. Org. Chem.* **2000**, 37–49; (i) Gu, K.; Yang, G.; Zhang, W.; Liu, X.; Yu, Z.; Han, X.; Bao, X. *J. Organomet. Chem.* **2006**, *691*, 1984–1992; (j) Barluenga, J.; Garcia-Garcia, P.; De Saa, D.; Fernandez-Rodrighez, M. A.; De La Rua, R. B.; Ballesteros, A.; Aguilar, E.; Tomas, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2610–2612.
13. Barluenga, J.; Tomas, M.; Lopez-Pelegrin, J. A.; Rubio, E. *Tetrahedron Lett.* **1997**, *38*, 3981–3984.
14. (a) Aumann, R.; Jasper, B.; Läge, M.; Krebs, D. *Chem. Ber.* **1994**, *127*, 2475–2482; (b) Ortin, Y.; Lugan, N.; Mathieu, R. *Dalton Trans.* **2005**, 1620–1636.
15. *General procedure*: A CH_2Cl_2 solution of carbenes **3** was left at room temperature under N_2 for 24 h. The blue solution progressively turned red (for **3a–c**) and colourless (for **3d–f**). The solution was chromatographed (silica gel diethylether–petroleum ether 30/70) to give the expected cyclopentenone **4** or (and) **5**. For **3d** an ester coming from $W(CO)_5$ substitution by O was also isolated in low yield.
    Selected spectroscopic data: **4c** (Scheme 4, Table 2) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (18H, s, $C(CH_3)_3$), 2.81 (2H, s, H_1), 4.14 (5H, s, C_5H_5), 4.37 (2H, s, $H_{3'}$ and $H_{5'}$), 4,52 (2H, s, C_5H_4), 4.60 (2H, s, C_5H_4), 6.07 (1H, s, H_2),. ^{13}CNMR (125 MHz, $CDCl_3$) δ 29.1 (CH_3), 35.0 ($C_{\mathrm{q}t\mathrm{Bu}}$), 47.5 ($C_{4'}$), 51.0 ($C_4$), 68.1 ($C_5H_4$), 70.1 ($C_5H_5$), 71.7 ($C_5H_4$), 78.0 ($C_{\mathrm{qFc}}$), 94.9 ($C_{3'}$ and $C_{5'}$), 121.1(C_2), 159.6 ($C_{2'}$ and $C_{6'}$), 174.7 (C_3), 209.9 (CO). IR (KBr): ν 2973, 1690, 1593, 1359, 1256, 1168, 1090, 823 cm^{-1}. HRMS (EI): $C_{27}H_{32}O_2Fe$ M^+ requires 444.1751, found 444.1735.
    Compound **5f** (Scheme 4, Table 2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (18H, s, $C(CH_3)_3$), 2.64 (2H, d, $^2J = 18.5$ Hz, $H_{3'}$ and $H_{5'}$), 3.04 (2H, s, H_1), 3.15 (2H, d, $^2J = 18.5$ Hz, $H_{3'}$ and $H_{5'}$), 3.85 (3H, s, OCH_3), 6.51 (1H, s, H_2), 6.93 (2H, d, $^3J = 7.0$ Hz, $H_{\mathrm{Ph}(para)}$), 7.62 (2H, d, $^3J = 7.0$ Hz, $H_{\mathrm{Ph(meta)}}$). ^{13}CNMR (125 MHz, $CDCl_3$) δ 26.6 ($C(CH_3)_3$), 42.7 ($C_{3'}$ and $C_{5'}$), 43,1 ($C_{3'}$ and $C_{5'}$), 43.7 ($C(CH_3)_3$), 44.0 ($C_{4'}$), 55.6 (OCH_3), 113.0 ($C_{\mathrm{Ph}(ortho)}$), 122.7 (C_2), 126.3 (C_{ipso}), 129.4 $C_{\mathrm{Ph}(meta)}$), 162.0 ($C_{\mathrm{Ph}(para)}$), 170.0 (C_3), 210.0 (C_1), 214.0 ($C_{2'}$ and $C_{6'}$). IR (KBr): ν 1706, 1681, 1594, 1513, 1336, 1260, 1182, 831 cm^{-1}. HRMS (EI): $C_{24}H_{32}O_4$ [$M+Na^+$] requires 407.2198, found 407.2198. NOESY experiment, performed on **4a**, showed the through space proximity of the methylene hydrogens and the β pyran hydrogens. This is in favour of the proposed structure.
16. Balaban, T. S.; Balaban, A. T. *Tetrahedron Lett.* **1997**, *28*, 1341–1344.
17. ROESY experiment performed on carbene **3c** (−40 °C, $CDCl_3$), showed ROE between the hydrogen atom borne by the carbon 2 (Scheme 4, $\delta = 7.70$ ppm) and the hydrogen atom of the ferrocenyl group and consequently confirmed the proposed stereochemistry for the C–C double bond bearing the ferrocenyl and carbene groups. This result is in accordance with the stereochemistry proposed by Aumann[3e] for analogous heterocyclic carbenes formed by the reaction between phenyl alkynylcarbene and methylene dihydrocyanoquinoléines.
18. Rezgui, F.; Amri, H.; Moncef El Gaied, M. *Tetrahedron* **2003**, *59*, 1369–1380.
19. Li, J.; Ma, J. P.; Liu, F.; Wu, X.-W.; Dong, Y.-B.; Huang, R. Q. *Organometallics* **2008**, *27*, 5446–5452.
20. Zora, M.; Ash Tumay, T.; Büyükgüngör, O. *Tetrahedron* **2007**, *63*, 4018–4026.
21. Gomez-Callego, M.; Mancheno, M. J.; Sierra, M. *Acc. Chem. Res.* **2005**, *38*, 44–53.