ORGANOMETALLICS

ARTICLE

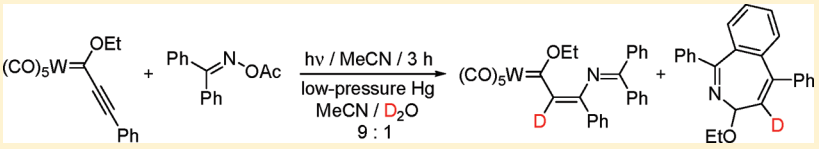
pubs.acs.org/Organometallics

Photochemically Driven Addition of Iminyl Radicals to Alkynyl Fischer Carbene Complexes†

Marina Blanco-Lomas, Alegría Caballero, Pedro J. Campos, Héctor F. González, Susana López-Sola, Laura Rivado-Casas, Miguel A. Rodríguez,* and Diego Sampedro

Departamento de Química, Universidad de La Rioja, Grupo de Síntesis Química de La Rioja, Unidad Asociada al CSIC, Madre de Dios, 51, E-26006, Logroño, Spain

ABSTRACT:



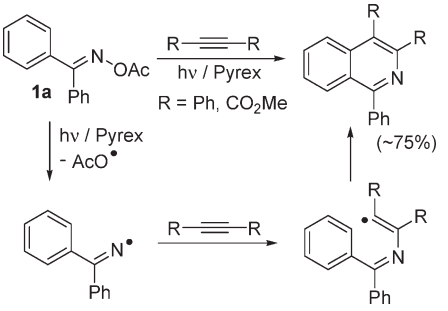
Nitrogen-centered radicals, generated by the action of UV light, are capable of reacting with alkynyl Fischer carbene complexes in two ways, 1,2- and 1,4-addition. Our results constitute the first reported example of a photochemically driven reaction of this kind.

INTRODUCTION

Radicals have shown impressive potential in synthesis.[1] We recently described[2] the use of acyloximes in the photochemical synthesis of isoquinoline derivatives in a two-step, one-pot reaction sequence. First, the iminyl radical is easily generated by a nitrogen−oxygen bond cleavage. The addition of this radical to unsaturated moieties then gives the heterocyclic compounds with ease in good yields.[2] This reaction mechanism has been further explored by means of theoretical calculations[3] and EPR studies.[4] Several groups are able to react in the intramolecular version, such as aryl, heteroaryl, alkenyl, or alkynyl,[2] while the intermolecular reaction works particularly well with alkynes to give isoquinolines (Scheme 1).[2a] This fact, together with our experience in the photochemistry of imine Fischer carbene complexes,[5] prompted us to study the reactivity of iminyl radicals with alkynyl Fischer carbene complexes.

A survey of the literature showed that metal carbene complexes have been extensively used as synthons in organic and organometallic synthesis.[6] However, as far as we know, only four papers have been published on additions of radicals to unsaturated Fischer carbene complexes. All of these reactions were carried out under thermal conditions and none under photochemical ones. The strategy to add alkyl radicals, generated from epoxides and $[Cp_2TiCl]_2$, to α,β-unsaturated carbenes was developed by Merlic[7] and was also used by Dötz to prepare carbohydrate-modified fused pyranosylidene complexes,[8] while Sierra used Et_3B in the presence of traces of oxygen to produce an ethyl radical that adds to the carbene complex.[9] The lack of examples is not surprising considering that carbenes often react with several types of reagents for radical generation or are incompatible with the reaction conditions to create such species.[10] Sierra also attempted to promote this kind of reaction by forming the radical through irradiation (tungsten lamp or sunlight) of Barton esters,[11] but this process resulted in recovery of unreacted or oxidized metal−carbene complex.[9] We report here the first successful results for the photochemically induced addition of an iminyl radical to unsaturated metal−carbene complexes.

Scheme 1. Iminyl Radical Addition to Alkynes



RESULTS AND DISCUSSIONS

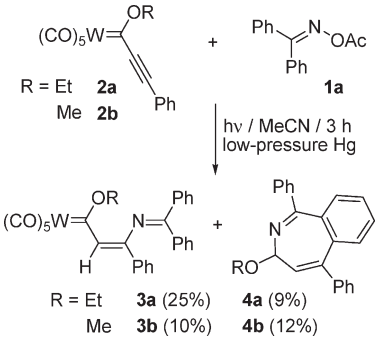
In our first attempt we reproduced the previous reaction conditions that successfully yielded isoquinolines. Irradiation of a solution of benzophenone *O*-acetyloxime (**1a**) and pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**2a**) was performed, at room temperature, with a 400 W medium-pressure mercury lamp through Pyrex under an Ar atmosphere. However, we found that the same reaction conditions were not appropriate in this case since only decomposition of the carbene complex occurred.

In our previous experiments, alkynes were used in excess to easily capture the forming radical and to improve the product yields. In this case, excess alkynyl carbene complex acts as an internal filter, preventing formation of the iminyl radical.[12] As we were unable to irradiate the oxime derivative selectively, we

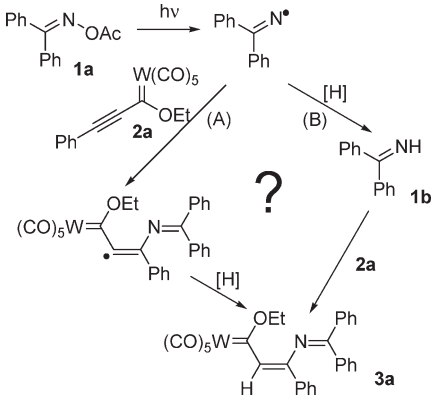
Received: May 24, 2011
Published: June 08, 2011

dx.doi.org/10.1021/om200438y | *Organometallics* 2011, 30, 3677–3682

Scheme 2. Iminyl Radical Addition to Alkynylcarbene Complexes



Scheme 3. Radical versus Nucleophilic Addition

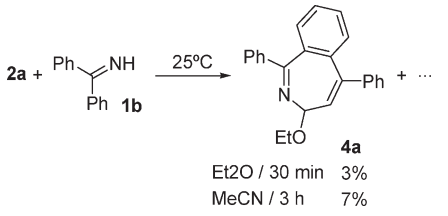


modified the reaction conditions by using a 1:1 reactant ratio and a low-pressure Hg lamp.[13] Under these conditions, irradiation in acetonitrile for 3 h led to the consumption of **1a** and **2a** and the formation of the new carbene complex **3a**, identified by spectroscopic data and comparison with similar complexes,[14,15] together with another product, identified as the seven-membered compound **4a** (Scheme 2).

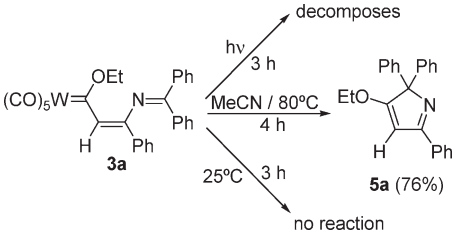
As we were limited by the relative absorption of the two reactants, the study of the effect of diverse reaction conditions on the reaction outcome was limited. In all cases low-pressure Hg lamps and a 1:1 ratio between reactants were used. Higher carbene complex ratios led to a decrease in the reaction yields, and higher acyloxime ratios contributed to an increase in the formation of **4a**. We also tried diverse oxime derivatives under our best reaction conditions in order to test the influence of the acyl moiety on the iminyl radical formation. The use of benzophenone *O*-benzoyl- or (*p*-methoxybenzoyl)oxime did not affect either of the results, the products or the yields, while the use of benzaldehyde *O*-acetyloxime as the iminyl radical precursor led only to decomposition of the starting materials. This is not surprising, as it is known[2,3] that iminyl radicals with α-hydrogen atoms are unstable and easily yield nitriles, and we could check that carbene **2a** decomposes under the direct action of UV light. However, the use of methoxy carbene **2b** gave **3b** and **4b** in 10% and 12% yields, respectively (Scheme 2).

To explore the photochemical nature of the reaction, we performed a test at room temperature in the dark. After 3 h of stirring only traces of **3a** were obtained, together with a large amount of unreacted starting compounds **1a** and **2a**, as

Scheme 4. Nucleophilic Addition of Imine 1b to Carbene Complex 2a



Scheme 5. Reactivity of Compound 3a



determined by the ^{1}H spectrum of the crude reaction mixture. This result demonstrates that the photochemical process is much faster than the thermal one and supports the fact that the reaction shown in Scheme 2 should be induced by the action of ultraviolet light. However, as shown in Scheme 3, once the radical is formed, it could evolve by direct radical addition to carbene **2a** (path A) or by hydrogen abstraction from the medium, followed by nucleophilic addition of benzophenone imine **1b** to **2a** (path B).

In contrast to the thermal reaction of imines with Fischer alkylcarbenes, which takes place with replacement of alkoxy by the imino group,[16] compounds with similar structures to carbene **3a** can also be obtained through nucleophilic addition of imines to alkynylcarbene complexes.[14] Moreover, complexes of type **3** cyclize to 2*H*-pyrroles upon heating at 50−55 °C in tetrahydrofuran solution. However, while the nucleophilic addition of imines to chromium complexes is well known, only one example has been described for the analogous process with a tungsten complex bearing a *tert*-butyl group.[14] Considering that the reaction with the phenyl derivative tungsten complex has not been described, we performed the reaction between carbene **2a** and benzophenone imine **1b**. After 30 min stirring in diethyl ether (de Meijere procedure)[14] or 3 h in acetonitrile we observed the formation of the seven-membered cycle **4a**, which could be isolated in 3% or 7% yield, respectively, together with a large amount of benzophenone and various unidentified products, but neither carbene nor starting carbene **2a** was detected in the crude reaction mixture (Scheme 4). These results rule out path B to explain the formation of carbene **3a** and, consistently, **3a** could be formed after initial addition of the iminyl radical to carbene **2a**.

On the other hand, **4a** could also be formed from **3a** either thermally or photochemically. As additional assays, isolated **3a** was irradiated in acetonitrile for 3 h, but this resulted in decomposition without the formation of **4a**, while stirring for 3 h did not alter starting material **3a**. However, heating complex **3a** in acetonitrile at 80 °C for 4 h led to 2*H*-pyrrole **5a** in 76% yield, a finding consistent with the literature,[14] but cycle **4a** was not detected (Scheme 5).

dx.doi.org/10.1021/om200438y |*Organometallics* 2011, 30, 3677–3682

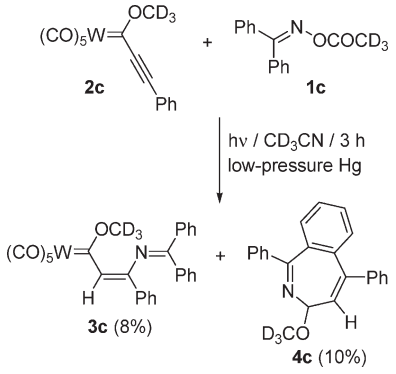
In any case, it can be stated that all of the assays provide indirect evidence for the radical addition to carbene **2**. In an effort to find direct evidence, we irradiated a mixture of **1a** and **2a** in the presence of radical trappers such as TEMPO and Ph_2Se_2, but the reaction yielded complex mixtures in which a carbene with a structure like **3** could not be detected, probably due to interaction of these trappers with the iminyl radical.

On the other hand, bearing in mind that a hydrogen atom could be abstracted from the medium, the reaction in a deuterated medium should give the analogous deuterated carbene. Irradiation of **1a** and **2a** was performed using tetrahydrofuran-d_8 or acetonitrile-d_3 as solvent, but **3a** was obtained once again rather than the corresponding deuterated compound. We continued by replacing the methyl group in the carbene and acyloxime by the trideuteromethyl one. As shown in Scheme 6, the photoreaction of **1c** and **2c** in acetonitrile-d_3 once again led to **3c** and **4c**.

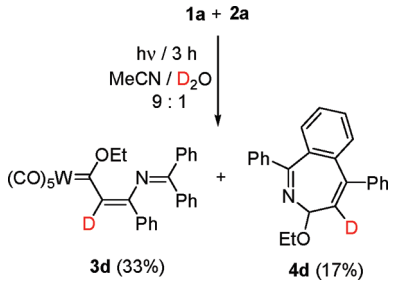
These results prompted us to consider that hydrogen incorporation into the structure could be a polar proccess, instead of a radical one, and traces of water present in the reaction medium should be enough to trap a proton.[17] Therefore, we performed the irradiation of **1a** and **2a** in acetonitrile but in the presence of deuterated water (9:1 ratio). This reaction gave compounds **3d** and **4d**, where a deuterium has been incorporated into both structures (Scheme 7).

Although a definitive reaction pathway cannot be established yet, tentative working proposals for the formation of **3** and **4** are

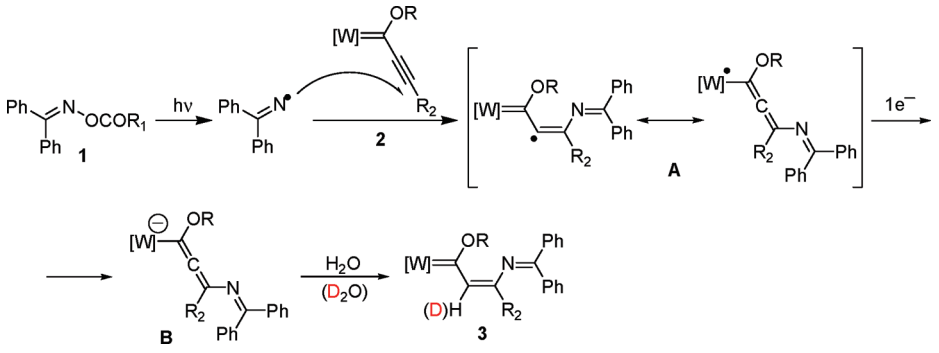
Scheme 6. Irradiation in a Deuterated Medium



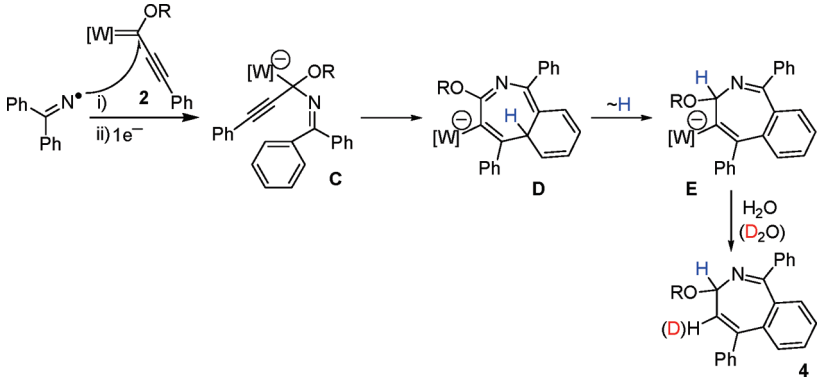
Scheme 7. Incorporation of a Deuterium Atom



Scheme 8. Proposed Mechanism for the Formation of Carbenes 3

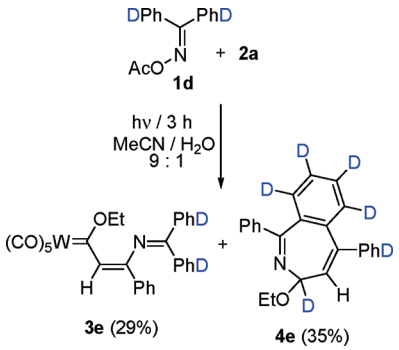


Scheme 9. Proposed Mechanism for the Formation of Azepines 4



dx.doi.org/10.1021/om200438y |*Organometallics* 2011, 30, 3677–3682

Scheme 10. Deuterium Migration



displayed in Schemes 8 and 9, respectively. First, as mentioned above, thermal reaction between acyloxime **1a** and carbene **2a** led to only traces of **3a** after 3 h of stirring. Moreover, carbene **3a** was not detected in the thermal reaction between imine **1b** and **2a** (Scheme 4). We therefore propose that irradiation of acyloxime **1** should generate the iminyl radical. This would attack carbene **2** at the alkynyl carbon (1,4-addition) to form intermediate **A**, which can be represented by two resonance structures (Scheme 8). A photoinduced electron transfer[18] could then occur to give carbene anion **B**, which is able to react with traces of H_2O or D_2O to yield **3**.

In relation to the seven-membered cycle, although the participation of the thermal reaction between imine **1b** (which should be generated by a hydrogen abstraction on the iminyl radical from the medium) and **2** cannot be ruled out (Scheme 4), heterocycles **4** were obtained in up to 17% yield. As a result, we suggest a similar mechanism to that proposed for carbenes **3**. The formation of azepine **4** is thought to occur by subsequent 1,2-addition of the iminyl radical to the carbene carbon of **2** and photoinduced electron transfer[18] to form the species **C** (Scheme 9). A 1,2-metal migration, promoted by the methoxy group, would cause simultaneous ring closure with one of the iminic phenyl groups to form intermediate **D**.[17,19] A subsequent hydrogen shift regenerates the aromaticity and **4** would form after hydrolysis or deuterolysis.

To test the effect of temperature on the addition product ratio, the irradiation was performed at −20 °C, but, unfortunately, there were no significant changes compared with the process at room temperature. Finally, the proposal for the formation of azepines **4** was supported by the use of the acyloxime of benzophenone-d_{10} **1d** as the starting material (Scheme 10). In this case azepine **4e** was formed in 35% yield after deuterium migration from **D** to **E**. The higher yield of **4e** could be rationalized considering that an inverse isotope effect at the position of deuteration is expected because of the change from sp^2 to sp^3 hybridization.[20]

CONCLUSION

In summary, it has been shown that a nitrogen-centered radical, generated photochemically, is able to participate in a 1,4-addition to alkynylcarbene complexes to give a 5-aza-1-metalla-1,3,5-hexatriene, while radical 1,2-addition leads to azepines.

EXPERIMENTAL SECTION

Representative Experimental Procedure. In a typical experiment 0.2 mmol of the carbene complex and 0.2 mmol of the acyloxime were dissolved in 10 mL of the appropriate solvent (commercial grade). The solution was deoxygenated by bubbling with Ar and either irradiated (cabinet photoreactor equipped with 16 low-pressure mercury lamps of 8 W) or stirred at room temperature for the time specified for each case. The solvent was removed in vacuo, and the products were purified by column chromatography (silica gel, hexane/AcOEt).

Benzophenone Trideuteroacetyloxime (1c) (ref 21). Yield: 213 mg, 88%. ^{1}H NMR: δ 7.47−7.16 (m, 10H) ppm. ^{13}C NMR: δ 168.4, 164.3, 134.4, 132.2, 130.6, 129.4, 128.7, 128.5, 128.3, 128.1, 18.7 (m, CD_3) ppm. UV: λ 210, 252 nm (ε = 9100, 16 250 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{15}H_{10}D_3NO_2$ + Na): calcd 265.1025, measd 265.1027.

Bis(perdeuterophenyl)methanone acetyloxime (1d) (ref 21). Yield: 239 mg, 96%. ^{1}H NMR: δ 2.07 (s, 3H) ppm. ^{13}C NMR: δ 168.5, 164.3, 134.4, 132.1, 130.5−127.2 (m, CD), 19.4 ppm. UV: λ 212, 252 nm (ε = 9120, 16 330 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{15}H_3D_{10}NO_2$ + Na): calcd 272.1447, measd 272.1466.

Pentacarbonyl(1-trideuteromethoxy-3-phenyl-2-propynylidene)tungsten(0) (2c) (ref 22). Yield: 452 mg, 16%. ^{1}H NMR: δ 7.65−7.25 (m, 5H) ppm. ^{13}C NMR: δ 283.9 (C-1), 205.6, 197.4 (C═O), 132.9, 131.7, 129.0, 121.0 ppm. C-2, C-3, and CD_3 not observed. UV: λ 245, 290, 314, 357, 465 nm (ε = 32 450, 13 180, 9250, 3150, 12 590 M^{-1} cm^{-1}). Exact mass MALDI(−) ($C_{15}H_5D_3O_6W$): calcd 471.001, measd 471.184.

Pentacarbonyl{(2*Z*)-3-[(diphenylmethylene)amino]-1-ethoxy-3-phenyl-2-propenylidene}tungsten(0) (3a). Yield: 33 mg, 25%. ^{1}H NMR: δ 7.64−7.30 (m, 15H), 7.18 (s, 1H, H-2), 4.66 (q, 2H, J = 6.0 Hz), 1.26 (t, 3H, J = 6.0 Hz) ppm. ^{13}C NMR: δ 296.4 (C-1), 204.1, 198.2 (C═O), 164.2 (C═N), 150.0, 137.6, 136.3, 130.7, 130.6, 128.8, 128.5, 128.3, 127.9, 127.6, 125.8 (C-2), 78.8, 15.2 ppm. IR: ν 2059, 1980, 1928 (W−CO), 1662 (C═C), 1604 (C═N), 1219 (C−O) cm^{-1}. UV: λ 246, 289, 350, 451 nm (ε = 32 910, 9880, 5430, 10 210 M^{-1} cm^{-1}). Exact mass MALDI(−) ($C_{29}H_{21}NO_6W$): calcd 663.088, measd 663.085.

Pentacarbonyl{(2*Z*)-3-[(diphenylmethylene)amino]-1-methoxy-3-phenyl-2-propenylidene}tungsten(0) (3b). Yield: 13 mg, 10%. ^{1}H NMR: δ 7.47−7.26 (m, 15H), 7.12 (s, 1H, H-2), 4.34 (s, 3H) ppm. ^{13}C NMR: δ 296.5 (C-1), 204.0, 198.1 (C═O), 164.8 (C═N), 150.3, 137.8, 136.3, 130.7, 128.8, 128.7, 128.6, 128.3, 127.7, 124.5 (C-2), 68.9 ppm. Exact mass MALDI(−) ($C_{28}H_{19}NO_6W$): calcd 649.072, measd 649.013.

Pentacarbonyl{(2*Z*)-3-[(diphenylmethylene)amino]-1-trideuteromethoxy-3-phenyl-2-propenylidene}tungsten(0) (3c). Yield: 11 mg, 8%. ^{1}H NMR: δ 7.47−7.28 (m, 15H), 7.12 (s, 1H, H-2) ppm. ^{13}C NMR: δ 296.5 (C-1), 204.0, 198.1 (C═O), 164.8 (C═N), 150.3, 137.8, 136.3, 130.7, 128.8, 128.7, 128.6, 128.3, 127.7, 124.5 (C-2) ppm. CD_3 not observed. Exact mass MALDI(−) ($C_{28}H_{16}D_3NO_6W$): calcd 652.090, measd 652.014.

Pentacarbonyl{(2*Z*)-2-deutero-3-[(diphenylmethylene)-amino]-1-ethoxy-3-phenyl-2-propenylidene}tungsten(0) (3d). Yield: 44 mg, 33%. ^{1}H NMR: δ 7.55−7.25 (m, 15H), 4.65 (q, 2H, J = 7.2 Hz), 1.33 (t, 3H, J = 7.2 Hz) ppm. ^{13}C NMR: δ 296.2 (C-1), 204.1, 198.3 (C═O), 164.2 (C═N), 150.0, 137.5, 136.3, 130.7, 128.8, 128.5, 128.3, 127.9, 127.6, 126.5 (t, DC-2, J = 7 Hz), 78.7, 15.2 ppm. Exact mass MALDI(−) ($C_{29}H_{20}DNO_6W$): calcd 664.094, measd 664.031.

Pentacarbonyl{(2*Z*)-3-[(diperdeuterophenylmethylene)-amino]-1-ethoxy-3-phenyl-2-propenylidene}tungsten(0) (3e). Yield: 39 mg, 29%. ^{1}H NMR: δ 7.55 (d, 2H, J = 6.0 Hz), 7.40−7.27 (m, 3H), 7.18 (s, 1H, H-2), 4.66 (q, 2H, J = 6.0 Hz), 1.26 (t, 3H, J = 6.0 Hz) ppm. ^{13}C NMR: δ 296.3 (C-1), 204.1, 198.2 (C═O), 164.2 (C═N), 149.9, 137.5, 136.0, 130.5, 129.0, 128.8, 128.5, 128.3, 127.9, 125.8 (C-2), 78.7, 15.1 ppm. Exact mass MALDI(−) ($C_{29}H_{11}D_{10}NO_6W$): calcd 673.148, measd 673.171.

(1*Z*,4*Z*)-3-Ethoxy-1,5-diphenyl-3*H*-benzo[*c*]azepine (4a). Yield: 6 mg, 9%. ^{1}H NMR: δ 7.59−7.30 (m, 14H), 6.44 (d, 1H, J = 4.5 Hz), 4.43 (d, 1H, J = 4.5 Hz), 4.15−4.07 (m, 1H), 3.60−3.50 (m,

1H), 1.38 (t, 3H, J = 7.5 Hz) ppm. ^{13}C NMR: δ 163.5 (C═N), 140.5, 140.4, 140.2, 139.0, 136.9, 133.4 (═CH), 129.8, 129.7, 129.3, 129.0, 128.9, 128.3, 128.0, 127.8, 127.7, 126.1, 88.8, 63.1, 15.3 ppm. IR: ν 1667 (C═C), 1604 (C═N), 1196 (C−O) cm^{-1}. Exact mass ESI(+) ($C_{24}H_{21}NO$ + H): calcd 340.1701, measd 340.1689.

(1*Z*,4*Z*)-3-Methoxy-1,5-diphenyl-3*H*-benzo[*c*]azepine (4b). Yield: 8 mg, 12%. ^{1}H NMR: δ 7.62−7.26 (m, 14H), 6.41 (d, 1H, J = 4.5 Hz), 4.33 (d, 1H, J = 4.5 Hz), 3.61 (s, 3H) ppm. ^{13}C NMR: δ 163.6 (C═N), 140.4, 140.4, 140.1, 139.2, 136.8, 133.0 (═CH), 130.1, 129.9, 129.8, 129.3, 129.0, 128.9, 128.6, 128.3, 128.0, 127.8, 126.1, 90.0, 55.2 ppm. Exact mass ESI(+) ($C_{23}H_{19}NO$ + H): calcd 326.1545, measd 326.1540.

(1*Z*,4*Z*)-3-Trideuteromethoxy-1,5-diphenyl-3*H*-benzo[*c*]-azepine (4c). Yield: 7 mg, 10%. ^{1}H NMR: δ 7.62−7.24 (m, 14H), 6.41 (d, 1H, J = 4.5 Hz), 4.33 (d, 1H, J = 4.5 Hz) ppm. ^{13}C NMR: δ 163.4 (C═N), 140.2, 140.1, 139.8, 138.8, 136.6, 132.8 (═CH), 130.1, 129.9, 129.7, 129.3, 129.0, 128.9, 128.6, 128.3, 128.0, 127.7, 125.8, 89.6 ppm. CD_3 not observed. Exact mass ESI(+) ($C_{23}H_{16}D_3NO$ + H): calcd 329.1726, measd 329.1731.

(1*Z*,4*Z*)-4-Deutero-3-ethoxy-1,5-diphenyl-3*H*-benzo[*c*]azepine (4d). Yield: 12 mg, 17%. ^{1}H NMR: δ 7.61−7.30 (m, 14H), 4.43 (s, 1H), 4.17−4.08 (m, 1H), 3.59−3.53 (m, 1H), 1.37 (t, 3H, J = 7.5 Hz) ppm. ^{13}C NMR: δ 163.5 (C═N), 140.4, 140.4, 140.1, 138.9, 136.9, 133.0 (t, ═CD, J = 20 Hz), 129.8, 129.7, 129.3, 129.0, 128.9, 128.3, 128.0, 127.8, 126.2, 88.8, 63.1, 15.3 ppm. Exact mass ESI(+) ($C_{24}H_{20}DNO$ + H): calcd 341.1762, measd 341.1759.

(1*Z*,4*Z*)-3,6,7,8,9-Pentadeutero-3-ethoxy-5-(perdeuterophenyl)-1-phenyl-3*H*-benzo[*c*]azepine (4e). Yield: 24 mg, 35%. ^{1}H NMR: δ 7.35−7.26 (m, 5H), 6.44 (s, 1H), 4.15−4.08 (m, 1H), 3.58−3.51 (m, 1H), 1.38 (t, 3H, J = 7.5 Hz) ppm. ^{13}C NMR: δ 163.5 (C═N), 140.5, 140.3, 139.9, 139.0, 136.8, 133.2 (═CH), 128.9, 128.3, 127.8, 88.4 (t, CD, J = 21 Hz), 63.0, 15.2 ppm. Exact mass ESI(+) ($C_{24}H_{11}D_{10}NO$ + H): calcd 350.2305, measd 350.2324.

AUTHOR INFORMATION

Corresponding Author

*E-mail: miguelangel.rodriguez@unirioja.es.

ACKNOWLEDGMENT

This work was partially supported by the Spanish MEC (CTQ2007-64197). M.B.-L., A.C., and H.F.G. thank the Spanish MEC, CSIC, and CAR, respectively, for their fellowships.

DEDICATION

†This article is dedicated to Prof. J. Barluenga on the occasion of his 70th birthday.

REFERENCES

(1) Selected reviews on the chemistry of radicals: Perchyonok, T. V. In *Radical Reactions in Aqueous Media*; The Royal Society of Chemistry: Cambridge, U.K., 2010. Togo, H. In *Advanced Free Radical Reactions for Organic Synthesis*; Elsevier: Oxford, U.K., 2004. Zard, S. Z. In *Radical Reactions in Organic Synthesis*; Oxford University Press: Oxford, U.K., 2003. Tumanskii, B.; Kalina, O. In *Radical Reactions of Fullerenes and their Derivatives*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001. *Radicals in Organic Synthesis*; Renaud, P.; Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001. Curran, D. P.; Porter, N. A.; Giese, B. In *Stereochemistry of Radical Reactions*; VCH: Weinheim, Germany, 1996.

(2) (a) Alonso, R.; Campos, P. J.; García, B.; Rodríguez, M. A. *Org. Lett.* **2006**, *8*, 3521. (b) Alonso, R.; Caballero, A.; Campos, P. J.; Rodríguez, M. A. *Tetrahedron* **2010**, *66*, 8828.

(3) Alonso, R.; Campos, P. J.; Rodríguez, M. A.; Sampedro, D. *J. Org. Chem.* **2008**, *73*, 2234.

(4) Portela-Cubillo, F.; Alonso-Ruiz, R.; Sampedro, D.; Walton, J. C. *J. Phys. Chem. A* **2009**, *113*, 10005.

(5) Campos, P. J.; Sampedro, D.; Rodríguez, M. A. *Organometallics* **2000**, *19*, 3082. Campos, P. J.; Sampedro, D.; Rodríguez, M. A. *Tetrahedron Lett.* **2002**, *43*, 73. Campos, P. J.; Sampedro, D.; Rodríguez, M. A. *Organometallics* **2002**, *21*, 4076. Campos, P. J.; Sampedro, D.; Rodríguez, M. A. *J. Org. Chem.* **2003**, *68*, 4674. Sampedro, D.; Caro, M.; Rodríguez, M. A.; Campos, P. J. *J. Org. Chem.* **2005**, *70*, 6705. Campos, P. J.; Caro, M.; López-Sola, S.; Sampedro, D.; Rodríguez, M. A. *J. Organomet. Chem.* **2006**, *691*, 1075.

(6) Selected reviews on the chemistry of Fischer carbene complexes: Dötz, K. H.; Stendel, J., Jr. *Chem. Rev.* **2009**, *109*, 3227. Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539. Gómez-Gallego, M.; Mancheño, M. J.; Sierra, M. A. *Acc. Chem. Res.* **2005**, *38*, 44. Barluenga, J.; Santamaría, J.; Tomás, M. *Chem. Rev.* **2004**, *104*, 2259. Herndon, J. W. *Coord. Chem. Rev.* **2004**, *248*, 3. Barluenga, J.; Flórez, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1. Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. de Meijere, A.; Schirmer, H.; Duestsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964.Books: Metal Carbenes in Organic Synthesis. in *Topics in Organometallic Chemistry*; Dötz, K. H., Ed.; Wiley: New York, 2004; Vol. 13. *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*; Bertrand, G., Ed.; Marcel Dekker: New York, 2002.

(7) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 9855. Merlic, C. A.; Xu, D.; Nguyen, M. C.; Truong, V. *Tetrahedron Lett.* **1993**, *34*, 227.

(8) Dötz, K. H.; Gomes da Silva, E. *Tetrahedron* **2000**, *56*, 8291.

(9) Mancheño, M. J.; Ramírez-López, P.; Gómez-Gallego, M.; Sierra, M. A. *Organometallics* **2002**, *21*, 989.

(10) Examples: Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995**, *36*, 1011. Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995**, *36*, 1007. Mak, C. C.; Tse, M. K.; Chan, K. S. *J. Org. Chem.* **1994**, *59*, 3585. Mak, C. C.; Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2143.

(11) Barton, D. H. R.; Crich, D.; Kretzschmar, G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 39. Barton, D. H. R. *Tetrahedron* **1992**, *48*, 2529.

(12) Carbene complex **2a** strongly absorbs at 252 nm (ε = 32 700), the wavelength of maximum absorption for the benzophenone acetyloxime **1a** (ε = 16 300).

(13) The low-pressure Hg lamp has an emission maximum at 254 nm.

(14) Funke, F.; Duetsch, M.; Stein, F.; Noltemeyer, M.; de Meijere, A. *Chem. Ber.* **1994**, *127*, 911.

(15) Aumann, R.; Jasper, B.; Laege, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502.

(16) Knauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744.

(17) Some metalated zwitterionic intermediates incorporate a hydrogen (deuterium) atom in the presence of water (D_2O). See: Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695. Barluenga, J. *Pure Appl. Chem.* **1999**, *71*, 1385. Barluenga, J.; Rodríguez, F.; Fañanás, F. J.; Flórez, J. *Top. Organomet. Chem.* **2004**, *13*, 59. Barluenga, J.; Martínez, S. *ARKIVOC* **2006**, 129.

(18) The photoinduced electron transfer from imine derivatives is well documented. See, for instance: Liu, H.; Li, B.; Liu, D.; Xu, Z. *Chem. Phys. Lett.* **2001**, *350*, 441. Kumar, A.; Ali, A.; Rao, C. P. *J. Photochem. Photobiol. A: Chem.* **2006**, *177*, 164.

(19) This metal migration has been invoked by Barluenga to rationalize the formation of azepines, from 1-azadienes and alkynyl carbenes of chromium, and seven-membered carbocycles. See: Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; Carbajo, R. J.; López-Ortiz, F.; García-Granda, S.; Pertierra, P. *Chem.—Eur. J.* **1996**, *2*, 88. Barluenga, J.; García-García, P.; Fernández-Rodríguez, M. A.; Aguilar, E.; Merino, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 5875.

(20) See, for example: Mitchell, K. H.; Rogge, C. E.; Gierahn, T.; Fox, B. G. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 3784.

(21) Obtained from 1 mmol of oxime and 1.3 mmol of the corresponding acetyl chloride. See ref 2b.

(22) Obtained from 6 mmol of tungsten hexacarbonyl, using $CF_3SO_3CD_3$ as electrophile: Vázquez, M. A.; Reyes, L.; Miranda, R.; García, J. J.; Jiménez-Vázquez, H. A.; Tamariz, J.; Delgado, F. *Organometallics* **2005**, *24*, 3413.