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Microwave-Assisted Reactivity of a Fischer Alkynyl Carbene Complex with Benzylidene Anilines

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This article is dedicated to Professor Joaquin Tamariz as a tribute for his 40 years as a Mexican researcher.

Abstract. The reaction between the Fischer carbene complex $(CO)_5Cr{=}C(OEt)C{\equiv}CPh$ and various benzylidene anilines $RCH{=}NR^1$ was promoted by microwave irradiation, generating stable cross-conjugated metallahexatrienes in 45-70 % yield. Compared to conventional heating, the present conditions provided shorter reaction times with moderate yields. The geometrical configuration and the most stable conformation for each of the Fischer carbene complexes and their oxidation products were established by NMR and DFT analysis. The reaction mechanism was explored by DFT calculations of the potential energy surface, suggesting a 1,4-addition/ring closure/electrocyclic opening cascade process.
Keywords: Fischer carbene complexes; benzylidene anilines; microwave irradiation; DFT analysis; electronic effect.

Resumen. Se reporta la reactividad entre el carbeno de Fischer $(CO)_5Cr{=}C(OEt)C{\equiv}CPh$ y las bencilidén anilinas, $RCH{=}NR^1$, empleando irradiación de microondas. Los resultados indican que el calentamiento por microondas generó metalohexatrienos cruzados estables en rendimientos de 45-70 %, mostrando además, que los nuevos complejos se obtienen en tiempos de reacción más cortos y rendimientos moderados en comparación con las condiciones de calentamiento convencional. La configuración geométrica y la conformación más estable para los complejos carbénicos de Fischer y de sus derivados oxidados fueron establecidos por medio de RMN y DFT. La exploración de la superficie de energía potencial por cálculos DFT mostró que el proceso consistió en una reacción en cascada incluyendo una secuencia de adición-1,4, cierre de anillo y apertura electrocíclica.
Palabras clave: Complejos carbénicos de Fischer; bencilidén anilinas; irradiación de microondas; análisis DFT; efecto electrónico.

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Introduction

Transition metal Fischer carbene complexes undergo cycloaddition reactions with a variety of substrates, and the growing body of research on their use is creating a broad new field in chemistry [1-8]. Even the simplest carbene complexes have exhibited great versatility[9]. The scope of the reaction increases in the event of the formation of an unsaturated system and is controlled by the type of substituents[10-14]. As a result, these organometallic complexes are capable of reacting with imines and many other molecules. Imines are important building blocks because they can contain not only nucleophilic or electrophilic sites but also a combination of the two, thus allowing for different reaction pathways in some cases[15-17]. Usually, this reactivity favours the synthesis of cyclic compounds in a few steps[15,16,18-23].

The reactivity of imines and carbene complexes has been reported by various authors. Imines were reacted with simple Fischer-type carbenes by Hegedus via thermal and photochemical routes, leading to new carbenic complexes and lactam nuclei, respectively [23]. On the other hand, de Meijere found that chromium alkynyl carbene complexes react with imines to produce the Michael adduct, which undergoes cyclization in thermal conditions to generate 2*H*-pyrroles (Scheme 1**(a)**) [24]. Meanwhile, Aumman [15] obtained Michael adducts and mesoionic pyrrolium carbonyltungstates by the reaction of imines with alkynyl chromium(0) carbene complexes (Scheme 1**(b)**). Subsequently, Sampedro´s group [16,25] conducted a complete computational mechanistic study of the same reaction to afford potential molecular switches and motors. In a later publication, this group documented the reaction of oxime derivatives and alkynyl Fischer carbene complexes to furnish four distinct types of nitrogenated heterocycles [26,27] (Scheme 1**(c)** and **(e)**). Yu achieved [28] the regioselective [3+2] annulation of azomethine imines with 1-alkynyl Fischer carbene complexes to synthesize versatile functionalized *N*,*N*-bicyclic pyrazolidin-3-ones (Scheme 1**(d)**). Along the same lines, our group has described the reaction of alkynyl Fischer carbene complexes with *α*-imino glycine methyl esters to provide 1,2,3,5-tetrasubstituted pyrroles (Scheme 1**(f)**) [11].

A search of the literature revealed few reports on energy sources other than conventional heating to test the reactivity of Fischer-type carbenes, except for the extensive investigation on the photochemistry of these complexes[29-33]. In 2002, Magennis *et al.* [34] established an advantage for a Dötz reaction when assisted by microwave energy versus the traditional thermal heating method. This reaction was also carried out by utilizing resin-bound Fischer carbenes subjected to microwave irradiation, followed by an oxidative reaction to generate 1,4-naphthoquinones [35]. Uracil-containing Fischer carbenes [36,37] and 1,3-dienol esters [38] have been prepared with microwave irradiation as well.

Therefore, investigating the behavior of Fischer carbenes in chemical reactions promoted by microwave energy is a relevant approach. In the methodologies developed by our group for the reaction of alkynyl and vinyl(alkoxy)carbene complexes under thermal conditions, substituents proved to play an important role in reactivity and selectivity during the synthesis of a variety of compounds, such as *ortho*- and *para*-quinones [39], phenols [12,40,41], furans, pyran-2-ones [42], 4-amino-1-azadienes [14], and pyrroles. The aim of the current contribution was to explore the reactivity of alkynyl(ethoxy)carbene complex **1** with benzylidene anilines **2a-p** under microwave irradiation.

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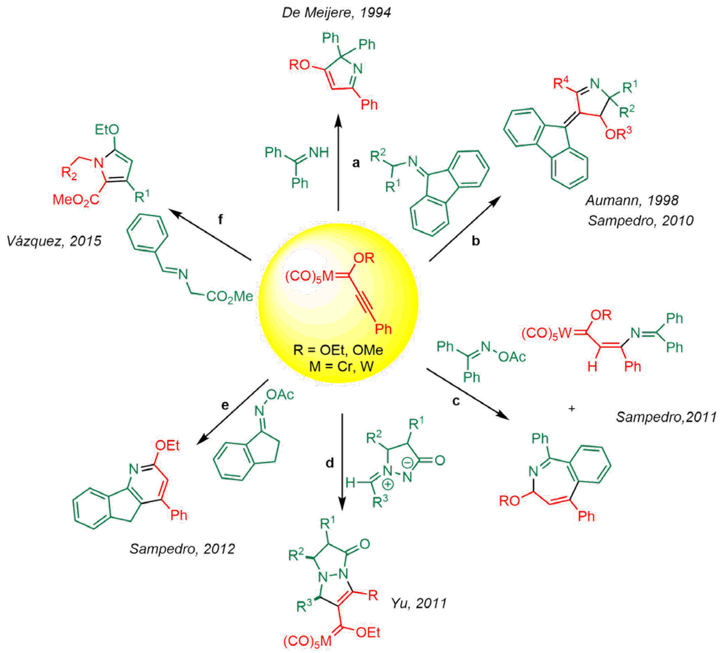

Scheme 1. Synthesis of a variety of heterocyclic compounds with alkynyl(alkoxy)carbene complexes.

Experimental

Chemistry

All solvents and reagents were purchased from Sigma-Aldrich and used without further purification. The products were purified by column chromatography with silica gel (MN Kieselgel 60, 230-400 mesh), employing ethyl acetate and *n*-hexane as eluents in different proportions. To identify the compounds, the mixture was submitted to thin-layer chromatography (TLC, utilizing aluminum sheets and silica gel 60 F/UV$_{254}$) visualized with UV light. Melting points were measured on a digital Electrothermal 90100 melting point apparatus. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ascend 500 MHz or a Bruker Ultrashield 600 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent. Chemical shifts are expressed in ppm, relative to tetramethylsilane as the internal reference. Infrared (IR) spectra were captured on potassium bromide plates with a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. Spectra from high-resolution mass spectrometry (HRMS) were acquired by carrying out electrospray ionization on a Bruker micrOTOF-Q II device, electron nebulization ionization on a Bruker QTOF mass spectrometer, and electron ionization techniques (70 eV) on a Jeol JSM-GC Mate II. X-ray data were collected on an Oxford Diffraction Gemini ‘A’ diffractometer with a CCD area detector. Microwave irradiation was performed in a Discover SP CEM microwave apparatus. The alkynyl(ethoxy)carbene complex of chromium **1** and the benzylidene anilines **2a-p** were prepared by the reported methods [43].

General method

Alkynyl(ethoxy)carbene complex **1** and one of the benzylidene anilines **2a-p** (1.5:1 mol equiv) were added to a reaction vessel containing anhydrous tetrahydrofuran (THF) (5 mL) under nitrogen atmosphere. Subsequently, the mixture was heated at 66 ºC with microwave irradiation (150 W) for 5 h. The reaction was monitored by TLC until completion. Purification of the crude mixtures by column chromatography over silica gel (*n*-hexane/EtOAc, 99:1) gave the corresponding products **3a-n**. Compounds **5** and **6** were identified by NMR, and the results were compared to information in the literature [14,44,45].

Pentacarbonyl-(*Z*)-2-phenyl-2-{[(*E*)-(phenyl)(phenylimino)methyl]} (ethoxy)carbene chromium(0) (3a). According to the general method, the reaction between **1** (0.30 g, 0.85 mmol) and imine **2a** (0.10 g, 0.57 mmol) provided **3a** (0.18 g, 60 %) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2061, 1988, 1936, 1712, 1593 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.74 (t, *J* = 6.6 Hz, 3H, H-18), 4.68 (bs, 1H, H-17), 4.86 (bs, 1H, H-17), 6.28 (s, 1H, H-3), 6.62 (d, *J* = 7.8 Hz, 2H, H-6), 6.87-6.92 (m, 1H, H-8), 7.06-7.11 (m, 2H, H-7), 7.14-7.17 (m, 2H, H-14), 7.22-7.26 (m, 2H, H-10), 7.30-7.38 (m, 6H, H-11, H-12, H-15, H-16). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 75.5 (C-17), 120.9 (C-6), 123.8 (C-8), 128.3 (C-11), 128.3 (C-7), 128.7 (C-15), 129.0 (C-9), 129.2 (C-10), 129.5 (C-16), 130.2 (C-12, C-14), 130.3 (C-3), 134.1 (C-13), 149.5 (C-2), 149.7 (C-5) 166.0 (C-4), 216.6 (CO*cis*), 224.3 (CO*trans*), 353.4 (Cr = C*carb*). HRMS (EI) calcd for $C_{29}H_{21}NO_6Cr$ $[M]^+$ 531.0774, found 531.0766.

Pentacarbonyl-(*Z*)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl)methyl]-3-phenyl}(ethoxy)carbene chromium(0) (3b). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2b** (0.12 g, 0.571 mmol) delivered **3b** (0.20 g, 65 %) as a red solid (mp 92-94 °C). FT-IR (CH_2Cl_2) ν_{max} 2061, 1988, 1932, 1605, 1566 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.72 (t, *J* = 7.2 Hz, 3H, H-18), 3.70 (s, 3H, OMe) 4.65 (bs, 1H, H-17), 4.82 (bs, 1H, H-17), 6.22 (s, 1H, H-3), 6.60 (d, *J* = 9.0 Hz, 2H, H-7), 6.64 (d, *J* = 9.0 Hz, 2H, H-6), 7.15 (d, *J* = 6.6 Hz, 2H, H-14), 7.24-7.29 (m, 2H, H-10), 7.30-7.35 (m, 3H, H-15, H-16), 7.36-7.41 (m, 3H, H-11, H-12). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 55.3 (OMe), 75.5 (C-17), 113.6 (C-6), 123.2 (C-7), 128.5 (C-11), 128.7 (C-12, C-15), 129.0 (C-16), 129.2 (C-3), 129.3 (C-10), 130.1 (C-14), 133.7 (C-13), 134.6 (C-9), 142.5 (C-5), 150.0 (C-2), 156.6 (C-8), 164.6 (C-4) 216.6 (CO*cis*), 224.4 (CO*trans*), 353.5 (Cr = C*carb*). HRMS (EI) calcd for $C_{30}H_{23}CrNO_7$ $[M]^+$ 561.0880, found 561.0873.

Pentacarbonyl-(*Z*)-2-{[(*E*)-(4-chlorophenylimino)(phenyl)methyl]-3-phenyl}(ethoxy)carbene chromium(0) (3c). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2c** (0.12 g, 0.571 mmol) afforded **3c** (0.14 g, 45 %) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2061, 1989, 1933, 1583, 1567 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.73 (t, *J* = 7.2 Hz, 3H, H-18), 4.66 (bs, 1H, H-17), 4.81 (bs, 1H, H-17), 6.29 (s, 1H, H-3), 6.55 (d, *J* = 8.4 Hz, 2H, H-6), 7.05 (d, *J* = 8.4 Hz, 2H, H-7), 7.14-7.19 (m, 2H, H-14), 7.21-7.26 (m, 2H, H-10), 7.30-7.39 (m, 6H, H-11, H-12, H-15, H-16). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 75.5 (C-17), 122.3 (C-6), 128.5 (C-11), 128.5 (C-7), 128.7 (C-15), 129.1 (C-10), 129.2 (C-12), 129.7 (C-16), 130.2 (C-14), 130.7 (C-3), 133.4 (C-13), 133.8 (C-9), 148.2 (C-5), 149.2 (C-2), 166.6 (C-8), 166.6 (C-4), 216.6 (CO*cis*), 224.1 (CO*trans*), 353.2 (Cr = C*carb*). HRMS (EI) calcd for $C_{29}H_{20}ClCrNO_6$ $[M]^+$ 565.0384, found 565.0377.

Pentacarbonyl-(*Z*)-3-(fluorophenyl)-2-{[(*E*)-(phenylimino)(phenyl)methy]} (ethoxy)carbene chromium(0) (3d). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2d** (0.113 g, 0.571 mmol) furnished **3d** (0.20 g, 66 %) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2061, 1988, 1940, 1704, 1599 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.73 (t, *J* = 7.0 Hz, 3H, H-18), 4.65 (bs, 1H, H-17), 4.86 (bs, 1H, H-17), 6.24 (s, 1H, H-3), 6.62 (d, *J* = 8.5 Hz, 2H, H-6), 6.87-6.92 (m, 1H, H-8), 7.00-7.05 (m, 2H, H-15), 7.06-7.11 (m, 2H, H-7), 7.12-7.16 (m, 2H, H-14) 7.21- 7.25 (m, 2H, H-10), 7.30-7.35 (m, 3H, H-11, H-12). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 75.6 (C-17), 115.9 (C-15, *J* = 25.8 Hz), 120.8 (C-6), 123.8 (C-8), 128.2 (C-7), 128.3 (C-11), 128.7 (C-13, *J* = 1.2 Hz) 128.8 (C-3), 129.0 (C-12), 129.1 (C-10), 132.0 (C-14, *J* = 10.0 Hz), 134.0 (C-9), 149.4 (C-2), 149.6 (C-5), 164.3 (C-16, *J* = 300.7 Hz), 165.9 (C-4), 216.5 (CO*cis*), 224.0 (CO*trans*), 353.3 (Cr = C*carb*). HRMS (EI) calcd for $C_{29}H_{20}FNO_6Cr$ $[M]^+$ 549.0680, found 549.0686.

Pentacarbonyl-(*Z*)-3-(4-chlorophenyl)-2-{[(*E*)-(phenyl)-(phenylimino)methyl}](ethoxy)carbene chromium(0) (3e). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2e** (0.12g, 0.571 mmol) produced **3e** (0.17 g, 53 %) as a red solid (mp 101-103 °C). FT-IR (CH_2Cl_2) ν_{max} 2061, 1989, 1940, 1716, 1582 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.73 (t, *J* = 7.2 Hz, 3H, H-18), 4.64 (bs, 1H, H-17), 4.85 (bs, 1H, H-17), 6.21 (s, 1H, H-3), 6.61 (d, *J* = 7.8 Hz, 2H, H-6), 6.88-6.93 (m, 1H, H-8), 7.07-7.12 (m, 4H, H-7, H-14), 7.21-7.25 (m, 2H, H-10), 7.30-7.37 (m, 5H, H-11, H-12, H-15). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.8 (C-18), 75.6 (C-17), 120.9 (C-6), 124.0 (C-8), 127.7 (C-12), 128.3 (C-7), 128.5 (C-3), 129.0 (C-11), 129.1 (C-10), 131.2 (C-15), 131.2 (C-15), 132.1 (C-13), 133.9 (C-9), 135.7 (C-16), 149.6 (C-5), 165.9 (C-

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2), 167.4 (C-4), 216.4 (CO*cis*), 224.0 (CO*trans*), 352.9 (Cr = C*carb*). HRMS (EI) calcd for $C_{29}H_{20}ClNO_6Cr$ $[M]^+$ 565.0384, found 565.0370.

Pentacarbonyl-(*Z*)-3-(4-methoxyphenyl)-2-{[(*E*)-(phenyl)(phenylimino)methyl]}(ethoxy)carbene chromium(0) (3f). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2f** (0.12 g, 0.571 mmol) provided **3f** (0.20 g, 64 %) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2060, 1938, 1601 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.72 (t, *J* = 6.6 Hz, 3H, H-18), 3.81 (s, 3H, OMe) 4.64 (bs, 1H, H-17), 4.84 (bs, 1H, H-17), 6.22 (s, 1H, H-3), 6.61 (d, *J* = 7.2 Hz, 2H, H-6), 6.82-6.93 (m, 3H, H-8, H-14), 7.05-7.13 (m, 4H, H-7, H-15), 7.20-7.25 (m, 2H, H-10), 7.28-7.34 (m, 3H, H-11, H-12). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 55.3 (OMe), 75.3 (C-17), 114.2 (C-14), 120.9 (C-6), 123.6 (C-8), 126.3 (C-13), 128.2 (C-11), 128.3 (C-7), 128.9 (C-12), 129.2 (C-10), 129.9 (C-3), 131.9 (C-15), 134.2 (C-9), 147.7 (C-2), 149.9 (C-5), 160.8 (C-16), 165.9 (C-4), 216 (CO*cis*), 224.4 (CO*trans*), 354.4 (Cr = C*carb*). HRMS (EI) calcd for $C_{30}H_{23}CrNO_7$ $[M]^+$ 561.0880, found 561.0883.

Pentacarbonyl-(*Z*)-3-(4-methylphenyl)-2-{[(*E*)-(phenyl)(phenylimino)methyl]}(ethoxy)carbene chromium(0) (3g). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2g** (0.11 g, 0.571 mmol) generated **3g** (0.16 g, 52 %) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2060, 1986, 1939, 1715, 1605 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.72 (t, *J* = 7.2 Hz, 3H, H-18), 2.34 (s, 3H, Me), 4.65 (bs, 1H, H-17), 4.84 (bs, 1H, H-17), 6.24 (s, 1H, H-3), 6.61 (d, *J* = 7.8 Hz, 2H, H-6), 6.86-6.92 (m, 1H, H-8), 7.02-7.11 (m, 4H, H-7, H-14), 7.15 (d, *J* = 7.8 Hz, 2H, H-15), 7.22-7.26 (m, 2H, H-10) 7.29- 7.35 (m, 3H, H-11, H-12), ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 21.3 (Me), 75.4 (C-17), 120.9 (C-6), 123.7 (C-8), 128.2 (C-11), 128.3 (C-7), 128.9 (C-12), 129.2 (C-10), 129.5 (C-15), 130.2 (C-3), 130.3 (C-14) 130.8 (C-13), 134.2 (C-9), 140.0 (C-16), 148.7 (C-2), 149.8 (C-5), 165.9 (C-4), 216.7 (CO*cis*), 224.4 (CO*trans*), 353.9 (Cr = C*carb*). HRMS (EI) calcd for $C_{30}H_{23}CrNO_6$ $[M]^+$ 545.0930, found 545.0925.

Pentacarbonyl-(*Z*)-3-(furan-2-yl)-2-{[(*E*)-(phenyl)(phenylimino)methyl]}(ethoxy)carbene chromium(0) (3h). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2h** (0.09 g, 0.571 mmol) promoted the formation of **3h** (0.14 g, 49 %) as a red solid (mp 95-97 °C). FT-IR (CH_2Cl_2) ν_{max} 2059, 1986, 1929, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.66 (t, *J* = 6.0 Hz, 3H, H-18), 4.60 (bs, 1H, H-17), 4.71 (bs, 1H, H-17), 6.01 (s, 1H, H-3), 6.43 (s, 1H, H-16), 6.45 (s, 1H, H-15), 6.61 (d, *J* = 7.8 Hz, 2H, H-6), 6.87-6.92 (m, 1H, H-8), 7.04-7.11 (m, 2H, H-7), 7.20-7.26 (m, 2H, H-10), 7.28-7.35 (m, 3H, H-11, H-12), 7.53 (s, 1H, H-14). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.7 (C-18), 75.1 (C-17), 112.8 (C-15), 115.0 (C-3), 115.3 (C-16), 121.0 (C-6), 123.8 (C-8), 128.3 (C-11), 128.3 (C-7), 129.0 (C-12), 129.2 (C-10), 133.8 (C-9), 146.1 (C-16), 146.2 (C-2), 149.7 (C-5), 149.8 (C-13), 165.0 (C-4), 216.8 (CO*cis*), 224.6 (CO*trans*), 350.0 (Cr = C*carb*). HRMS (EI) calcd for $C_{27}H_{19}CrNO_7$ $[M]^+$ 521.0567, found 521.0557.

Pentacarbonyl-(*Z*)-3-(furan-2-yl)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl) methyl]}(ethoxy)carbene chromium(0) (3i). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2i** (0.11 g, 0.571 mmol) led to **3i** (0.21 g, 69%) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2059, 1986, 1931, 1603, 1578 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.57 (t, *J* = 6.0 Hz, 3H, H-18), 3.61 (s, 3H, OMe), 4.50 (bs, 1H, H-17), 4.61 (bs, 1H, H-17), 5.88 (s, 1H, H-3), 6.32 (s, 1H, H-16), 6.37 (s, 1H, H-15), 6.51 (d, *J* = 9.0 Hz, 2H, H-7), 6.55 (d, *J* = 9.0 Hz, 2H, H-6), 7.14-7.22 (m, 2H, H-10), 7.25-7.33 (m, 3H, H-11, H-12), 7.43 (s, 1H, H-14). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.6 (C-18), 55.2 (OMe), 75.0 (C-17), 112.7 (C-15), 113.6 (C-6), 114.2 (C-3), 114.9 (C-16), 123.3 (C-7), 128.5 (C-11), 128.9 (C-12), 129.1 (C-10), 134.3 (C-9), 142.5 (C-5), 145.8 (C-14), 146.6 (C-2), 149.9 (C-13), 156.6 (C-8), 163.6 (C-4), 216.9 (CO*cis*), 224.7 (CO*trans*), 350.0 (Cr = C*carb*). HRMS (EI) calcd for $C_{28}H_{21}CrNO_8$ $[M]^+$ 551.0672, found 551.0660.

Pentacarbonyl-(*Z*)-3-(4-bromophenyl)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl)methyl]}(ethoxy)carbene chromium(0) (3j). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2j** (0.16 g, 0.571 mmol) resulted in **3j** (0.19 g, 53 %) as a red oil. FT-IR (CH_2Cl_2) ν_{max} 2061, 1989, 1934, 1605, 1584 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz,): δ 1.72 (t, *J* = 6.6 Hz, 3H, H-18), 3.70 (s, 3H, OMe), 4.60 (bs, 1H, H-17), 4.81 (bs, 1H, H-17), 6.13 (s, 1H, H-3), 6.58 (d, *J* = 7.0 Hz, 2H, H-7), 6.64 (d, *J* = 7.0 Hz, 2H, H-6), 7.02 (d, *J* = 6.5 Hz,

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2H, H-14), 7.22- 7.28 (m, 2H, H-10), 7.36-7.42 (m, 3H, H-11, H-12), 7.46 (d, *J* = 6.5 Hz, 2H, H-15). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.7 (C-18), 55.2 (OMe), 75.6 (C-17), 113.6 (C-6), 123.3 (C-7), 123.9 (C-16), 127.6 (C-3), 128.6 (C-11), 129.1 (C-12), 129.1 (C-10), 131.3 (C-14), 131.9 (C-15), 132.6 (C-13), 134.5 (C-9), 142.3 (C-5), 150.4 (C-2), 156.7 (C-8) 164.5 (C-4), 216.6 (CO*cis*), 224.2 (CO*trans*), 353.0 (Cr = C*carb*). HRMS (EI) calcd for $C_{30}H_{22}BrNO_7Cr$ [M]$^+$ 638.9985, found 638.9980.

Pentacarbonyl-(*Z*)-3-(4-chlorophenyl)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl)methyl]}(ethoxy)carbene chromium(0) (3k). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2k** (0.139 g, 0.571 mmol) gave **3k** (0.17 g, 50 %) as a red oil. FT-IR (CH$_2$Cl$_2$) ν_{max} 2061, 1989, 1935, 1605 cm^{-1}. ^{1}H NMR (CDCl$_3$, 600 MHz,): δ 1.72 (t, *J* = 6.6 Hz, 3H, H-18), 3.70 (s, 3H, OMe) 4.61 (bs, 1H, H-17), 4.81 (bs, 1H, H-17), 6.15 (s, 1H, H-3), 6.58 (d, *J* = 8.4 Hz, 2H, H-7), 6.64 (d, *J* = 9.0 Hz, 2H, H-6), 7.08 (d, *J* = 8.4 Hz, 2H, H-14), 7.23-7.27 (m, 2H, H-10), 7.29-7.34 (m, 2H, H-15), 7.36-7.40 (m, 3H, H-11, H-12). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.7 (C-18), 55.3 (OMe), 75.6 (C-17), 113.6 (C-6), 123.3 (C-7), 127.6 (C-3), 128.6 (C-11), 128.9 (C-15), 129.0 (C-12), 129.1 (C-10), 131.1 (C-14), 132.2 (C-16), 134.5 (C-9), 135.5 (C-13), 142.3 (C-5), 150.3 (C-2), 156.7 (C-8), 164.4 (C-4) 216.6 (CO*cis*), 224.2 (CO*trans*), 353.1 (Cr = C*carb*). HRMS (EI) calcd for $C_{30}H_{22}ClCrNO_7$ [M]$^+$ 595.0490, found 595.0489.

Pentacarbonyl-(*Z*)-3-(4-methoxyphenyl)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl)methyl]}(ethoxy)carbene chromium(0) (3l). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2l** (0.13 g, 0.571 mmol) delivered **3l** (0.23 g, 70 %) as a red solid (mp 46-48 °C). FT-IR (CH$_2$Cl$_2$) ν_{max} 2060, 1932, 1604 cm^{-1}. ^{1}H NMR (CDCl$_3$, 600 MHz,): δ 1.70 (t, *J* = 7.2 Hz, 3H, H-18), 3.69 (s, 3H, OMe), 3.80 (s, 3H, OMe), 4.61 (bs, 1H, H-17), 4.81 (bs, 1H, H-17), 6.16 (s, 1H, H-3), 6.57 (d, *J* = 9.0 Hz, 2H, H-7), 6.63 (d, *J* = 9.0 Hz, 2H, H-6), 6.85 (d, *J* = 8.4 Hz, 2H, H-15), 7.09 (d, *J* = 8.4 Hz, 2H, H-14), 7.23-7.27 (m, 2H, H-10), 7.34-7.38 (m, 3H, H-11, H-12). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.8 (C-18), 55.3 (OMe, OMe), 75.3 (C-17), 113.6 (C-6), 114.2 (C-15), 123.1 (C-7), 126.5 (C-13), 128.4 (C-11), 128.8 (C-3), 129.0 (C-12), 129.2 (C-10), 131.8 (C-14), 134.7 (C-9), 142.7 (C-5), 148.2 (C-4), 156.4 (C-8), 160.7 (C-16), 164.6 (C-2), 216.8 (CO*cis*), 224.4 (CO*trans*), 354.4 (Cr = C*carb*). HRMS (EI) calcd for $C_{31}H_{25}NO_8Cr$ [M]$^+$ 591.0985, found 591.0972.

Pentacarbonyl-(*Z*)-3-(4-methylphenyl)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl)methyl]}(ethoxy)carbene chromium(0) (3m). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2m** (0.12 g, 0.571 mmol) afforded **3m** (0.20 g, 62 %) as a red oil. FT-IR (CH$_2$Cl$_2$) ν_{max} 2060, 1987, 1932, 1606 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz,): δ 1.71 (t, *J* = 7.0 Hz, 3H, H-18), 2.34 (s, 3H, Me), 3.69 (s, 3H, OMe), 4.62 (bs, 1H, H-17), 4.80 (bs, 1H, H-17), 6.19 (s, 1H, H-3), 6.58 (d, *J* = 8.5 Hz, 2H, H-7), 6.63 (d, *J* = 9.0 Hz, 2H, H-6), 7.05 (d, *J* = 8.0 Hz, 2H, H-14), 7.14 (d, *J* = 8.0 Hz, 2H, H-15), 7.24-7.28 (m, 2H, H-10), 7.34-7.39 (m, 3H, H-11, H-12). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.7 (C-18), 21.3 (Me), 55.3 (OMe), 75.3 (C-17), 113.6 (C-6), 123.2 (C-7), 128.4 (C-11), 128.9 (C-12), 129.2 (C-10), 129.3 (C-3), 129.4 (C-15), 130.1 (C-14), 130.9 (C-13), 134.7 (C-9), 139.8 (C-16), 142.5 (C-5), 149.1 (C-2), 156.5 (C-8) 164.6 (C-4), 216.7 (CO*cis*), 224.4 (CO*trans*), 353.9 (Cr = C*carb*). HRMS (EI) calcd for $C_{31}H_{25}NO_7Cr$ [M]$^+$ 575.1036, found 575.1045.

Pentacarbonyl-(*Z*)-2-{[(*E*)-(4-chlorophenylimino)(phenyl)methyl]-3-(4-methoxyphenyl)}(ethoxy)carbene chromium(0) (3n). According to the general method, the reaction between **1** (0.30 g, 0.856 mmol) and imine **2n** (0.13 g, 0.571 mmol) furnished **3n** (0.170 g, 50 %) as a red oil. FT-IR (CH$_2$Cl$_2$) ν_{max} 2060, 1931, 1604, 1580 cm^{-1}. ^{1}H NMR (CDCl$_3$, 600 MHz,): δ 1.71 (t, *J* = 6.6 Hz, 3H, H-18), 3.82 (s, 3H, OMe) 4.62 (bs, 1H, H-17), 4.80 (bs, 1H, H-17), 6.22 (s, 1H, H-3), 6.54 (d, *J* = 8.4 Hz, 2H, H-6), 6.86 (d, *J* = 9 Hz, 2H, H-15), 7.04 (d, *J* = 8.4 Hz, 2H, H-7), 7.10 (d, *J* = 8.4 Hz, 2H, H-14), 7.20-7.24 (m, 2H, H-10), 7.32-7.37 (m, 3H, H-11, H-12). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.7 (C-18), 55.4 (OMe), 75.3 (C-17), 114.3 (C-15), 122.4 (C-6), 128.4 (C-7), 128.4 (C-11), 129.0 (C-8), 129.1 (C-12), 129.2 (C-10), 130.4 (C-3), 132.0 (C-14), 133.9 (C-9), 144.9 (C-13), 147.4 (C-2), 148.3 (C-5), 160.9 (C-16), 166.6 (C-4), 216.7 (CO*cis*), 224.1 (CO*trans*), 354.1 (Cr = C*carb*). HRMS (EI) calcd for $C_{30}H_{22}ClCrNO_7$ [M]$^+$ 595.0490, found 595.0490.

Ethyl (*E*)-3-(4-methoxyphenyl)-2-{[(*E*)-(4-methoxyphenylimino)(phenyl)methyl]}acrylate (10b). Compound **3l** (0.25g, 0.422 mmol) in THF (5 mL) was irradiated with visible light (fluorescent lamp, 22 watts, Osram) at room temperature for 48 h. The solvent was then removed under vacuum and the residue was separated by flash column chromatography (*n*-hexane/EtOAc, 99:1), obtaining **10b** (0.1 g, 59 %) as a pale-yellow solid. FT-IR (CH_2Cl_2) ν_{max} 2934, 1731, 1689, 1238, 1168 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.1 Hz, 3H, H-18), 3.66 (s, 3H, OMe), 3.71 (s, 3H, OMe), 4.06 (m, *J* = 7.1 Hz, 2H, H-17), 6.75-6.56 (m, 6H, Ar), 7.45-7.26 (m, 5H, Ar), 7.69 (s, 1H, H-3), 7.92 (d, *J* = 7.5 Hz, 2H, Ar). ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (C-18), 16.0 (C-17), 55.5 (OMe), 55.6 (OMe), 76.8, 77.0, 77.3, 114.3, 114.4, 114.8, 115.1, 125.5, 125.6, 128.5, 128.8, 129.7, 131.7, 132.0, 132.9, 133.7, 190.8 (C-1). HRMS (ESI) calcd for $C_{26}H_{26}NO_4$ $[M+H]^+$ 416.1862 found 416.1865.

X-ray structure determination

Crystal data and refinement details for **10b** are included in supplementary information. Single crystals were generated by the slow diffusion of *n*-hexane in a $CHCl_3$ solution with **10b** at 4 ºC. The pale-yellow crystal of compound **10b** was mounted on glass fibers. Data was collected at 20 ºC on an Agilent SuperNova (single source at offset, Eos) S2 diffractometer using Mo Kα radiation (graphite crystal monochromator, λ 0.71073 Å). Hydrogen atoms were placed in idealized positions, and their atomic coordinates refined. An empirical absorption correction was applied based on spherical harmonics (implemented in SCALE3 ABSPACK scaling algorithm). The structure was solved with the SHELXT program package [46-48] running under the OLEX2 1.5 environment [49]. CCDC 2192850 contains the supplementary crystallographic data for this paper, which can be acquired free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

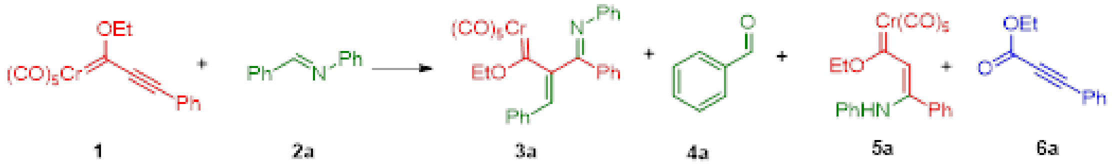
Computational details

All the stationary points along the reaction mechanisms were established by the density functional theory (DFT) at the M06-L level of theory [50] on the Gaussian 09 suite of programs [51], with the 6-311++G** basis set [52] for non-heavy atoms and the LANL2TZ effective core potential [53] for Cr atoms. The level of theory herein employed provides a good description of the thermochemistry, chemical kinetics (transition state energy), non-covalent interactions, and dissociation energy for organometallic compounds [51,54]. All the stationary points and transition state points were re-optimized with a non-explicit solvent model by means of the polarizable continuum model (PCM) [55,56]. The solvent considered for all the calculations was THF. The minima and transition states along the potential energy surface were optimized by performing a frequency calculation for each compound. The intrinsic reaction coordinate (IRC) was computed with Berny optimization to confirm the connection along a minimum energy path of reactants, intermediates, adducts, and products. Free energies at 363.15 K were calculated by including the corresponding thermal corrections to Gibbs free energies (TCGE).

Results and discussion

To initiate the reactivity study, benzylidene aniline **2a** [43] and Fischer carbene complex **1** were utilized as model reagents [57]. Four anhydrous solvents (toluene, benzene, methyl *t*-butyl ether (MTBE), and THF) were tested to avoid the hydrolysis of **2a** (Table 1, entries 1-4). Under thermal conditions, various products were detected by ^1H NMR. For example, ester **6a** resulted from the oxidation of **1** [44,45], benzaldehyde **4a** from the hydrolysis of **2a**, and enamine **5a** from the 1,4-addition of aniline to **1** [14].

Table 1. Optimization of the reaction conditions of Fischer carbene **1** and imine **2a**.[a]



Entry	Solvent	t (h)	T (°C)	Source	3a(%)	4a(%)	5a(%)	6a(%)
1	toluene	24	111	thermal	traces	traces	40	20
2	benzene	2	80	thermal	18	traces	28	10
3	MTBE	17	55	thermal	17	traces	20	15
4	THF	1	66	thermal	20	traces	30	25
5[b]	neat	1	111	thermal	22	traces	15	30
6[b]	neat	1	80	IR/25 Volts	15	traces	10	10
7[b]	neat	9	80	MW	trace	traces	30	50
8	THF	5	66	MW	60	traces	10	5
9	CH_3CN	5	82	MW	30	traces	10	15
10	toluene	5	111	MW	traces	traces	25	30

[a] Complex **1** (1.5 equiv) and **2a** (1 equiv), N_2, 5 mL of solvent. [b] No solvent.

The spectroscopy data (HPLC and NMR) of the isolated product **3a** were different than the expected result [15,25]. The ^1H NMR spectrum of **3a** showed signals for three aromatic rings located between 7.38 and 6.62 ppm, as well as a singlet at 6.28 ppm attributed to a vinyl proton. In the ^{13}C NMR spectrum, a signal at 353.4 ppm indicated the existence of a carbene carbon (Cr = C*carb*), and the signals in 216.6 and 224.3 ppm evidenced the presence of CO*cis* and CO*trans* groups. Hence, the structure of **3a** corresponds to a new vinyl chromium carbene complex α-substituted by an (*E*)-phenyl(phenylimino)methyl group (*i.e*, a cross-conjugated metallatriene system, Table 1). Furthermore, the HRMS analysis is in agreement with the proposed structure of **3a**.

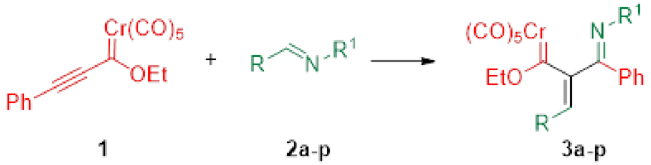
Other experiments were carried out to improve the yield of **3a**. With thermal heating and THF (entry 4), the low yield at 1 h did not improve when the reaction was monitored over the next few hours. Under neat conditions, infrared irradiation as the source of heat afforded a mixture of products comparable to those found with the thermal procedure, while microwave irradiation promoted the formation of only traces of the same (Table 1, entries 5-7). With microwave energy as the source of heat, the reactions performed in a sealed vessel furnished **3a** in yields of 60 % and 30 % when using polar solvents (THF and CH_3CN, respectively), and only a trace amount with toluene (Table 1, entries 8-10). This outcome may be due to the main properties of microwave energy, being dipolar polarization and ionic conduction [58]. Accordingly, the polar solvents probably provoke an efficient dipolar polarization effect over the generation and stabilization of polar species during the proposed reaction mechanism (Scheme 4).

Under the optimized conditions, the scope of the methodology was explored by modifying the aromatic substituents of the benzylidene aniline (**2a-p**) while keeping **1** as the phenyl alkyne carbene complex (Table 2). The new complexes **3a-n** were achieved in 45-70 % yields. Prolonging the irradiation time led to the decomposition of the carbene complex and only traces of the target compound.

The products were separated by column chromatography over silica gel, and their structures were established by ^1H, ^{13}C, 2D, and nuclear Overhauser effect (NOE) NMR experiments as well as IR and HRMS.

In all cases, complexes **3a-n** were obtained as single *Z* (double bond)/*E* (imino group) isomers, along with the corresponding by-products indicated in Table 1.

Table 2. Scope of the synthesis of the new cross-conjugated metallahexatrienes **3a-p**[a]



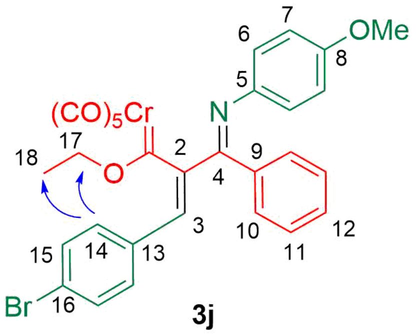
Entry	Benzylidene aniline	R	R^1	Yield (%)
1	**2a**	C_6H_5	C_6H_5	**3a** (60)
2	**2b**	C_6H_5	*p*-$OMeC_6H_4$	**3b** (65)
3	**2c**	C_6H_5	*p*-ClC_6H_4	**3c** (45)
4	**2d**	*p*-FC_6H_4	C_6H_5	**3d** (66)
5	**2e**	*p*-ClC_6H_4	C_6H_5	**3e** (53)
6	**2f**	*p*-$OMeC_6H_4$	C_6H_5	**3f** (64)
7	**2g**	*p*-MeC_6H_4	C_6H_5	**3g** (52)
8	**2h**	C_4H_3O	C_6H_5	**3h** (49)
9	**2i**	C_4H_3O	*p*-$OMeC_6H_4$	**3i** (69)
10	**2j**	*p*-BrC_6H_4	*p*-$OMeC_6H_4$	**3j** (53)
11	**2k**	*p*-ClC_6H_4	*p*-$OMeC_6H_4$	**3k** (50)
12	**2l**	*p*-$OMeC_6H_4$	*p*-$OMeC_6H_4$	**3l** (70)
13	**2m**	*p*-MeC_6H_4	*p*-$OMeC_6H_4$	**3m** (62)
14	**2n**	*p*-$OMeC_6H_4$	*p*-ClC_6H_4	**3n** (50)
15	**2o**	C_6H_5	*p*-$NO_2C_6H_4$	**3o** (0)
16	**2p**	*p*-$NO_2C_6H_4$	C_6H_5	**3p** (0)

[a]Complex **1** (1.5 equiv) and **2a-p** (1 equiv) in THF (5 mL) under N_2, MW (150 W), 66 ºC, 5h.

The impact of the electronic effect of the different aromatic groups of the imines on the efficiency of the reaction is illustrated in Table 2, although a quantitative structure-reactivity relationship was not established. A relatively low yield of complex **3c** resulted from the presence of the chlorine atom (a weak electron donating group) in imine **2c** (Table 2, entry 3) compared to a greater yield of complex **3b** derived from the methoxy group (a stronger electron donating group) in the imine of **2b** (Table 2, entry 2). The yield of complexes **3a** and **3b** were 60 % and 65 %, respectively (Table 2, entries 1 and 2), despite the lack of substituents in the phenyl rings of **2a** (*vide infra*). On the other hand, electron donor groups in the imines **2l** and **2m** (R and R^1) increased the yield of complexes **3l** and **3m** (Table 2, entries 12 and 13). The combination of electron donating and electron withdrawing groups in the imines **2j**, **2k**, and **2n** afforded slightly lower yields of **3j**, **3k**, and **3n** (53, 50, and 50%, respectively) compared to **3a** (60 %), the latter furnished by the reaction with the unsubstituted imine **2a**. In contrast, when the imine bore a strong electron withdrawing group, such as **2o** and **2p** (R = *p*-

$NO_2C_6H_4$, R^1 = *p*-$NO_2C_6H_4$), the reaction did not occur. Due to these differences in reactivity, the electronic effects of the substituents in imines **2** were analyzed by theoretical studies (*vide infra*).

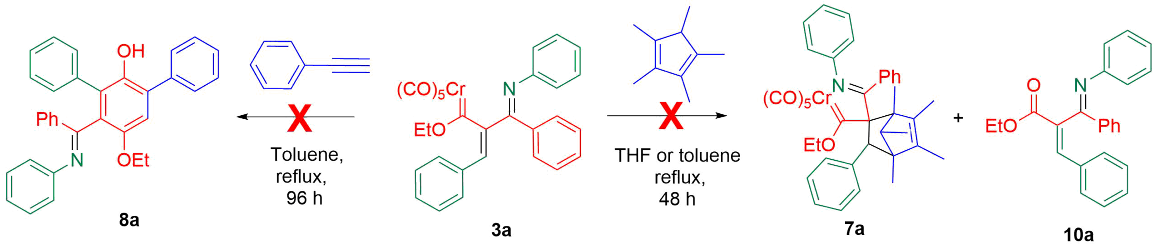
Even though it was not possible to obtain the crystalline structures of **3a-n** by single crystal X-ray diffraction, NOE spectroscopy (NOESY and ROESY) experiments provided sufficient evidence to determine the conformation. Accordingly, complex **3j** exhibited a NOE effect of the vinyl proton H-3 and the CH_3CH_2O group (protons H-17 and H-18) by irradiating the aromatic proton H-14 (7.02 ppm) (Fig. 1), indicating a *Z* configuration of the double bond C-C. Neither proton H-17 nor H-18 showed a NOE effect with H-6 or H-7, which suggests that the *N*- anisyl ring of the imine moiety remains distant from the metal center.



3j

Fig. 1. NOESY for complex **3j**.

It is reported that metallatrienes are precursors of cyclopentadienes [58], indenes [59], naphthalenes [60], homopyrroles [61], and other carbo- and heterocycles [22]. Hence, some experiments were conducted to evaluate the reactivity of the new metallatrienes **3a-n**. The reaction of **3a** and pentamethylcyclopentadiene was attempted under the [4+2] cycloaddition conditions previously described. The reaction did not proceed in THF or toluene at reflux for 48 h, and a consequence, the starting materials were recovered. The results of the Dötz reaction of phenylacetylene with **3a** in toluene was also examined after refluxing for 96 h. The ^1H NMR analysis of the crude reaction mixture did not show the expected transformation, but the oxidation product **10a** was detected (Scheme 2).



Scheme 2. Exploration of the reactivity of complex **3a**.

With the objective of forming a six-membered cycle in complex **3l**, further experiments were performed with UV and visible light irradiation to attain the insertion of CO and the subsequent cyclization to phenol **9a**. Nevertheless, the desired product was not found and only the oxidized compound **10b** was isolated, afforded in a moderate yield of 59 % (Scheme 3). Despite there being an α,β-unsaturated system in complexes **3a-n**, indicating susceptibility to Dötz benzannelation, such a reaction did not take place for **3l**, probably because of the steric effect of the bulky substituents.

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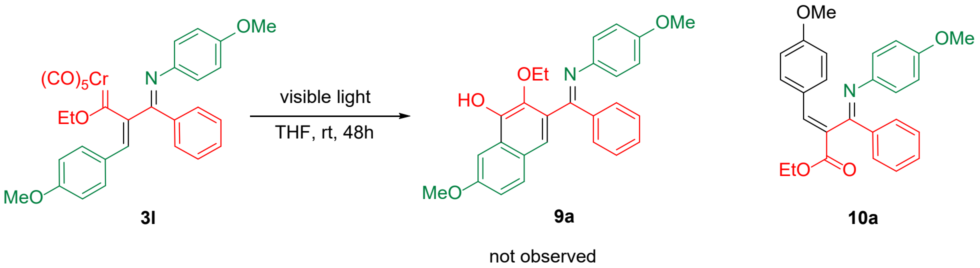


Scheme 3. Conversion of **3l** into ethyl acrylic ester **10b**.

A crystal sample was obtained by the slow diffusion of *n*-hexane in a $CHCl_3$ solution with **10b** at 4 ºC. The crystallized compound fits in the monocyclic crystal system. The space group P21/c and unit cell parameters are a = 17.0269(12) Å, b = 9.6109(5) Å, and c = 14.1952(8) Å, as well as $\alpha = 90°$, $\beta = 104.895(7)°$, $\gamma = 90°$, and a volume of 2244.9(2) Å^3. According to the crystalline structure of **10b**, oxidation of **3l** and removal of the steric hindrance of the bulky $Cr(CO)_5$ group leads to isomerization of the double bond of this compound to the *E* configuration [torsion angle: C1-C2-C6-C21 = 72.78°]. Moreover, the ester group adopts the *s-cis* conformation and the imino moiety is orthogonal to the double bond (Fig. 2).

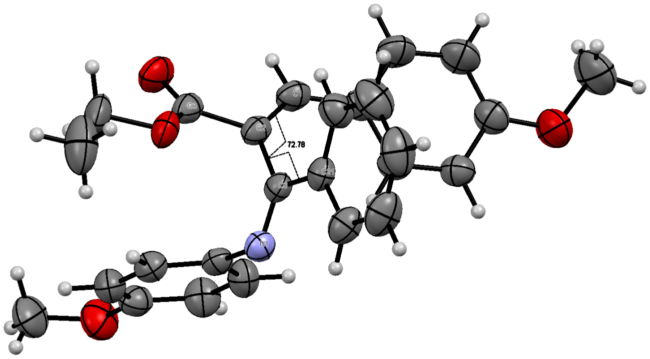
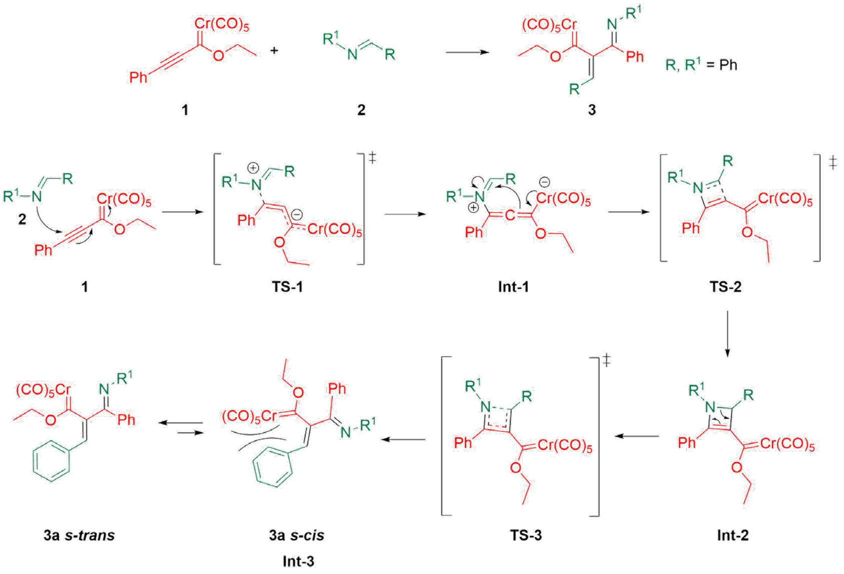


Fig. 2. Molecular structure of **10b** with 50 % probability ellipsoids.

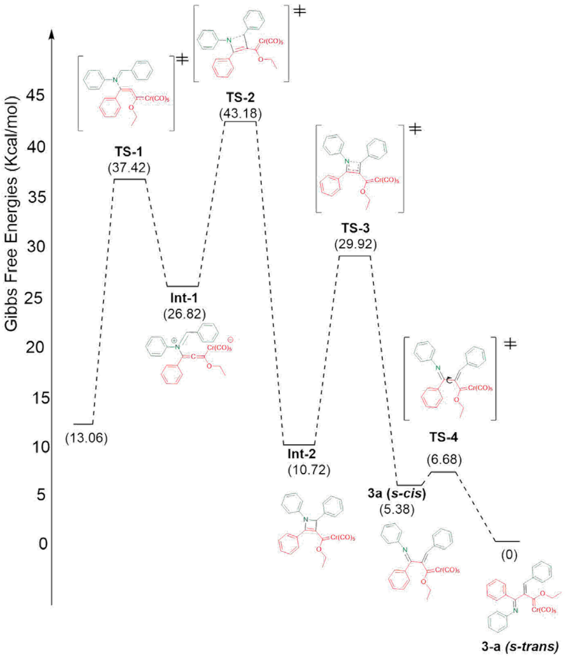
Computational analysis

Reaction between the Fischer alkynyl carbene complex and benzylidene anilines

Considering the experimental findings, a computational study was performed to account for the mechanism of formation of the new compounds **3a-n**. The potential energy surface was calculated for the proposed four-step mechanism (Scheme 4), involving three intermediates and three transition states (Scheme 5). The first step consists of the 1,4-addition of the nitrogen atom of the imine to the alkynyl Fischer carbene, leading to transition state **TS-1** with an N-C$_\beta$ bond distance of 1.95 Å and an activation energy ($\Delta G^{\neq}$) of 37.42 kcal/mol. Afterwards, intermediate 1 (**Int-1**) is generated, with a reactant energy (ΔG^{o}) of 13.76 kcal/mol. **Int-1** undergoes an intramolecular attack by the carbenic anion and is converted into the iminium moiety by passing through the cyclic **TS-2**, which is the rate-determining step ($\Delta G^{\neq} = 43.18$ kcal/mol). The distance of the C-C$_\beta$ bond formed is 2.24 Å for **Int-1** but only 1.40 Å for intermediate 2 (**Int-2**). The latter exhibits much greater stability than **Int-1** ($\Delta G^{o} = 16.10$ kcal/mol). Subsequently, the thermally allowed electrocyclic opening of the aza-cyclobutene of **Int-2** brings about transition state 3 (**TS-3**) with an activation barrier ($\Delta G^{\neq}$) of 29.92 kcal/mol, which in turn evolves into **3a** (*s-cis*) with a dihedral angle of 68.83° (Figures 3 and 4). Interestingly, greater stability (-5.38 kcal/mol) was found for the *s-trans* than the *s-cis* conformation of **3a**. To find the transition state barrier associated with the rotation, a SCAN of the dihedral rotation was performed (Scheme 6), using 18 steps spanning an interval of 0-180 degrees (consisting of 10 degrees for each step), starting from the *s-cis* and arriving to the *s-trans* conformation. The energetic profile shows two minima: the **3a** *s-cis* structure at 68.83º and the more stable **3a** *s-trans* conformer with an activation energy (ΔG≠) of 1.30 kcal/mol between both rotamers. The stability of the *s-trans* conformer is in agreement with the experimental results for compound **3a**.



Scheme 4. Proposed reaction mechanism for the generation of **3a**.



Scheme 5. Energetic profile of the Gibbs free energies (kcal/mol) relative to the energy of product at the M06L/6311++G**/Cr=LANL2TZ/SCRF=THF level of theory.

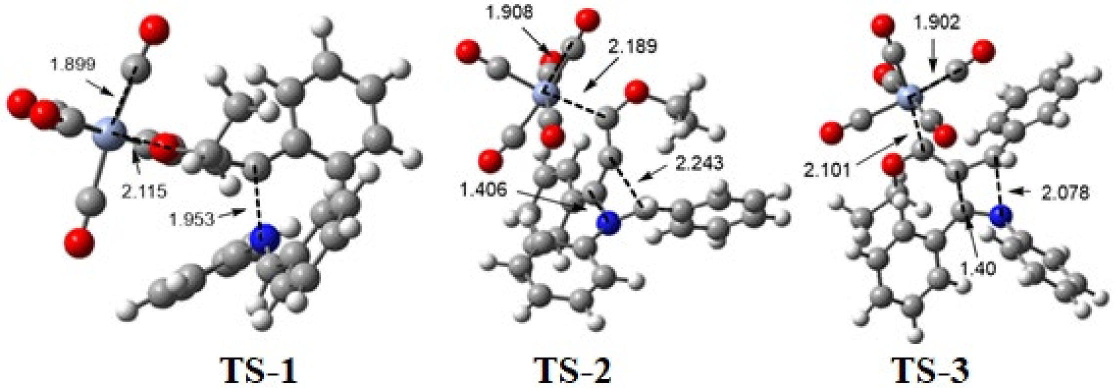


Fig. 3. Structures corresponding to the transition states **TS-1**, **TS-2**, and **TS-3** at the M06-L/6-311++G**/Cr=LANL2TZ/SCRF=THF level of theory. Bond distances are given in Å. Color code of the spheres pictured: hydrogen atoms in white, carbon atoms in grey, nitrogen atoms in blue, oxygen atoms in red, and chromium atoms in light blue.

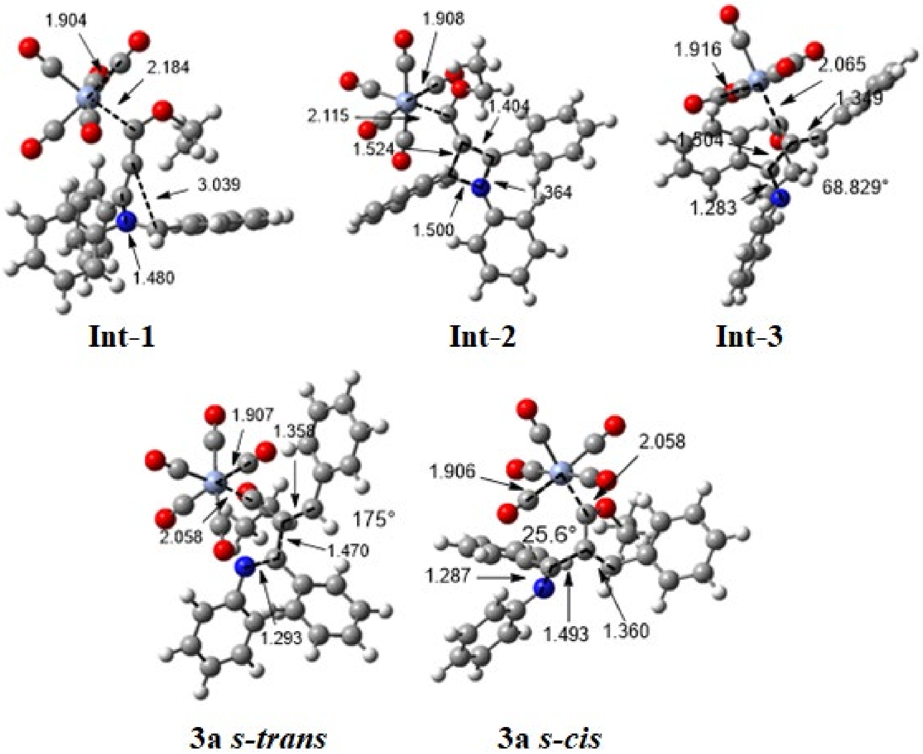
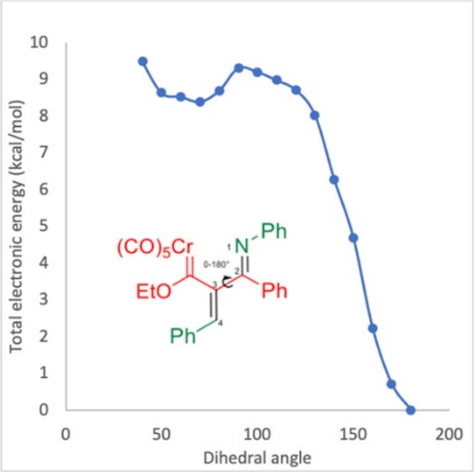


Fig. 4. Optimized structures of intermediates **Int-1**, **Int-2**, and **Int-3**, as well as products **3a** (*s-cis*) and **3a** (*s-trans*) at the M06-L/6-311++G**/Cr=LANL2TZ/SCRF=THF level of theory. Bond distances are given in Å. Color code of the spheres depicted: hydrogen atoms in white, carbon atoms in grey, nitrogen atoms in blue, oxygen atoms in red, and chromium atoms in light blue.



Scheme 6. Energetic profile of the scan of dihedral rotation for the *cis-trans* transformation.

A comparative study was carried out to explore the impact of the R and R^1 substituents on the aromatic system of benzylidene anilines **2a**-**p**. Apparently, the R^1 substituent did not have any relevant effect on the 1,4-addition, and the electronic effect of the R substituent was not relevant in the reactivity of the entire process (see supplementary data).

Conclusions

Microwave irradiation promoted the reaction between the Fischer carbene complex of Cr(0) (**1**) and benzylidene anilines **2a-n**, obtaining moderate yields of new, stable, and polysubstituted Fischer carbenes with a cross-conjugated system. In all cases, complexes **3a-n** were afforded as single *Z* (double bond)/*E* (imino group) isomers, while the oxidation product **10a** changed to the *E* (double bond)/*E* (imino group) configuration. The computational study of the reaction mechanism revealed that the formation of the dihydroazete intermediate (**Int-2**) is the rate-determining step of the reaction. The proposed mechanism involves a 1,4-addition/ring closure/electrocyclic opening cascade reaction. The reaction did not proceed in any of the compounds **2** that had an electron withdrawing group in the aromatic ring of the imine moiety. Even though complexes **3a-n** did not evolve into the Diels-Alder or the Dötz products (probably because of the great steric effects exhibited by the organometallic compounds), these kinds of structures are interesting from a synthetic and theoretical point of view. Further research on Fischer carbene complexes of W(0) and Mo(0) with different substituents is currently under way, and the results will be reported in due course.

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