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Mono- and Bimetallic Zwitterionic Chromium(0) and Tungsten(0) Allenyls

Elena A. Giner,[†,∥] Alicia Santiago,[†,∥] Mar Gómez-Gallego,*[,†,∥] Carmen Ramírez de Arellano,[‡,∥] Rebecca C. Poulten,[§] Michael K. Whittlesey,[§] and Miguel A. Sierra*[,†,∥]

[†]Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

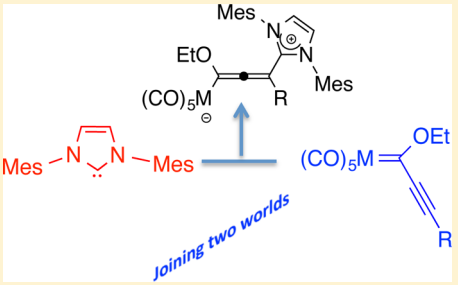
[‡]Departamento de Química Orgánica, Facultad de Química, Universidad de Valencia, 46100-Valencia, Spain

[§]Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

[∥]Centro de Innovación en Química Avanzada, ORFEO−CINQA, Madrid, Spain

Supporting Information

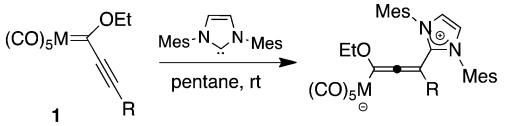
ABSTRACT: A series of stable chiral (racemic), formally neutral, zwitterionic mono- and bimetallic $M(CO)_5[C(OEt)=C=CR(NHC)]$ (M = Cr, W) σ-allenyls are ready available by the addition of N-heterocyclic carbenes (NHCs) to Cr(0) and W(0) alkynyl Fischer carbene complexes. Different classes of NHCs, (e.g., 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, and their six- and seven-membered analogues and 1,3-bis(dimethyl)imidazol-2-ylidene) were employed as nucleophiles in these C−C bond-forming reactions yielding the novel complexes in essentially quantitative yields. A systematic experimental and computational study of the electronic properties of the Cr- and W-allenyls shows that their UV−vis spectra are directly influenced by the structure of the heterocyclic moiety derived from the NHC (ring size, substituents on the N atoms) and by the nature of the metal fragment (Cr/W). The electron-releasing nature of these complexes allows them to participate in electron-transfer reactions in the ground state, leading to a type of charged α,β-unsaturated Fischer carbenes that incorporate an NHC fragment in their structure.



INTRODUCTION

The special properties of N-heterocyclic carbenes (NHCs), like ambiphilicity (σ-donor and π-acceptor character), strong basicity, and moderate nucleophilicity,[1] have found widespread applications in organic and organometallic chemistry, not just in the design of new catalysts but also as components for medicinal, luminescent, and functional materials.[2] Their role as organocatalysts is now well-recognized,[3] and their affinity for metals has converted them into habitual ligands in homogeneous metal catalysis,[4] in most cases being a superior alternative to the classical phosphine ligands.[5] However, the reactivity of NHCs as simple nucleophiles in C−C bond-forming reactions is largely unknown. In this context, our interest has been directed to a study of the compatibility of NHCs as nucleophiles with metal complexes having several reactive centers. In preliminary results,[6] we reported the synthesis of stable chromium and tungsten zwitterionic η^1-allenyl complexes **2a−c**, by the addition of 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) to the corresponding alkynyl Fischer carbene complex **1**, at room temperature and in quantitative yields (Scheme 1). The efficient synthesis of compounds **2a−c** demonstrates that despite the high affinity of NHCs to bind metals,[7] the thermodynamically favorable CO exchange from metal carbonyls,[8] and their ability to displace carbene ligands in goup 6 Fischer ($M(CO)_5L$) carbenes,[9,10] it is possible to combine a NHC with an electrophilic group 6 alkynyl Fischer carbene complex to make a C−C bond.

Scheme 1. [a]



Mes = 2,4,6-trimethylphenyl

2a M = Cr, R = Ph[a]
2b M = Cr, R = Fc[a]
2c M = W, R = Ph[a]
2d M = Cr, R = 2-thienyl
2e M = Cr, R = 4-BrC_6H_4
2f M = Cr, R = 4-MeC_6H_4
2g M = Cr, R = 4-$OMeC_6H_4$
2h M = Cr, R = 4-$NMe_2C_6H_4$
2i M = Cr, R = 4-$CF_3C_6H_4$

[a]See ref 6.

Compounds **2** constitute a new type of formally neutral zwitterionic η^1-metal allenyls, a class of compounds that, due to their elusive character, have been scarcely studied.[11−13] In this regard, the stability of metal allenyls **2** offers an excellent opportunity to obtain more information about their structures,

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their physicochemical properties, as well as to establish the main features of their reactivity. In this work, we explore the scope of the addition of NHCs to α,β-unsaturated Fischer mono- and biscarbene complexes, undertaken as a study to establish the influence of the substituents in both reagents and the nature of the metal fragment on their structures, electronic properties, and reactivity.

RESULTS AND DISCUSSION

To study the effect of the substituent in the aromatic ring attached to the triple bond, complexes **2d**−**2i** were prepared following our previously reported method.[6] Thus, reaction of IMes with the corresponding Cr(0) and W(0) alkynyl Fischer carbene complexes **1** in pentane, at room temperature, affords metal−allenyl complexes **2** in quantitative yields (Scheme 1). All new complexes were obtained as yellow solids and were fully characterized by NMR and mass spectrometry (MS) analysis. As for the previously reported parent complex **2a**, compounds **2d**−**2i** show the characteristic diastereotopic protons of the ethoxy group in the ^{1}H NMR spectra (multiplets at ca. 1.97 and 2.50 ppm, respectively), noticeably shielded compared to the starting carbene (the CH_2 protons in the ethoxy group in alkynyl carbenes **1** appear as a quartet at ca. 4.5 ppm). Also significant are the ^{13}C NMR signals of the M−C carbon (C1) at ca. 200 ppm, the central allenyl carbon (C2) at ∼155−160 ppm, and the terminal carbon (C3) at 79−88 ppm (Table 1). The effect of the metal fragment on the chemical shift of the allene carbons is remarkable. The most deshielded signal in simple allenes corresponds to the central carbon atom (at ca. 200−220 ppm),[14] whereas in metal allenyls **2**, this signal corresponds to the neighboring position to the metal. The change from Cr to W in the $M(CO)_5$ moiety (complex **2c**)[6] also causes the deshielding of the M−C (C1) signal. Results in Scheme 1 and Table 1 indicate that the reaction is not strongly influenced by the *p*-substituent at the aromatic ring and hence the electrophilicity of the conjugated position (C3) in the starting alkynyl Fischer carbene. The addition of the NHC works well regardless of the electronic nature of the substituent placed in the para position of the phenyl ring in C3 (electron-donating or electron-withdrawing groups). The incorporation of an electron-rich heteroaromatic ring (2-thienyl) or a ferrocenyl group at the conjugated position of the alkynyl carbene also has a negligible effect on the reaction course, although an effect is noticeable in terms of the C3 ^{13}C NMR chemical shifts, which are shielded (2-thienyl, **2d**) and deshielded (ferrocenyl, **2b**), respectively, compared to the rest of the compounds of the series (Table 1). Regarding the IR data, no significant changes were observed in the C═C═C and CO stretching bands with the electronic properties of the aryl substituent at C3.

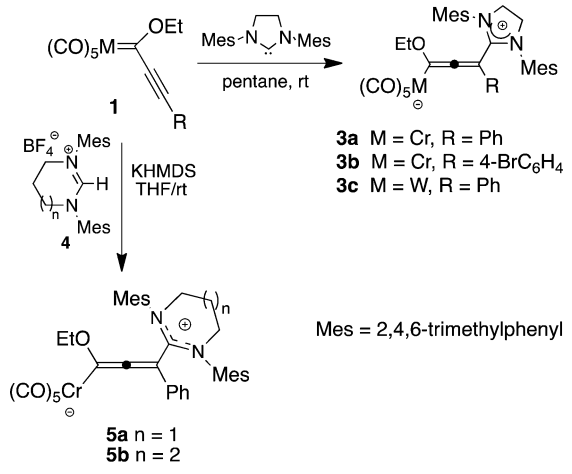
Given the influence of the ring size, N-substituent bulk, and N−C−N angle on the electronic properties of NHCs,[1,3b,15] other types of NHCs were also tested. Saturated NHCs are more basic than their unsaturated counterparts, and the increase of the ring size is translated into larger N−C−N angles and higher steric congestion.[1,16] Reaction of Cr(0) and W(0) alkynyl carbenes **1a**, **1e**, and **1c** and 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene afforded the expected metal allenyls **3a**−**c** in quantitative yields (Scheme 2, Table 1). The study of the effect of the enlargement in the NHC ring was achieved by reaction of alkynyl carbene **1a** with the corresponding six- and seven-membered NHC carbenes, generated in situ from their BF_4^- pyrimidinium/diazepinium salts **4** and potassium bis(trimethylsilyl)amide (KHMDS) in tetrahydrofuran (THF), at room temperature and in quantitative yields. The ring expansion of the heterocyclic fragment in metal allenyls **5a**−**b** causes significant shielding of the signals of the ethoxy group in ^{1}H NMR spectra compared to their five-membered counterparts **3**. In fact these signals appear now at ∼1.7 and 2.1 ppm, respectively, while the

Table 1. ^{13}C{^{1}H} NMR Chemical Shifts (ppm in $CDCl_3$) and IR Data (cm^{-1}) of Metal Allenyls 2, 3, 5, and 6

compound	C1	C2	C3	ν(C═C═C) and ν(CO)
2a[a]	201.3	160.1	84.9	2040(17), 1959(20), 1907(100), 1868(56)
2b[a]	199.4	155.8	88.9	2038(13), 1953(16), 1907(100), 1861(60)
2d	199.6	159.2	79.2	2040(27), 1958(27), 1907(100), 1857(69)
2e	199.5	160.3	83.2	2041(27), 1958(27), 1912(100), 1867(81)
2f	200.5	159.6	84.4	2040(25), 1956(25), 1909(100), 1864(67)
2g	200.8	159.4	84.0	2040(36), 1959(36), 1902(100), 1865(81)
2h	201.0	158.9	84.6	2046(31), 1919(br)(100), 1865(67)
2i	199.6	160.7	83.6	2042(43), 1962(31), 1911(100), 1874(81)
2c[a]	209.1	155.3	85.9	2051(23), 1961(39), 1904(100), 1857(78)
3a[a]	198.6	170.1	85.7	2042(16), 1965(22), 191(100), 1853(61)
3b	196.7	170.5	84.3	2043(75), 1963(80), 1922(100), 1865(95)
3c	207.2	170.0	85.9	2053(24), 1968(29), 1907(100), 1845(67)
5a	208.4	167.8	91.4	2041(21), 1965(29), 1904(100), 1849(64)
5b	216.4	158.5	93.1	2040(31), 1964(31), 1905(100), 1855(64)
6a	176.0	147.3	106.5	2038(31),1963(35),1903(100), 1859(67)
6b	176.0	147.3	106.5	2037(23),1948(28), 1906(100), 1854(66)
6c	178.7	146.6	106.2	2038(27), 1964(36), 1907(100), 1844(87)
6d	182.4	145.6	105.7	2050(17),1961(22), 1900(100), 1855(51)

[a]See ref 6.

Scheme 2



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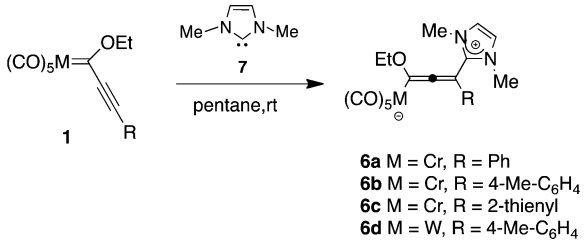
analogous compounds **3** showed signals at ~2.0 and 2.6 ppm, respectively. Also, in the ^{13}C NMR spectra, the signals of M−C carbon (C1) in "enlarged" derivatives **5a−b** are noticeably deshielded (10−18 ppm) compared to their five-membered counterparts **3** (Table 1). The central allenyl carbon (C2) is less affected, but the extreme position (C3) moves up to 91.4 and 93.1 ppm, respectively (compare with the signals at 79−88 ppm in complexes **1b**). The less effective electron donation from the N-atoms to stabilize the neighboring cationic center, as well as the effect of the bulkier ring on the structure of the allene, could be the origin of these observations.[16]

The impact of the N-substituents was addressed next. Addition of 1,3-bis(dimethyl)imidazol-2-ylidene (IMe_2, **7**) to alkynyl carbenes **1a**, **1d**, **1f**, and **1j** afforded metal allenyls **6a−d** in 81% to quantitative yields and as brownish solids (Scheme 3). Reaction times and yields were unaffected by using either

Scheme 3



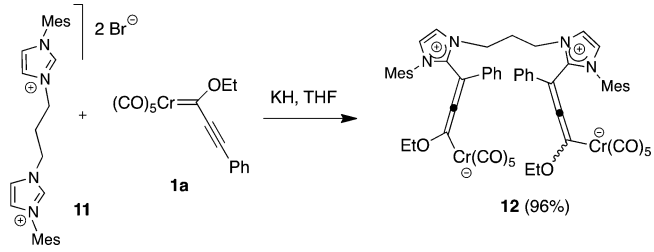
6a M = Cr, R = Ph
6b M = Cr, R = 4-Me-C_6H_4
6c M = Cr, R = 2-thienyl
6d M = W, R = 4-Me-C_6H_4

the free, freshly prepared **7**,[17] or the carbene generated in situ from the 1,3-dimethylimidazolium iodide salt and KH in THF.[18] Compounds **6** were characterized by spectroscopic analysis. The replacement of the bulky mesityl groups by methyl arms in the heterocyclic moiety allows a higher conformational freedom of the molecule, which is reflected in the signals of the NMR spectra. Thus, the ^1H NMR signals of the protons of the ethoxy group in compounds **6**, although still diastereotopic, almost overlap and appear noticeably deshielded (at ~4 ppm) compared to the IMes derivatives **2** (see above). Other changes evident in the $^{13}C\{^1H\}$ NMR spectra were the shielding of the signals of the allenyl system (C1 ~20 ppm and C2 ~15 ppm relative to compounds **2**) and the strong deshielding (~24 ppm) of the signals of the allenyl-carbon (C3). The latter is probably due to the increase of the positive character of the NCN carbon in Me_2Im-compounds **6**.

The preparation of zwitterionic bis-metal allenyls was tested next. Double nucleophilic addition of IMes or SIMes, to the corresponding chromium bis-alkynyl carbene complexes **8**, led to the formation of bis-allenyl metal complexes **9** and **10** as yellow solids in almost quantitative yields (Scheme 4).

In an alternative approach to bis-metal allenyls, the bis-allenyl complex **12**, having a flexible tether between the nitrogen atoms, was obtained in 96% yield by reaction of alkynyl carbene **1a** and a bis-NHC-carbene generated in situ from the dibromide salt **11** and KH (Scheme 5).

Scheme 5

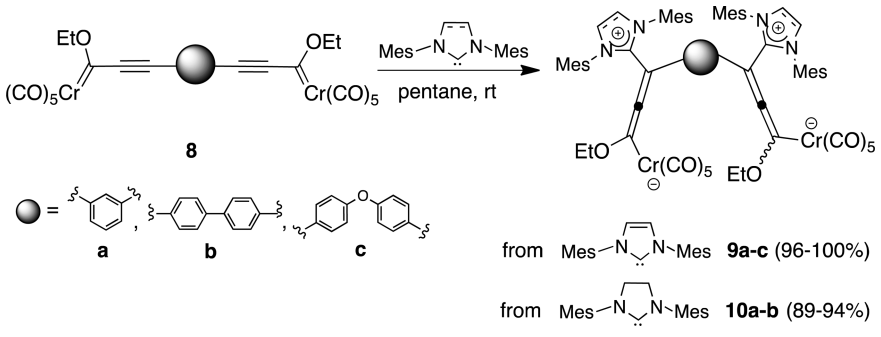


All the allenyl metals prepared through this work are chiral compounds obtained as *racemic* mixtures. The incorporation of two allenyl fragments within the same molecule in compounds **9**, **10**, and **12** should then lead to diastereomeric mixtures, at least a symmetrical meso form and an *enantiomeric pair*. The NMR spectra of the bis-allenyl metals confirm this fact. Compounds **9b,c**, **10b**, and **12** having flexible tethers, show well-resolved signals with little splitting in the ^1H and ^{13}C NMR spectra, the chemical shifts being similar to those of the monometallic counterparts. The combination of the bulky IMes and the short, rigid 1,3-substituted phenyl ring as tether in bis-allenyl metal complexes **9a** and **10a** leads to more complex ^1H NMR spectra, with broad and noticeably split signals, in accord with structures possessing little conformational mobility.

All compounds prepared through this work (**2**, **3**, **5**, **6**, **9**, **10**, **12**, **13**) are perfectly stable in the solid state at room temperature, and they do not need to be handled under special conditions. They do not require Schlenck techniques; they are not air sensitive and can be stored as solids in perfect conditions. In solution they are stable in Et_2O, THF, and hexanes but slowly decompose when left to stand in CH_2Cl_2 or $CHCl_3$ solution.

Finally, further structural information on the different types of σ-metal allenyls prepared through this work was gained by a computational study (B3LYP/def2-SVP method) of **2a**, **3a**, **5a**, **5b**, and **6a**, as the extent of the coplanarity between the NHC moiety and the attached sp^2 carbon could give information about the Lewis donor/imidazolium character of the NHC units. Our calculations indicate a torsion angle of 41.47° in the

Scheme 4



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gas phase for the IMes derivative **2a**, a value considerably higher than that obtained in the crystal structure (16.97°, see ref 6) and consistent with the expected greater packing of the molecules in the crystalline form. The replacement of the bulky mesityl groups by methyl groups does not affect seriously the calculated torsion angle (40.46° in **6a**). Finally, the incorporation of a saturated NHC of different ring size provokes changes in the torsion angles from 11.75° in **3a** to 42.40° in **5a** and 20.44° in **5b**.

Electronic Structure of the Allenyl Metal Complexes. Information about the electronic structure of metal allenyl complexes prepared through this work was obtained by UV−vis spectroscopy (Table 2).

Table 2. UV−vis Excitation Energies (λ_{max} in nm) and Calculated Oscillator Strengths (f, in parentheses) for Mono- and Bis-Metal Allenyl Complexes

entry	complex	λ_1/nm[a]	λ_2/nm[a]
1	**1a**[c]	281	497
2	**1b**[c]	309	487, 544
3	**1c**	290	495
4	**2a**	338 (344, 0.123)	424 (404, 0.002)
		338[b]	413[b]
5	**2e**	334 (345, 0.125)	429 (407, 0.002)
6	**2f**	339 (346, 0.133)	424 (404, 0.001)
7	**2g**	342 (344, 0.125)	423 (402, 0.003)
8	**2h**	354 (345, 0.135)	416 (404, 0,002)
9	**2i**	336 (347, 0.133)	433 (407, 0.001)
10	**2b**	315	417
11	**2d**	336 (331, 0.373)	424 (436, 0.020)
12	**2c**	347	403
13	**3a**	341 (360, 0.130)	451 (427, 0.001)
14	**3b**	336 (363, 0.134)	453 (426, 0.001)
15	**3c**	347	408
16	**5a**	343 (339, 0.054)	440 (401, 0.007)
17	**5b**	350 (broad) (357, 0.155)	472 (467, 0.002)
18	**6a**[c]		334 (371, 0.017, 333, 0.061)
19	**6b**[c]		335
20	**6c**[c]		333
21	**6d**[c]		340
22	**9a**	328	418
23	**9b**	339	427
24	**9c**	338	419
25	**10a**[b]	336	430
26	**10b**[b]	334	429
27	**12**[c]		343

[a]The first value corresponds to experimental data (recorded at room temperature in Et_2O with a concentration of 1×10^{-4} M unless specified). The first value in parentheses corresponds to the computed TD-CAM-B3LYP/def2-SVP gas-phase vertical excitation energies. The second one is the corresponding oscillator strength f. [b]Data recorded at room temperature in THF, with a concentration 1×10^{-4} M. [c]Data recorded at room temperature in THF, with a concentration 1×10^{-5} M.

Metal allenyl complexes **2a−i** bearing 1,3-bis(2,4,6-trimethylphenyl)imidazolium moieties show two main absorptions around 340 and 430 nm (data obtained in Et_2O in 1×10^{-4} M solutions, Figure 1). The assignment of the absorption bands was made by time-dependent (TD) density functional theory (DFT) calculations using the TD-CAM-B3LYP/def2-SVP method. Data in Table 2 (which include the calculated

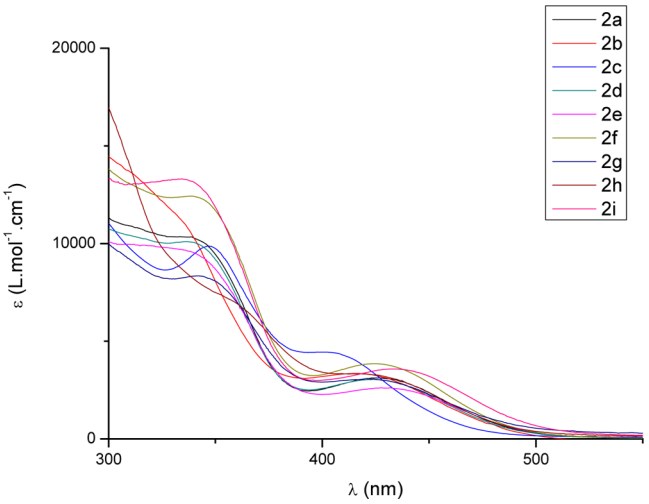

Figure 1. Room-temperature UV−vis spectra of complexes **2a−i** (Et_2O, concentration ca. 1×10^{-4} mol L^{-1}).

oscillator strengths of the main absorptions) show a good agreement between the calculated vertical excitation energies and the wavelengths of the absorption maxima in the experimental UV−vis spectra. The deviation of the calculated from the experimental values is in the range of 10−40 nm (the calculated data are red-shifted compared to the experimental measurements). The TD-CAM-DFT calculations indicate that the bands in the range of 430 nm are mainly due to the promotion of one electron from the metal-centered highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). As depicted in Figure 2 for compound **2a**, the HOMO should be viewed as π-molecular orbital mainly located at the metal fragment, whereas the LUMO is a π^*-orbital mostly distributed on the imidazolium salt. The observed bands can thus be assigned to metal-to-ligand charge transfer (MLCT) transitions possessing remarkable $\pi-\pi^*$ character. On the other hand, the bands at ∼340 nm can be assigned, on the basis of the TD-CAM-DFT calculations, to metal-centered HOMO−1 to LUMO transitions. Compared to the starting chromium alkynyl carbene complexes **1a−c** (Table 2, entries 1−3) the UV−vis spectra of the metal−allenyl species **2** show a remarkable blue shift of the MLCT band (from 490 to 430 nm) and a red shift of the ligand field (LF) band (from 290 to 340 nm).[19a] The origin of these shifts may be due to the loss of the partial double bond character of the starting complexes and replacement by a M−C single bond in the allenyl complexes. This effect has been reported previously by us for Cr(0) and W(0) carbene complexes having donor or acceptor substituents attached to the M═C moiety.[19b]

As expected, and taking into account the distribution of the HOMO and LUMO orbitals involved in the MLCT transition (Figure 2), the substituents attached to the aryl group in compounds **2** have very little influence on this absorption band. However, the data in Table 2 show that the higher energy LF band is somewhat influenced by electronic effects. Thus, the presence of π electron donating substituents in the para position of the phenyl group causes a slight red shift in this band, which moves from 338 nm in the unsubstituted compound **2a** (R = H entry 4) to 342 nm in **2g** (R = OMe, entry 7) and 354 nm in **2h** (R = NMe_2, entry 8). Replacement of the phenyl group at C3 by ferrocenyl (**2b**) causes a

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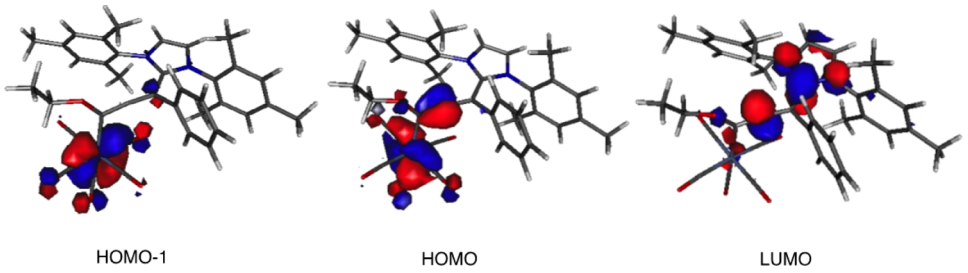

Figure 2. Calculated DFT (B3LYP/def2-SVP level) HOMO−1, HOMO and LUMO orbitals of compound **2a** (isosurface value 0.04).

noticeable blue shift to 315 nm (entry 10). These effects may be explained by taking into account the participation of the C3 position (next to the aryl group) in the description of the HOMO−1 of the allene (the origin of this UV transition; see Figure 2). This participation is missing in the HOMO (the origin of the MLCT absorption). Finally, the nature of the metal fragment ($Cr(CO)_5$, $W(CO)_5$) has an effect on the MLCT band, which is blue-shifted in the tungsten complex **2c** (424 cm in **2a** cf. 403 nm in **2c**, entry 12). This was previously reported by us[19] in M(0) carbene complexes.

UV−vis absorption spectra of metal−allenyls **3** and **5** bearing (*saturated*) 1,3-bis(2,4,6-trimethylphenyl)imidazolinium, pyrimidinium, and diazepinium moieties are displayed in Figure 3.

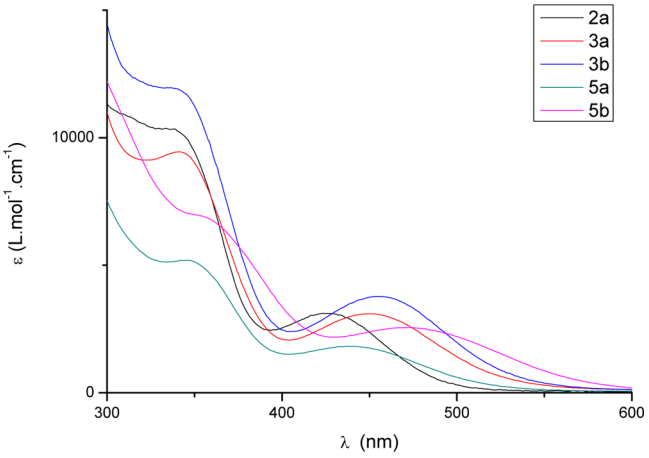

Figure 3. UV−vis absorption spectra of compounds **3a−b** and **5a−b** (Et_2O, concentration ca. 1×10^{-4} mol L^{-1}). Compound **2a** is included for comparison.

Although the general pattern is similar to those of the *unsaturated* counterparts **2** (see above), there is a remarkable red shift observed in their MLCT bands. Thus, **3a** and **3b** show MLCT absorptions at 451 and 453 nm, respectively, ∼30 nm red-shifted compared with those of the structurally related **2a** and **2e** (compare entries 13−14 and 4−5). The effect is particularly evident when the heterocyclic ring is enlarged. Thus, **5b**, having a seven-membered ring, shifts the MLCT band to 472 nm (entry 17). The structural changes made in the cationic heterocyclic moiety (imidazolinium, pyrimidinium, diazepinium) undoubtedly influence the energy of the LUMO [−1.56 eV for **2a** but −1.69 eV (**3a**), −1.76 (**3b**), −1.66 eV (**5a**), and −1.90 eV (**5b**)] and are the origin of the red shifts observed in the MLCT bands. Finally, the UV−vis spectra of the bis-allenyl metal complexes **9** and **10** (entries 22 to 26 in Table 2, Figure S1 in the Supporting Information) show similar absorptions to those of the corresponding monoallenyl derivatives, as would be expected considering that the metallic moieties are independent of each other.

Replacement of the bulky mesityl by methyl groups in the imidazolium moiety causes evident changes in the UV spectra of compounds **6** compared to the structurally related compounds **2** (Table 2, entries 18−21 and Figure 4). In this

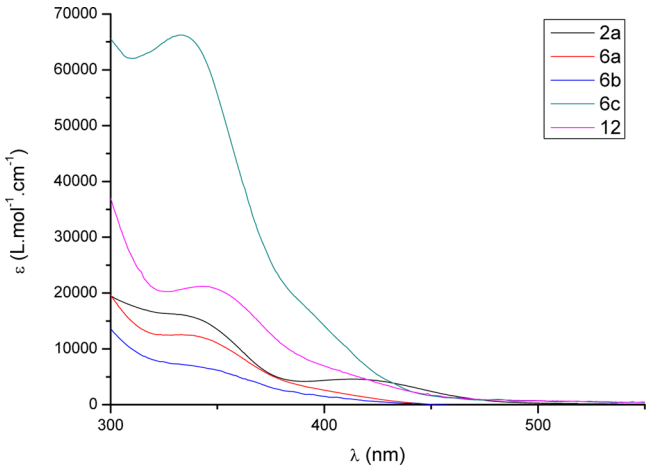

Figure 4. UV−vis absorption spectra of compounds **6a−c** and **12** (THF, concentration ca. 1×10^{-5} mol L^{-1}). UV−vis spectrum of compound **2a** recorded in the same conditions is included for comparison.

case for solubility reasons, the spectra were recorded in THF. The LF and MLCT bands observed in compounds **2** are replaced by a single absorption at ∼330−340 nm, assigned by TD-DFT calculations to a combination of HOMO to LUMO (53%) and HOMO−1 to LUMO (29%) transitions.

The frontier molecular orbitals distribution of **6a** (Figure 5) is similar to that depicted in Figure 2 for **2a**, with the HOMO and HOMO−1 centered on the metal fragment and the LUMO mostly located on the heterocyclic moiety. As a consequence, replacement of the mesityl groups by methyl groups in **6a** should affect the LUMO more; this in fact causes a rise in energy (−1.56 eV in **2a** but −1.40 eV in **6a**), whereas the HOMO hardly changes (−4.86 eV in **2a** and −4.80 eV in **6a**). The increase in the HOMO−LUMO gap could explain the strong blue shift observed for the MLCT band in **6a−d** compared to their IMes counterparts **2**. The UV−vis spectrum of bis-allenyl metal complex **12** derived from a bis-NHC carbene tethered with a flexible (C_3H_6) alkyl chain (entry 27 in Table 2) follows a similar pattern.

Reactivity. In agreement with our preliminary studies[6] the metal allenyls prepared through this work are essentially unreactive toward nucleophiles/electrophiles in the ground state. However, their zwitterionic character and the fact that the

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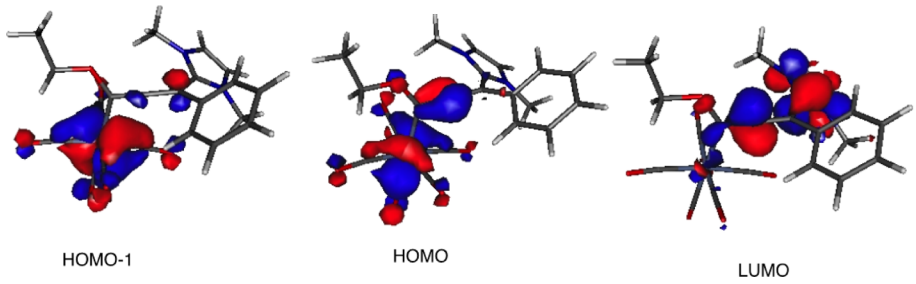


Figure 5. Calculated HOMO−1, HOMO, and LUMO orbitals of compound **6a** (isosurface value 0.04).

HOMO is mostly localized on the metal fragment makes them interesting substrates on which to test electron-transfer reactions. In this context, their electrochemical properties were addressed first. Thus, cyclic voltammograms of **2a**, **2c**, and **6a** were measured in CH_3CN solution with tetrabutylammonium perchlorate as supporting electrolyte, using Ag/AgCl as reference electrode (data are collected in Table 3 and shown in Figure 6). All show three main oxidation events, accompanied by other low-intensity waves in the case of the IMes derivatives. To gain more information about the oxidation process, a DFT investigation (B3LYP/def2-SVP) was conducted on **2a** and **6a**. As expected, the calculations assign the first oxidation wave in both cases to the loss of one electron from the metal-centered HOMO, leading to a radical cation in which the electronic density is still mainly located on the metal fragment (spin densities 0.98 e^- for **2a**$^{\bullet+}$ and 1.03 e^- for **6a**$^{\bullet+}$, respectively). Data in Table 3 also indicate that the change of the metal (Cr/W) increases the E_{pa} values, whereas the replacement of the mesityl groups by methyl groups in the imidazolium moiety facilitates the first oxidation of the complex.

Table 3[a]

compound	E_{pa}^1	E_{pa}^2	E_{pa}^3
2a	0.51	0.88[b]	1.42 (sh 1.11)
2c	0.60	1.28	
6a	0.36	0.88[b]	1.43

[a]Oxidation potentials in CH_3CN/0.1M[^{n}Bu$_4$N]ClO_4; 298 K, Ag/AgCl 3 M as reference and a Pt wire counter electrode (scan rate 0.1 V/s). [b]$E_{1/2}$.

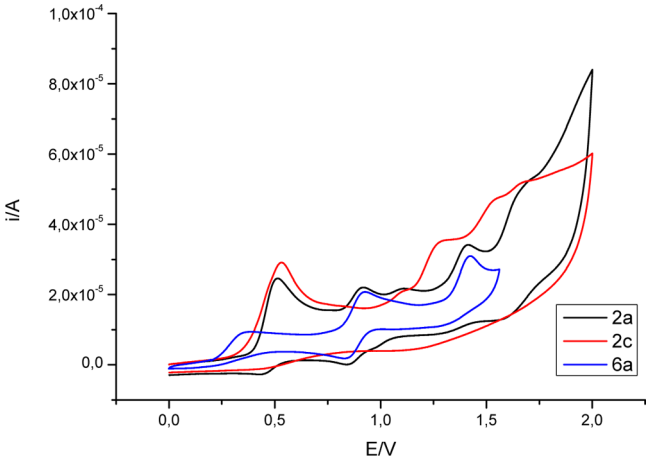
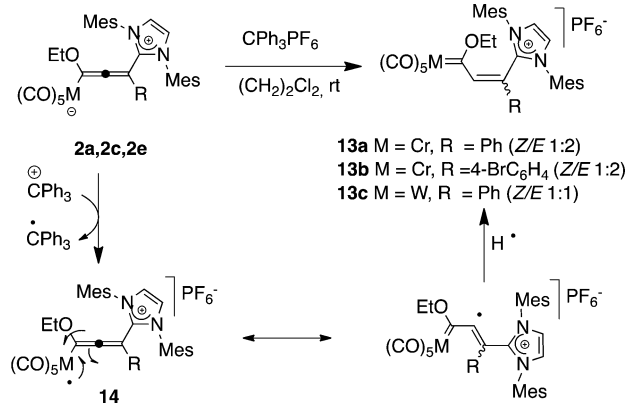


Figure 6. Cyclic voltammograms of **2a**, **2c**, and **6a** in CH_3CN/0.1 M [NBu_4]ClO_4 using Ag/AgCl 3 M as reference and a Pt wire counter electrode (scan rate 0.1 V/s).

Chemical reactivity toward the oxidant [Ph_3C]PF_6 was tested next. Reaction with chromium or tungsten alkenyl complexes **2a**, **2c**, and **2e**, in 1,2-dichloroethane at room temperature led quantitatively to the α,β-unsaturated Fischer carbenes **13** as mixtures of *Z*/*E* isomers (Scheme 6). Consistent with the above discussion about the oxidation process, the reactions could be interpreted as involving initial loss of one electron from the metal fragment to give the radical cation **14**, followed by capture of a hydrogen radical at the conjugated position (presumably from the solvent). Similar reactivity was observed using [Cp_2Fe] (PF_6) in THF as oxidant, although with lower yields due to the extensive oxidation of the reaction products.

Scheme 6



The structure of compounds **13a−c** was established by spectroscopic analysis. Being Fischer carbenes, the ^{13}C NMR spectra of the Cr(0) complexes **13a−b** show the characteristic signals for the C−M carbon at ca. 335 ppm together with those of the CO ligands (CO_{trans} ca. 224 ppm, CO_{cis} ca. 215 ppm). These signals are deshielded, as expected, in the case of the W(0) complex **13c** (305 ppm for the C−W and 202 and 196 ppm for the CO ligands, respectively). Also characteristic are the signals corresponding to the methylene protons of the ethoxy group that appear as quartets in the range of 4.3−5.2 ppm. The different solubility of the *Z*/*E* isomers allowed the confirmation of the structure of ***Z*-13a** by X-ray diffraction (Figure 7). A suitable crystal of ***Z*-13a**·$CHCl_3$, obtained by $CHCl_3$/pentane liquid diffusion, was used for X-ray structure determination. ***Z*-13a**·$CHCl_3$ shows two independent molecules in the asymmetric unit. In the crystal, the alkene moiety is distorted from planarity for both independent cations, with C(2)−C(6)−C(7)−C(8) and C(21)−C(6)−C(7)−C(8) torsion angles of 12.4(8)/10.0(8)° and 10.9(5)/ 9.0(5)°,

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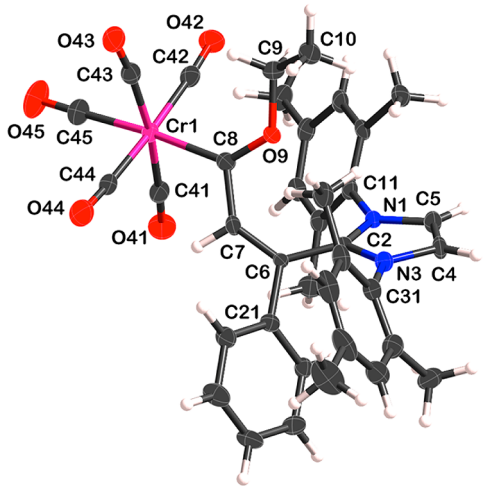

Figure 7. Thermal ellipsoid plot (50% probability level) and labeling scheme of one of the two independent cations of **Z-13a**·$CHCl_3$. Selected bond distances (Å): Cr(1)−C(8) 2.051(5), C(2)−C(6) 1.474(6), C(6)−C(7) 1.360(6), C(6)−C(21) 1.490(6), C(7)−C(8) 1.473(6).

respectively. Compared to the starting allenyl complex **2a** the distance Cr−C distance is reduced (from 2.18 to 2.05 Å in **13a**), but the Csp^2−NHC distances are almost identical (1.46 Å in **2a** and 1.47 Å in **13a**).

CONCLUSIONS

In summary, a series of of chiral (racemic), stable, formally neutral, zwitterionic mono- and bimetallic chromium and tungsten allenyls can be prepared in quantitative yield by addition of NHCs to Cr(0) and W(0) alkynyl Fischer carbenes. The reaction provides an example of the use of different types of NHCs as simple nucleophiles in C−C bond forming reactions. A study of the electronic properties of the metal allenyls prepared through this work shows that their UV−vis spectra are influenced by the structure of the heterocyclic moiety derived from the NHC (ring size, substituents on the N-atoms) and by the nature of the metal fragment (Cr/W). Although our previous investigations showed that this new class of compounds was only reactive in the excited (T_1) state, their reductor character allows them to participate in electron-transfer reactions in the ground state, leading to a new type of α,β-unsaturated Fischer carbenes.

EXPERIMENTAL GENERAL

Flame-dried glassware was used for moisture-sensitive reactions, and anhydrous solvents were taken from a Pure Solvent PS-MD-5 apparatus. In the synthesis of the carbene precursors, silica gel (Merck: 230−400 mesh) was used as stationary phases for purification of crude reaction mixtures by flash column chromatography. NMR spectra were recorded at 25 °C in $CDCl_3$ on a 300 MHz (300 MHz for ^{1}H, 75 MHz for ^{13}C) and 500 MHz (500 MHz for ^{1}H, 126 MHz for ^{13}C) and 700 MHz (700 MHz for ^{1}H, 176 MHz for ^{13}C) spectrometers. Chemical shifts are given in parts per million relative to $CDCl_3$ (^{1}H, 7.27 ppm and ^{13}C, 77.00 ppm). IR spectra were taken on a mid-IR (8000−400 cm^{-1}) spectrometer as solid films by slow evaporation of the solvent using the attenuated total reflectance (ATR) technique. High-resolution (HR) MS experiments were conducted on an Accurate Mass Q-TOF system. UV−vis spectra were recorded in Et_2O or THF in concentrations of 1×10^{-4} M on an Agilent Technologies Cary 60 spectrometer, using quartz cells. Cyclic voltammograms were recorded at room temperature from CH_3CN solutions (dry and free of acid traces) containing 0.1 M $[NBu_4]ClO_4$ as supporting electrolyte, using an AUTOLAB PGSTAT302N potentiostat and Ag/AgCl 3 M as reference and a Pt wire counter electrode (scan rate 0.1 V/s).

Commercially available reagents were used without further purification. Compounds **1a** (M = Cr, R = Ph),[20] **1b** (M = Cr, R^1 = Fc),[21] **1c** (M = W, R = Ph),[20b] **1f** (M = Cr, R = 4-methyl),[22] **1g** (M = Cr, R = 4-methoxy),[22] **1h** (M = Cr, R = 4-dimethylamino),[23] **1j** (M = W, R = 4-methyl),[24] **2a**,[6] **2b**,[6] **2c**,[6] **3a**,[6] **4a**,[16d] **4b**,[16d] **8a**,[25] **8b**,[26] **8c**,[26] and **11**[27] were prepared according to reported procedures. For experimental details of the synthesis and characterization of Fischer alkynyl carbene complexes **1d** (M = Cr, R = 2-thienyl), **1e** (M = Cr, R = 4-Br) and **1i** (M = Cr, R = 4-CF_3) see the Supporting Information.

General Procedure for the Synthesis of Compounds 2, 3, 9, and 10. Under argon atmosphere, a solution of the corresponding alkynyl Fischer carbene **1** or bis-alkynyl Fischer carbene **8** and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes) or 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (SIMes) in pentane (previously distilled and degassed) was stirred at room temperature. The reaction was accompanied by a color change from red to yellow and the subsequent formation of a yellow precipitate. The solvent was decanted, and the obtained yellow solid washed with dry pentane and dried in vacuum. Compounds **2**, **3**, **9**, and **10** are stable in the solid state at room temperature and in solution in Et_2O, THF, and hexanes but dissociate to some extent to the starting components when left to stand in CH_2Cl_2 or CH_3CN solution. Samples in $CDCl_3$ solution are stable for their NMR analysis, although they slowly revert to some extent to the starting reagents if the solution is left to stand at room temperature.

Synthesis of ***2d****.* From a solution of alkynyl carbene **1d** (50 mg, 0.14 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (55 mg, 0.18 mmol) in 4 mL of pentane, **2d** (94 mg, quantitative yield) was obtained after 20 min at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (s, 2H, NC*H*=C*H*N), 6.95−6.87 (m, 4H, CH_{arom}), 6.87−6.80 (m, 1H, CH_{arom}), 6.75−6.64 (m, 2H, CH_{arom}), 2.63−2.50 (m, 1H, OC$H_2$$CH_3$), 2.30 (s, 6H, CH_3), 2.24−2.14 (m, 12H, CH_3), 1.96−1.86 (m, 1H, OC$H_2$$CH_3$), 0.76 (t, J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 226.2 (CO), 220.5 (CO), 199.6 (CCr), 159.2 (C2), 150.9 (C$_{arom}$), 140.6 (C$_{arom}$), 137.6 (C$_{arom}$), 135.2 (C$_{arom}$), 134.5 (C$_{arom}$), 134.2 (C$_{arom}$), 131.9 (C$_{arom}$), 129.9 (CH), 129.7 (CH), 129.2 (CH), 128.0 (CH), 124.1 (CH), 122.2 (CH), 120.4 (CH), 79.2 (C3), 67.6 (CH_2), 21.0 (CH_3), 18.5 (CH_3), 18.3 (CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3442, 2973, 2923, 2041, 1958, 1907, 1857, 1485, 1453, 668. Electrospray ionization (ESI) HRMS m/z: calcd. for $C_{35}H_{33}CrN_2O_6S$ $[M + H]^+$ 661.1464; found 661.1460.

Synthesis of ***2e****.* From a solution of alkynyl carbene **1e** (50 mg, 0.12 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (42 mg, 0.14 mmol) in 4 mL of pentane, **2e** (86 mg, quantitative yield) was obtained after 1 h at room temperature. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.11 (s, 2H, NC*H*=C*H*N), 7.07 (d, J = 8.2 Hz, 2H, CH_{arom}), 6.91−6.89 (m, 6H, CH_{arom}), 2.57−2.49 (m, 1H, OC$H_2$$CH_3$), 2.29 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.02−1.94 (m, 1H, OC$H_2$$CH_3$), 0.75 (t, J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 225.9 (CO), 220.3 (CO), 199.5 (CCr), 160.3 (C2), 150.3 (C$_{arom}$), 140.8 (C$_{arom}$), 135.8 (C$_{arom}$), 135.0 (C$_{arom}$), 134.4 (C$_{arom}$), 131.8 (C$_{arom}$), 130.4 (CH$_{arom}$), 129.8 (CH), 129.3 (CH), 128.4 (C$_{arom}$), 122.4 (CH), 119.4 (C$_{arom}$), 83.2 (C3), 67.8 (CH_2), 21.0 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3448, 2925, 2041, 1958, 1912, 1867, 1485, 1450, 667. ESI-HRMS m/z: calcd for $C_{37}H_{34}BrCrN_2O_6$ $[M + H]^+$ 733.1050; found 733.1028.

Synthesis of ***2f****.* From a solution of alkynyl carbene **1f** (50 mg, 0.14 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (52 mg, 0.17 mmol) in 5 mL of pentane, **2f** (94 mg, quantitative yield) was obtained after 20 min at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2H, NC*H*=C*H*N), 6.94−6.84 (m, 5H, CH_{arom}), 6.79−6.71 (m, 2H, CH_{arom}), 2.60−2.47 (m, 1H, OC$H_2$$CH_3$), 2.27 (s, 6H, CH_3), 2.25−2.21 (2 s, 12H, CH_3), 2.16 (s, 3H, CH_3), 2.01−1.89 (m, 1H, OC$H_2$$CH_3$), 0.74 (t, J = 7.0 Hz, 3H,

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OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 226.2 (CO), 220.5 (CO), 200.5 (CCr), 159.6 (C2), 151.0 (C_{arom}), 140.5 (C_{arom}), 135.3 (C_{arom}), 135.1 (C_{arom}), 134.5 (C_{arom}), 133.9 (C_{arom}), 132.0 (C_{arom}), 129.6 (CH), 129.1 (CH), 128.0 (CH), 126.8 (CH), 122.2 (CH), 84.4 (C3), 67.4 (CH_2), 21.0 (CH_3), 20.9 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3442, 2924, 2040, 1956, 1909, 1864, 1486, 1448, 668. ESI-HRMS m/z: calcd for $C_{38}H_{37}CrN_2O_6$: 669.2051 $[M + H]^+$; found 669.2047.

Synthesis of ***2g***. From a solution of alkynyl carbene **1g** (60 mg, 0.16 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (56 mg, 0.18 mmol) in 6 mL of pentane, **2g** (110 mg, quantitative yield) was obtained after 1 h at room temperature. ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 2H, NC*H*=C*H*N), 6.96−6.84 (m, 6H, CH_{arom}), 6.53−6.44 (m, 2H, CH_{arom}), 3.68 (s, 3H, OCH_3), 2.58−2.49 (m, 1H, OCH_2CH_3), 2.28 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.02−1.93 (m, 1H, OCH_2CH_3), 0.74 (t, J = 7.0 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 226.1 (CO), 220.5 (CO), 200.8 (CCr), 159.4 (C2), 151.0 (C_{arom}), 140.4 (C_{arom}), 135.2 (C_{arom}), 134.5 (C_{arom}), 132.0 (C_{arom}), 130.0 (C_{arom}), 129.7 (CH), 129.1 (CH), 128.2 (CH), 122.2 (CH), 112.8 (CH), 84.0 (C3), 67.3 (CH_2), 55.2 (OCH_3), 21.0 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 15.1 (CH_2CH_3). IR (ATR): ν cm^{-1} 3447, 2966, 2925, 2040, 1959, 1902, 1865, 1506, 1485, 1448, 668. ESI-HRMS m/z: calcd for $C_{38}H_{37}CrN_2O_7$ $[M + H]^+$ 685.2001; found 685.2016.

Synthesis of ***2h***. From a solution of alkynyl carbene **1h** (50 mg, 0.13 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (46 mg, 0.15 mmol) in 4 mL of pentane, **2h** (91 mg, quantitative yield) was obtained after 30 min at room temperature. ^1H NMR (700 MHz, $CDCl_3$) δ 7.06 (s, 2H, NC*H*=C*H*N), 6.91−6.83 (m, 6H, CH_{arom}), 6.33 (d, J = 8.0 Hz, 2H, CH_{arom}), 2.80 (s, 6H, NCH_3), 2.58−2.53 (m, 1H, OCH_2CH_3), 2.27 (s, 6H, CH_3), 2.23 (s, 12H, CH_3), 1.95−1.90 (m, 1H, OCH_2CH_3), 0.74 (t, J = 6.9 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 226.3 (CO), 220.6 (CO), 201.0 (CCr), 158.9 (C2), 151.5 (C_{arom}), 148.9 (C_{arom}), 140.2 (C_{arom}), 135.2 (C_{arom}), 134.6 (C_{arom}), 132.1, 129.7 (CH), 129.1 (CH), 127.8 (CH), 125.6 (C_{arom}), 122.1 (CH), 112.0 (CH), 84.6 (C3), 67.2 (CH_2), 40.8 (NCH_3), 21.0 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3414, 2979, 2923, 2111, 2046, 1919, 1865, 1524, 1484, 1445, 665. ESI-HRMS m/z: calcd for $[M + H]^+$ $C_{39}H_{40}CrN_3O_6$ 698.2317; found 698.2318.

Synthesis of ***2i***. From a solution of alkynyl carbene **1i** (55 mg, 0.13 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (48 mg, 0.16 mmol) in 5 mL of pentane, **2i** (96 mg, quantitative yield) was obtained after 40 min at room temperature. ^1H NMR (300 MHz, $CDCl_3$) δ 7.23−7.17 (m, 2H, NC*H*=C*H*N), 7.16−7.10 (m, 4H, CH_{arom}), 6.90−6.83 (m, 4H, CH_{arom}), 2.62−2.51 (m, 1H, OCH_2CH_3), 2.26 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.05−1.93 (m, 1H, OCH_2CH_3), 0.76 (t, J = 7.0 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 226.3 (CO), 220.6 (CO), 199.6 (CCr), 160.7 (C2), 150.5 (C_{arom}), 141.3 (C_{arom}), 135.4 (C_{arom}), 134.8 (C_{arom}), 132.1 (C_{arom}), 130.2 (CH), 129.6 (CH), 127.3 (CH), 124.7 (CH), 122.9 (CH), 83.6 (C3), 68.4 (CH_2), 21.3 (CH_3), 19.0 (CH_3), 18.8 (CH_3), 15.5 (CH_2CH_3). IR (ATR): ν cm^{-1} 3441, 2973, 2925, 2042, 1962, 1911, 1874, 1484, 1449, 1325, 665. ESI-HRMS m/z: calcd for $C_{38}H_{34}CrF_3N_2O_6$ $[M + H]^+$ 723.1770; found 723.1769.

Synthesis of ***3b***. From a solution of alkynyl carbene **1e** (50 mg, 0.12 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (43 mg, 0.14 mmol) in 5 mL of pentane, **3b** (88 mg, quantitative yield) was obtained after 30 min at room temperature. ^1H NMR (300 MHz, $CDCl_3$) δ 7.12−6.98 (m, 2H, CH_{arom}), 6.93−6.77 (m, 6H, CH_{arom}), 4.40−4.22 (m, 2H, NCH_2), 4.02−3.86 (m, 2H, NCH_2), 2.62−2.51 (m, 1H, OCH_2CH_3), 2.43 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.05−1.94 (m, 1H, OCH_2CH_3), 0.75 (t, J = 7.0 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 226.2 (CO), 220.2 (CO), 196.7 (CCr), 170.5 (C2), 157.4 (C_{arom}), 140.0 (C_{arom}), 136.5 (C_{arom}), 135.7 (C_{arom}), 134.6 (C_{arom}), 133.6 (C_{arom}), 130.6 (CH), 130.2 (CH), 129.9 (C_{arom}), 129.7 (CH), 120.0 (C_{arom}), 84.3 (C3), 69.5 (CH_2 CH_3), 50.4 (NCH_2), 21.3 (CH_3), 18.9 (CH_3), 15.6 (CH_2CH_3). IR (ATR): ν cm^{-1} 3423, 2971, 2923, 2043, 1963, 1922, 1865, 1516, 1490, 1459, 667. ESI-HRMS m/z: calcd for $C_{37}H_{36}BrCrN_2O_6$ $[M + H]^+$ 737.1145; found 735.1150.

Synthesis of ***3c***. From a solution of alkynyl carbene **1c** (50 mg, 0.10 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (35 mg, 0.11 mmol) in 5 mL of pentane, **3c** (87 mg, quantitative yield) was obtained after 30 min at room temperature. ^1H NMR (300 MHz, $CDCl_3$) δ 6.98 (m, 2H, CH_{arom}), 6.95−6.87 (m, 3H, CH_{arom}), 6.83 (m, 2H, CH_{arom}), 6.75 (m, 2H, CH_{arom}), 4.33 (m, 2H, NCH_2), 3.93 (m, 2H, NCH_2), 2.46 (s, 6H, CH_3), 2.36 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 1.85 (dd, J_1 = 9.1, J_2 = 7.0 Hz, 2H, OCH_2CH_3), 0.71 (t, J = 7.0 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 207.2 (CW), 205.4 (CO), 201.1 (CO), 170.0 (C2), 146.8 (C_{arom}), 139.4 (C_{arom}), 136.2 (C_{arom}), 136.0 (C_{arom}), 134.4 (C_{arom}), 133.1 (C_{arom}), 129.7 (CH), 129.4 (CH), 127.4 (CH), 127.2 (CH), 125.8 (CH), 86.0 (C3), 68.4 (CH_2CH_3), 50.0 (NCH_2), 20.9 (CH_3), 18.8 (CH_3), 18.7 (CH_2CH_3), 15.1 (CH_3). IR (ATR): ν cm^{-1} 3448, 2925, 2053, 1968, 1907, 1845, 1608, 1520, 1496, 590. ESI-HRMS m/z: calcd for $C_{37}H_{37}N_2O_6W$ $[M + H]^+$; 789.2161; found.789.2164.

General Procedure for the Synthesis of Compounds 5a,b. To a solution of alkynyl carbene **1a** and the BF_4 salt **4** in 5 mL of dry pentane was added KHMDS (1 M in THF). The reaction product precipitates in the medium once it is formed. After 30 min at room temperature, the solvent was removed, and the precipitated orange solid was washed with dry pentane. Compounds **5** are perfectly stable in the solid state at room temperature and in solution in Et_2O, THF, and hexanes but slowly decompose when left to stand in CH_2Cl_2 or $CHCl_3$ solution. Samples in $CDCl_3$ solution are stable for their NMR analysis.

Synthesis of ***5a***. From **1a** (43 mg, 0.12 mmol), BF_4 salt **4a** (50 mg, 0.12 mmol), and KHMDS (134 μL, 0.13 mmol, 1 M in THF), **5a** (96 mg, quantitative yield) was obtained as dark orange solid. ^1H NMR (300 MHz, $CDCl_3$) δ 6.94−6.58 (m, 9H, CH_{arom}), 4.04−3.84 (m, 2H, NCH_2), 3.61−3.46 (m, 2H, NCH_2), 2.57 (s, 6H, CH_3), 2.49−2.39 (m, 2H, $CH_2CH_2CH_2$), 2.24−2.14 (m, 12H, CH_3), 2.11−1.95 (m, 1H, OCH_2CH_3), 1.69−1.55 (m, 1H, OCH_2CH_3), 0.52 (t, J = 6.9 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 176 MHz) δ 226.1 (CO), 220.4 (CO), 208.4 (CCr), 167.8 (C2), 159.3 (C_{arom}), 139.0, 138.7, 138.7, 132.9, 130.0, 129.7, 127.1, 127.0, 125.0, (all CH_{arom}), 91.4 (C3), 66.9 (CH_2CH_3), 50.7 (NCH_2), 21.6 (CH_2), 20.8 (CH_3), 19.5 (CH_3), 19.4 (CH_3), 15.0 (CH_2CH_3). IR (ATR): ν cm^{-1} 3447, 2923, 2857, 2041, 1965, 1904, 1849, 1539, 1081, 1037, 668. ESI-HRMS m/z: calcd for $C_{38}H_{39}CrN_2O_6$ $[M + H]$ 671.2208; found 671.2203.

Synthesis of ***5b***. From **1a** (39 mg, 0.11 mmol), BF_4 salt **4b** (60 mg, 0.14 mmol), and KHDMS (156 μL, 0.16 mmol, 1 M in THF), **5b** (92 mg, quantitative yield) was obtained as dark orange solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.03−6.83(m, 7H, CH_{arom}), 6.65−6.51 (m, 2H, CH_{arom}), 4.19−4.03 (m, 2H, NCH_2), 3.95−3.82 (m, 2H, NCH_2), 2.64 (s, 6H, CH_3), 2.41 (s, 3H, CH_3), 2.24 (s, 9H, CH_3), 2.08−1.96 (m, 5H, $NCH_2CH_2CH_2CH_2N$ and OCH_2CH_3), 1.79−1.74 (m, 1H, OCH_2CH_3), 0.50 (t, J = 6.9 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 226.3 (CO), 220.2 (CO), 216.3 (CCr), 157.6 (C2), 138.9 (C_{arom}), 138.1 (C_{arom}), 133.5 (C_{arom}), 130.8 (C_{arom}), 130.4 (C_{arom}), 128.2 (C_{arom}), 127.4 (CH), 125.2 (CH), 93.1 (C3), 68.1 (CH_2CH_3), 56.8 (NCH_2), 25.3 (CH_2CH_2), 24.0 (CH_2CH_2), 20.7 (CH_3), 20.4 (CH_3), 15.19 (CH_2CH_3). IR (ATR): ν cm^{-1} 3443, 2971, 2924, 2040, 1964, 1905, 1855, 1519, 1481, 1438, 1209, 1081, 1053, 699.45; ESI-HRMS m/z: calcd for $C_{39}H_{41}CrN_2O_6$ $[M + H]^+$ 685.2365; found 685.2365.

General Procedure for the Synthesis of Compounds 6. *Method A. Synthesis of 1,3-Dimethylimidazol-2-ylidene (Me_2Im).* This compound was obtanied by a modification of the previously reported method.[17] 1,3-Di(methyl)imidazolium iodide[17] (32.0 g, 0.143 mol) and NaH (3.43 g, 0.143 mol) were dissolved at −78 °C in 200 mL of liquid NH_3. The ammonia was previously dried by passing the gas successively through a flask containing KOH flakes and through another containing 3 Å molecular sieves. The reaction mixture was stirred for 1 h at this temperature before the temperature was raised to room temperature to remove NH_3. The last traces of ammonia were eliminated in vacuo at room temperature. The yellow precipitate obtained was carefully distilled (avoiding overheating of the oil bath)

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at 150 °C and 1 × 10^{-2} mbar into a flask that was cooled with liquid nitrogen to give 1.87 g (43%) of a red, crystalline solid (at −30 °C). ^{1}H NMR (C_6D_6) δ 6.70 (s, 2H, NCHCHN), 3.43 (s, 6 H, CH_3). ^{13}C{^{1}H}NMR (C_6D_6) δ 214.55 (NCN), 120.24 (NCCN), 37.35 (CH_3). The free carbene was stored in the fridge as a solution in dry benzene (1M).

Reaction of (Me$_2$Im) with Alkynyl Carbenes. Under argon atmosphere, to a solution of the corresponding alkynyl carbene **1** (1 equiv) in pentane (previously distilled and degassed) was added the 1,3-dimethylimidazol-2-ylidene (Me_2Im; 2 equiv, 1 M solution in benzene), and the mixture was stirred at room temperature. The reaction was accompanied by the formation of a brownish precipitate. The solvent was decanted, and the obtained solid washed with dry pentane and dried in vacuum.

Method B. Generation in situ of 1,3-dimethylimidazol-2-ylidene (Me_2Im) was done according to the reported method.[18] 1,3-Dimethylimidazolium iodide (2.10 mmol) and KH (13.0 mmol) were placed in a Schlenk tube, and the suspension was stirred in THF (3 mL). Slow gas evolution was observed. After 4 h, effervescence had stopped, and Et_2O (10 mL) was added to ensure nearly complete precipitation of the generated potassium iodide. The THF/Et_2O solution of the 1,3-dimethylimidazol-2-ylidene was filtered and added dropwise to a 50 mL flask containing the carbene complex (1.00 mmol) dissolved in Et_2O (5 mL). The precipitate obtained was washed with dry pentane. Compounds **6** are perfectly stable in the solid state at room temperature and in solution in Et_2O, THF, and hexanes but slowly decompose when left to stand in CH_2Cl_2 or $CHCl_3$ solution. Samples in $CDCl_3$ solution are stable for their NMR analysis.

*Synthesis of **6a**. Following Method A.* From **1a** (50 mg, 0.14 mmol) in 5 mL of pentane and 1,3-dimethylimidazol-2-ylidene (1 M solution in benzene) (0.32 mL, 0.32 mmol). Compound **6a** was obtained as brownish powder (62 mg, quantitative yield).

Following Method B. From **1a** (100 mg; 0.29 mmol), potassium hydride (151 mg, 3.77 mmol), and 1,3 dimethylimidazolium iodide (134 mg, 0.60 mmol) in 0.85 mL of THF, compound **6a** (127 mg, quantitative yield) was obtained after 15 min at room temperature.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26−7.24 (m, 2H, CH_{arom}), 7.20−7.17 (m, 2H, CH_{arom}), 7.09−7.07 (m, 1H, CH_{arom}), 6.91 (s, 2H, NC*H*=C*H*N), 4.01 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 3.74 (s, 6H, CH_3), 1.39 (t, J = 7.1 Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 226.4 (CO), 220.7 (CO), 176.0 (CCr), 147.3 (C2), 146.4 (C_{arom}), 143.8 (C_{arom}), 128.0 (CH), 124.7 (CH), 124.4 (CH), 121.5 (CH), 106.5 (C3), 63.8 (CH_2CH_3), 37.2 (NCH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3424, 2973, 2038, 1963, 1903, 1859, 1576, 1515, 1483, 1446, 1237, 661. ESI-HRMS m/z: calcd for $C_{21}H_{18}CrN_2O_6$ 446.3735; found 306.2094 [M-5(CO)].

*Synthesis of **6b**.* Method A: From 60 mg (0.16 mmol) of **1f** in 5 mL of pentane and 1,3-dimethylimidazol-2-ylidene (1 M solution in benzene; 0.25 mL, 0.25 mmol), compound **6b** was obtained as dark orange powder (60 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, J = 8.1 Hz, 2H, CH_{arom}), 7.07 (d, J = 8.1 Hz, 2H, CH_{arom}), 6.90 (s, 2H, NC*H*=C*H*N), 4.05−3.95 (m, 2H, OCH_2CH_3), 3.72 (s, 6H, CH_3), 2.30 (s, 3H, CH_3), 1.38 (t, J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 226.4 (CO), 220.9 (CO), 176.1 (CCr), 146.5 (C2), 143.8 (C_{arom}), 143.3 (C_{arom}), 134.1 (C_{arom}), 128.7 (CH), 125.2 (CH), 121.5 (CH), 106.4 (C3), 63.8 (CH_2CH_3), 37.2 (NCH_3), 21.0 ($ArCH_3$), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3424, 3124, 2927, 2037, 1948, 1906, 1854, 1664, 1579, 1453, 1077, 1037, 665. ESI-HRMS m/z: calcd for $C_{22}H_{21}N_2O_6Cr$ [M + H]$^+$ 461.0799; found 461.0799.

*Synthesis of **6c**.* Method B. From 106 mg (0.47 mmol) of 1,3-di(methyl)imidazolium iodide, 115 mg (2.86 mmol) of potassium hydride, and 80 mg (0.22 mmol) of **1d** in 1 mL of dry diethyl ether, compound **6c** was obtained as pale yellow powder (96 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23−7.22 (m, 2H, CH_{arom}), 7.17−7.16 (m, 1H, CH_{arom}), 6.92 (s, 2H, NC*H*=C*H*N), 4.03−3.90 (m, 2H, OCH_2CH_3), 3.69 (s, 6H, CH_3), 1.40−1.35 (m, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 226.0 (CO), 221.0 (CO), 178.7 (CCr), 146.6 (C2), 144.9 (C_{arom}), 135.5 (C_{arom}), 127.8 (CH), 124.5 (CH), 121.5 (CH), 120.9 (CH), 106.2 (C3), 63.8 (CH_2CH_3), 37.1 (NCH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1}: 3446, 2974, 2926, 2038, 1964, 1907, 1844, 1576, 1114, 1074, 667. ESI-HRMS m/z: calcd for $C_{19}H_{17}CrN_2O_6S$ [M + H]$^+$ 453.0207; found 453.0196.

*Synthesis of **6d**.* Method B: From 95 mg (0.42 mmol) of 1,3-di(methyl)imidazolium iodide, 104 mg (2.69 mmol) of potassium hydride, and 100 mg (0.20 mmol) of **1j** in 1 mL of dry diethyl ether, compound **6d** was obtained as brown powder (117 mg, quantitative yield). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H, CH_{arom}), 7.09 (d, J = 8.0 Hz, 2H, CH_{arom}), 6.91 (s, 2H, NC*H*=C*H*N), 4.04−3.95 (m, 2H, OCH_2CH_3), 3.70 (s, 6H), 2.32 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 205.7 (CO), 201.7 (CO), 182.4 (CW), 145.7 (C2), 143.5 (C_{arom}), 134.9 (C_{arom}), 133.5 (C_{arom}), 128.7 (CH), 127.1 (CH), 121.4 (CH), 105.7 (C3), 63.9 (CH_2CH_3), 37.3 (NCH_3), 21.2 ($ArCH_3$), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1}: 3424, 2925, 2050, 1961, 1900, 1855, 1644, 1577, 1508, 1450, 1075, 821, 584. ESI-HRMS m/z: calcd for $C_{22}H_{21}N_2O_6W$ [M + H]$^+$ 593.0907; found 593.0900.

*Synthesis of Bis-Allenyl Complexes **9** and **10**.* These were prepared following the general methodology described for compounds **2** but using THF as solvent. The solid obtained after the removal of the solvent under vacuum was washed several times with pentane.

*Synthesis of **9a**.* From a solution of alkynyl carbene **8a** (50 mg, 0.08 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (54 mg, 0.18 mmol) in 5 mL of THF, compound **9a** (83 mg, 96%) was obtained after 15 min at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13−6.63 (m, 13.18H), 6.61−6.20 (m, 1.46H), 6.12−6.11 (m, 0.96H), 6.02−5.80 (m, 0.4H), (NC*H*=C*H*N, CH_{arom}), 2.69−2.59 (m, 2H, OCH_2CH_3), 2.33 (s, 7.08H), 2.27 (s, 5.86H), 2.21 (s, 4.83H), 2.17 (s, 1.71H), 2.10 (s, 10.40H), 1.91 (s, 6.12H), (CH_3), 1.64−1.59 (m, 2H, OCH_2CH_3), 0.88 (t, J = 6.9 Hz, 1.87H), 0.74 (t, J = 6.9 Hz, 3.60H), 0.59 (t, J = 7.0 Hz, 0.32H), (OCH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 176 MHz) δ 226.2 (CO), 226.0 (CO), 220.4 (CO), 219.8 (CO), 196.7 (CCr), 160.9 (C2), 150.2 (C_{arom}), 140.9 (CH), 136.5 (C_{arom}), 134.6 (C_{arom}), 134.1 (C_{arom}), 132.3 (C_{arom}), 130.0 (CH), 128.8 (CH), 126.4 (CH), 122.4 (CH), 83.2 (C2), 67.2 (CH_2CH_3), 21.1 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 15.3 (CH_2CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3442, 2974, 2924, 2041, 1959, 1906, 1867, 1485, 1449, 665. ESI-HRMS m/z: calcd for $C_{68}H_{63}Cr_2N_4O_{12}$ [M + H]$^+$ 1231.3296; found 1231.3252.

*Synthesis of **9b**.* From a solution of alkynyl carbene **8b** (50 mg, 0.07 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (44 mg, 0.15 mmol) in 4 mL of THF, compound **9b** (94 mg, quantitative yield) was obtained after 30 min at room temperature. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.15−6.82 (m, 20H, NC*H*=C*H*N, CH_{arom}), 2.65−2.56 (m, 2H, OCH_2CH_3), 2.25 (s, 36H, CH_3), 2.02−1.93 (m, 2H, OCH_2CH_3), 0.78 (t, J = 6.3 Hz, 6H, OCH_2CH_3). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 226.1 (CO), 220.5 (CO), 200.2 (CCr), 199.9 (C−Cr), 160.0 (C2), 150.6 (C_{arom}), 140.6 (C_{arom}), 135.1 (C_{arom}), 134.5 (C_{arom}), 131.9 (C_{arom}), 129.7 (CH), 129.1 (CH), 127.1 (CH), 125.7 (CH), 122.4 (CH), 84.2 (C3), 68.0 (CH_2CH_3), 21.0 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3443, 2973, 2922, 2041, 1958, 1906, 1867, 1488, 1451, 664. ESI-HRMS m/z: calcd for $C_{74}H_{67}Cr_2N_4O_{12}$ [M + H]$^+$ 1307.3625; found 1307.3660.

*Synthesis of **9c**.* From a solution of alkynyl carbene **8c** (50 mg, 0.07 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (51 mg, 0.17 mmol) in 5 mL of THF, compound **9c** (93 mg, quantitative yield) was obtained after 20 min at room temperature. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.10 (s, 2H, NC*H*=C*H*N), 7.09 (s, 2H, NC*H*=C*H*N), 7.00−6.95 (m, 4H, CH_{arom}), 6.93−6.88 (m, 8H, CH_{arom}), 6.45−6.40 (m, 4H, CH_{arom}), 2.63−2.56 (m, 2H, OCH_2CH_3), 2.30 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 2.25−2.20 (m, 24H, CH_3), 2.04−1.98 (m, 2H, OCH_2CH_3), 0.81−0.75 (m, 6H, OCH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 176 MHz) δ 226.1 (CO), 220.5 (CO), 220.4 (CO), 201.2 (CCr), 159.9 (C_{arom}), 155.4 (C_{arom}), 155.2 (C_{arom}), 150.0 (C_{arom}), 140.7 (C_{arom}), 140.6 (C_{arom}), 135.3 (C_{arom}), 135.1 (C_{arom}), 134.5 (C_{arom}), 134.5 (C_{arom}), 132.4 (C_{arom}), 132.1 (C_{arom}), 132.0 (C_{arom}), 131.9 (C_{arom}), 130.0 (CH), 129.7 (CH), 129.7 (CH), 129.2 (CH), 129.1 (CH), 129.1 (CH), 128.4 (CH), 128.1 (CH), 122.4 (CH), 122.3 (CH), 117.7 (CH), 117.5 (CH), 84.0 (C3), 67.6 (CH_2), 67.4 (CH_2CH_3), 21.1 (CH_3), 21.0 (CH_3), 18.6 (CH_3), 18.5 (CH_3),

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15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3444, 2973, 2924, 2041, 1959, 1907, 1868, 1495, 1451, 1233, 665. ESI-HRMS m/z: calcd for $C_{74}H_{67}Cr_2N_4O_{13}$ $[M + H]^+$ 1323.3574; found 1323.3515.

Synthesis of ***10a***. From a solution of alkynyl carbene **8a** (50 mg, 0.08 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (49 mg, 0.16 mmol) in 5 mL of THF, compound **10a** (70 mg, 89% yield) was obtained after 5 min at room temperature. ^1H NMR (700 MHz, $CDCl_3$) δ 7.03−6.66 (m, 9H), 6.49−6.43 (m, 0.7H), 6.39−6.33 (m, 0.5H), 6.01−5.93 (m, 0.9H), 5.82−5.71 (m, 0.8H), (CH_{arom}), 4.79−4.73 (m, 0.5H), 4.41−4.32 (m, 1H), 4.30−4.18 (m, 2.5H), 4.03−3.95 (m, 0.5), 3.88−3.70 (m, 3.5H), (NCH_2), 3.23−3.14 (m, 1H), 2.83−2.74 (m, 1H), (OCH_2CH_3), 1.61−2.00 (m, 36H, CH_3), 1.67−1.53 (m, 2H, OCH_2CH_3), 1.42−1.38 (m, 0.5H), 1.35−1.22 (m, 1.5H), 0.96−0.81 (m, 4H), (OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 226.0 (CO), 220.0 (CO), 219.9 (CO), 216.3 (CO), 193.4 (CCr), 184.2 (CCr), 170.0 (C2), 164.1 (C2), 156.3 (C_{arom}), 139.7 (C_{arom}), 139.3 (C_{arom}), 137.5 (C_{arom}), 137.1 (C_{arom}), 136.4 (C_{arom}), 136.2 (C_{arom}), 134.4 (C_{arom}), 134.3 (C_{arom}), 133.8 (C_{arom}), 133.4 (C_{arom}), 131.9 (C_{arom}), 131.3 (CH), 130.1 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 125.9 (CH), 83.8 (C3), 69.1 (CH_2CH_3), 68.5 (CH_2CH_3), 50.0 (NCH_2), 47.1 (NCH_2), 46.5 (NCH_2), 44.2 (NCH_2), 20.1 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 18.2 (CH_3), 17.9 (CH_3), 17.7 (CH_3), 15.5 (CH_2CH_3), 15.2 (CH_2CH_3), 14.1 (CH_2CH_3). IR (ATR): ν cm^{-1} 3775, 3699, 3660, 3634, 3576, 3454, 2923, 2042, 1909, 1860, 1829, 1604, 1520, 1493, 1444, 1382, 1356, 1284, 1213, 1067, 1036, 852, 666. ESI-HRMS m/z: calcd for $C_{58}H_{66}N_4O_2$ $[M\text{-}2(CrCO_5)]^+$ 850.5185; found 851.5195.

Synthesis of ***10b***. From a solution of alkynyl carbene **8b** (50 mg, 0.072 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (44 mg, 0.14 mmol) in 5 mL of THF, compound **10b** (88 mg, 94% yield) was obtained after 5 min at room temperature. ^1H NMR (700 MHz, $CDCl_3$) δ 7.04−6.93 (m, 6H, CH_{arom}), 6.85−6.82 (m, 6H, CH_{arom}), 6.76−6.72 (m, 4H, CH_{arom}), 4.32−4.28 (m, 4H, NCH_2), 3.97−3.90 (m, 4H, NCH_2), 2.62−2.54 (m, 2H, OCH_2CH_3), 2.46 (s, 10H, CH_3), 2.36 (s, 10H, CH_3), 2.18−2.20 (m, 16H, CH_3), 2.00−1.94 (m, 2H, OCH_2CH_3), 0.78−0.76 (m, 6H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 226.0 (CO), 220.0 (CO), 197.6 (CCr), 170.4 (C_{arom}), 164.1(C_{arom}), 156.8 (C_{arom}), 139.4 (C_{arom}), 138.4 (C_{arom}), 136.2 (C_{arom}), 134.3 (C_{arom}), 133.3 (C_{arom}), 129.8 (C_{arom}), 129.7 (CH), 129.5 (CH), 128.0 (CH), 125.6 (CH), 125.5 (CH), 84.9 (C3), 69.0 (CH_2), 68.9 (CH_2CH_3), 50.0 (CH_2CH_3), 20.9 (CH_3), 18.7 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 18.3 (CH_3), 15.3 (CH_2CH_3), 15.2 (CH_2CH_3). IR (ATR): ν cm^{-1} 3448, 2924, 2043, 1962, 1910, 1869, 1609, 1517, 1494, 1459, 1358, 1282, 1211, 1066, 1031, 666. ESI-HRMS m/z: calcd for $C_{74}H_{71}Cr_2$ N_4O_{12} $[M + H]^+$ 1312.3901; found 1312.3854.

Synthesis of Compound ***12***. The salt **11**[16d] (125 mg, 0.22 mmol) and KH (229 mg, 5.72 mmol) were placed in a Schlenk tube, and the suspension was stirred in THF (1 mL). Slow gas evolution was observed. After 4 h, effervescence had stopped, and Et_2O (2 mL) was added. The THF/Et_2O solution of the generated bis-NHC carbene was filtered and added dropwise via cannula to a 50 mL flask containing the carbene complex **1a** (76.2 mg, 0.22 mmol) dissolved in Et_2O (5 mL). The precipitate obtained was washed with dry pentane, to yield 118 mg (96%) of **12** as brown solid. ^1H NMR (700 MHz, $CDCl_3$) δ 7.23−7.19 (m, 4H), 7.13−7.06 (m, 6H), 7.02−6.95 (m, 2H), 6.89−6.81 (m, 4H), 6.76−6.72 (m, 2H), (CH_{arom} and NC*H*=C*H*N), 3.75−3.60 (m, 4H, NCH_2), 2.52−2.43 (m, 2H, CH_2), 2.36−2.33 (m, 2H, CH_2), 2.23 (s, 6H, CH_3), 2.19−2.16 (m, 2H, CH_2), 2.08−2.02 (m, 6H, CH_3), 1.99−1.95 (m, 6H, CH_3), 1.06−0.96 (m, 6H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 225.6 (CO), 224.7 (CO), 220.5 (CO), 211.4 (CCr), 202.4 (CCr), 184.2 (CCr), 175.9 (C_{arom}), 175.7 (C_{arom}), 146.5(C_{arom}), 146.3 (C_{arom}), 145.0 (C_{arom}), 141.5 (C_{arom}), 141.1 (C_{arom}), 139.9 (C_{arom}), 138.4 (C_{arom}), 137.0 (C_{arom}), 135.2 (C_{arom}), 134.4 (C_{arom}), 133.3 (C_{arom}), 132.6 (C_{arom}), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 127.7 (CH), 126.8 (CH), 126.5 (CH), 125.1 (CH), 124.6 (CH), 121.8 (CH), 121.4 (CH), 107.0 (C3), 106.8 (C3), 64.5 (CH_2CH_3), 46.8 (NCH_2), 45.50 (NCH_2), 29.7 (CH_2), 29.3 (CH_2), 21.1 (CH_3), 18.4 (CH_3), 17.8 (CH_3), 17.4 (CH_3), 14.6 (CH_2CH_3). IR (ATR): ν cm^{-1}: 3419, 2924, 2038, 1907, 1874, 1667. ESI-HRMS m/z: calcd for $C_{59}H_{53}Cr_2N_4O_{12}$ $[M + H]^+$ 1113.2468; found 1113.2495.

General Procedure for the Synthesis of Compounds 13. The corresponding metal allenyl (1 mmol) was dissolved in anhydrous 1,2-dichloroethane (67 mL) in a Schlenk flask; trityl hexafluorophosphate (1.2 mmol) was added, and the reaction mixture was stirred for 4−5 min. The solvent was removed under reduced pressure, and the solid formed was washed with dry diethyl ether.

Synthesis of ***13a***. Following the general procedure, from **2a** (60 mg, 0.09 mmol) and trityl hexafluorophosphate (43 mg, 0.11 mmol) in 6 mL of 1,2-dichloroethane, **13a** (70 mg, quantitative yield) was obtained as a *Z*/*E* isomeric mixture (1:2). ^1H NMR (700 MHz, $CDCl_3$) δ 7.76 (d, J = 2.8 Hz), 7.68 (s), 7.57 (s), 7.35−7.31 (m), 7.31−7.26 (m), 7.22−7.20 (m), 7.18−7.14 (m), 7.05 (s), 7.04−7.00 (m), 6.96−6.90 (m), 6.89 (s), 6.75 (s), 6.62 (d, J = 7.7 Hz, 12H, CH_{arom}, C*H*=C and NC*H*=C*H*N), 5.13 (q, J = 7.0 Hz, 1.33H, *E*-isomer), 4.50 (q, J = 7.1 Hz, 0.66H, *Z*-isomer), (2H, OCH_2CH_3), 2.36 (s), 2.31−2.22 (m), 2.14−2.10 (m), (18H, CH_3), 1.54 (t, J = 7.0 Hz, 2H, *E*-isomer), 0.83 (t, J = 7.1 Hz, 1H,-*Z* isomer), (3 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ: 336.4 (CCr), 332.2 (CCr), 224.4 (CO), 222.6 (CO), 215.1 (CO), 214.9 (CO), 147.0 (*C*H=C), 146.8 (C_{arom}), 146.3 (CH=*C*), 142.3 (C_{arom}), 142.0 (CH), 141.7 (C_{aromn}), 141.7 (C_{arom}), 141.1 (C_{arom}), 137.2 (C_{arom}), 136.6 (CH), 134.0 (C_{arom}), 133.6 (C_{arom}), 133.3 (C_{arom}), 133.1 (C_{arom}), 132.8 (C_{arom}), 130.9 (CH), 130.7 (CH), 130.6 (C_{arom}), 130.5 (CH), 130.3 (C_{arom}), 130.2 (C_{arom}), 130.2 (CH), 130.1 (CH), 130.0 (CH), 129.9 (CH), 129.3 (CH), 129.0 (C_{arom}), 128.7 (CH), 128.6 (CH), 128.3 (CH), 127.9 (CH), 127.9 (CH), 127.5 (CH), 127.3 (CH), 126.9 (CH), 126.7 (CH), 125.1 (CH), 116.0 (CH=*C*), 113.4 (CH=*C*), 82.0 (CH_2CH_3), 79.1 (CH_2CH_3), 21.2 (CH_3), 21.1 (CH_3), 21.0 (CH_3), 20.8 (CH_3), 19.8 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.2 (CH_3), 15.6 (CH_2CH_3), 13.7 (CH_2CH_3). IR (ATR): ν cm^{-1}: 3452, 3183, 2925, 2061, 1949, 1609. ESI-HRMS m/z: calcd for $C_{37}H_{35}CrN_2O_6$ 655.1895; found 655.1925.

Synthesis of ***13b***. Following the general procedure, from **2c** (60 mg, 0.082 mmol) and trityl hexafluorophosphate (48 mg, 0.12 mmol) in 6 mL of 1,2-dichloroethane **13b** (60 mg, quantitative yield) was obtained as a *Z*/*E* mixture of isomers (1:2). ^1H NMR (700 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.70 (s), 7.68 (s), 7.30−7.28 (m), 7.17(dd, J_1 = 8.3, J_2 = 2.2 Hz), 7.00 (s), 6.96 (s), 6.92 (s,), 6.83−6.76 (m), 6.49 (d, J = 8.3 Hz), (12 H, CH_{arom}, C*H*=C and NC*H*=C*H*N), 5.12 (q, J = 7.0 Hz, 1.33H), 4.55 (d, J = 7.1 Hz, 0.66H), (2H, OCH_2CH_3), 2.36−2.33 (m), 2.30 (s), 2.26 (s), 2.24 (s), 2.11 (s), 1.96−1.93 (m), (18H, CH_3), 1.53 (t, J = 7.1 Hz, 2H), 0.91 (t, J = 7.1 Hz, 1H), (3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 335.5 (CCr), 331.8 (CCr), 224.3 (CO), 222.4 (CO), 215.1 (CO), 214.8 (CO), 146.8 (*C*H=C), 146.2 (*C*H=C), 142.0 (C_{arom}), 141.7 (C_{arom}), 141.5 (C_{arom}), 141.4 (C_{arom}), 136.0 (C_{arom}), 133.6 (C_{arom}), 133.40 (C_{arom}), 133.1 (C_{arom}), 131.9 (CH), 131.5 (C_{arom}), 131.4 (CH), 130.9 (CH), 130.7 (CH), 130.5 (C_{arom}), 130.3 (C_{arom}), 130.2 (CH), 130.0 (CH), 129.3 (CH), 129.0 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.0 (CH), 126.8 (CH), 126.3 (CH), 125.2 (C_{arom}), 123.3 (C_{arom}), 114.4 (CH=*C*), 112.0 (CH=*C*), 79.1 (CH_2CH_3), 77.3 (CH_2CH_3), 21.0 (CH_3), 20.9 (CH_3), 19.8 (CH_3), 17.8 (CH_3), 15.6 (CH_2CH_3), 13.5 (CH_2CH_3). IR (ATR): ν cm^{-1}: 3446, 2925, 2855, 2061, 1954. ESI-HRMS m/z: calcd for $C_{37}H_{34}BrCrN_2O_6$ 735.0989; found 735.1002.

Synthesis of ***13c***. Following the general procedure, from **2e** (50 mg, 0.08 mmol) and trityl hexafluorophosphate (35 mg, 0.09 mmol) in 6 mL of 1,2-dichloroethane **13c** (50 mg, quantitative yield) was obtained as *Z*/*E* mixture of isomers (1:1). ^1H NMR (700 MHz, $CDCl_3$) δ 7.81 (s), 7.73 (s), 7.59 (d, J = 1.6 Hz), 7.56 (s), 7.33−7.29 (m), 7.19−7.13 (m), 7.08 (s), 7.06−7.03 (m), 6.98−6.96 (m), 6.91 (s), 6.84 (s), 6.77 (s), 6.68−6.64 (m), (11 H, CH_{arom}, C*H*=C and NC*H*=C*H*N), 4.84 (q, J = 7.1 Hz, 1H), 4.28 (q, J = 7.1 Hz, 1H), (2H, OCH_2CH_3), 2.38 (s), 2.30 (s), 2.28−2.25 (m), 2.16−2.12 (m), 2.09 (s), (18H, CH_3), 1.53 (t, J = 7.1 Hz, 1.5H), 0.80 (t, J = 7.1 Hz, 1.5H), (3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 307.81 (CW), 304.0 (CW), 202.9 (CO), 202.1 (CO), 196.1 (CO), 195.7 (CO), 152.3 (*C*H=C), 151.4 (*C*H=C), 141.7 (C_{arom}), 141.1 (C_{arom}), 134.0 (C_{arom}), 133.6

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(C_{arom}), 133.4 (C_{arom}), 133.0 (C), 131.0 (CH), 130.7 (CH), 130.6 (C_{arom}), 130.5 (CH), 130.4 (C_{arom}), 130.3 (C_{arom}), 130.2 (CH), 130.1 (CH), 130.0 (CH), 129.0 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.8, 127.7 (CH), 127.5 (CH), 127.0 (CH), 126.9 (C_{arom}), 126.8 (CH), 126.7 (CH), 125.1 (CH), 117.9 (CH=*C*), 116.3 (CH=C), 81.7 (CH_2CH_3), 79.3 (CH_2CH_3), 21.2 (CH_3), 21.1 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 19.9 (CH_3), 19.8 (CH_3), 17.9 (CH_3), 17.2 (CH_3), 15.3 (CH_2CH_3), 13.4 (CH_2CH_3). IR (ATR): ν cm^{-1}: 3445, 2924, 2071, 1946, 1929, 1635. ESI-HRMS *m/z*: calcd for $C_{37}H_{35}N_2O_6W$ 787.2005; found 787.1997.

Crsytallographic Data for *Z*-13a·CHCl$_3$. $C_{38}H_{36}Cl_3CrF_6N_2O_6$, *M* = 920.01, triclinic, *a* = 11.9124(3), *b* = 16.7703(4), *c* = 22.7908(10) Å, α = 76.840(3), β = 80.306(3), γ = 71.624(2)°, *V* = 4184.3(2) Å^3, space group $P\bar{1}$, *Z* = 4, *T* = 120(2) K, λ = 0.710 73 Å, Dcalcd =1.460 g cm^{-3}, μ = 0.576 cm^{-1}, 6162 reflections measured, 24 185 unique (R_{int} = 0.0788), crystal structure was solved by direct methods, and all non-hydrogen atoms refined anisotropically on F^2 using the programs SHELXT and SHELXL-2014,[28] one of the solvent molecules is disordered over two positions, both solvent molecules and anions were refined with appropriate similarity restraints (SAME) and with U value components restrained to be equal (RIGU, SIMU, ISOR), methyl group hydrogen atoms were included using a *rigid* model and other hydrogen atoms as *riding*, *R* (Fo, $I > 2\sigma(I)$) = 0.0979, *Rw* (Fo^2, all data) = 0.2562.

■ ASSOCIATED CONTENT

Supporting Information

Details for the synthesis of compounds **1d**, **1e**, and **1i**, computational details, UV−vis of compounds **9** and **10**, a CIF file containing X-ray crystallographic data for **Z-13a**·CHCl$_3$, and proton and carbon NMR spectra for all synthesized compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00492.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: margg@ucm.es. (M.G.G.)
*E-mail: sierraor@ucm.es. (M.A.S.)

Notes

The authors declare no competing financial interest.

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