7-(Dimethylamino)tricyclo[5.2.2.0^{1,6}]undecene Derivatives from β-Cyclohexenyl β-Dimethylamino-Substituted α,β-Unsaturated Fischer Carbenes

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When heated in pyridine at 80 °C, pentacarbonyl[(2*E*)-3-cyclohexenyl-3-(dimethylamino)-1-ethoxy-2-propen-1-ylidene]chromium (**1**-Cr) and -tungsten (**1**-W) complexes undergo 6π-electrocyclization and subsequent reductive elimination to yield the cyclohexane-annelated cyclopentadiene **6**, which equilibrates by 1,5-hydrogen shift with its more reactive isomer **7**. The latter molecule is efficiently trapped in Diels–Alder reactions with various alkynes **2** and styrenes **8** to give the cyclohexane-annelated norbornadiene **3** and norbornene derivatives respectively, with high regio- and diastereoselectivity in 15–91% yields. The enol ether moiety in compound **3** is particularly easily hydrolyzed, probably due to the through-space interaction between the two double bond moieties, so that the norbornenone derivatives **4** are isolated in all but one case after chromatographic purification. In this reaction, the tungsten complex **1**-W consistently gave lower yields than **1**-Cr. Arylalkynes with strongly electron-withdrawing groups and minimal steric congestion are particularly suitable reaction partners for **7**. The formation of bis-cycloadducts **10** from suitable diynes largely depends upon the steric and electronic properties of the corresponding alkynyl-substituted mono-cycloaddition products of type **4** or **11**. With the fluorenyl-substituted tricycle **4w** in acetonitrile at 25 °C, but not with **4y**, dual fluorescence is observed, with a red-shifted unstructured additional emission band with a dipole moment of 32 D, originating from intramolecular charge transfer. The molecule **2y** has an exceptionally large radiative rate constant of 13×10^8 s^{-1}.

Introduction

α,β-Unsaturated Fischer carbenes have established their broad versatility in organic synthesis.[1] Among a wide spectrum of easily accessible products from such metal complexes, 7-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-ones **4** were obtained from pentacarbonyl(3-cyclohexenyl-3-(dimethylamino)-1-ethoxy-2-propen-1-ylidene)chromium (**1**-Cr) and alkynes **2** in one step with high regio- and stereoselectivity (Scheme 1), as we communicated previously.[2] The initial products were actually the cycloadducts **3** as assigned on the basis of ^{1}H and ^{13}C NMR spectra of the crude products. However, hydrolysis of the enol ether moiety in **3** apparently occurred during chromatographic purification, and the corresponding ketones **4** were the only isolated products. In order to better understand this convenient access to these highly functionalized interesting tricycles, we have continued our efforts in this area. Especially, we have addressed the questions concerning the steric and electronic effects of the substituents on the incorporated alkynes **2**, and the influence of the nature of the transition metal in the carbene complexes **1** on this reaction. Here we report on these aspects and the full scope of this method.

Results and Discussion

β-(Dimethylamino)-substituted α,β-unsaturated Fischer carbene complexes **1** were prepared from lithiated 1-ethynyl-1-cyclohexene, the respective hexacarbonylmetal, triethyloxonium tetrafluoroborate and dimethylamine according to the previously developed one-pot procedure in excellent yields (94% for **1**-Cr[1] and 87% for **1**-W). As mentioned previously,[2] the cyclohexane-annelated cyclopentadiene **6** is formed via a 6π-electrocyclization, and the observed re-

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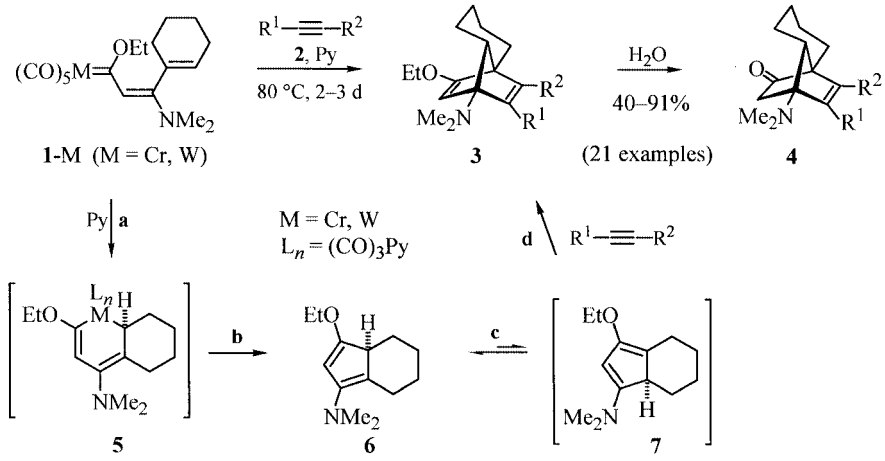


Scheme 1. One-pot synthesis of 7-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-ones **4** from complexes **1** and alkynes **2** as well as a mechanistic rationalization. **a**: 6π-electrocyclization. **b**: reductive elimination. **c**: 1,5-hydrogen shift. **d**: [4+2] cycloaddition. For details see Table 1

gional and facial selectivities in the Diels–Alder reactions of **7** with dienophiles **2** can be explained on the basis of a model proposed by Winterfeldt[3] (Scheme 2). The applied alkynes add onto the more reactive 1,3-diene **7** with *syn*-facial selectivity (with respect to the hydrogen in **7**) and, as far as the larger groups R_L are concerned, the *ortho*-selectivity rule (with respect to the dimethylamino group in **7**) is obeyed.[2]

As listed in Table 1, 31 out of 32 examples gave only the hydrolysis products **4**. However, the reaction of complex **1**-Cr with 1,4-diphenyl-1,3-butadiyne (**2q**) did not only yield the ketone **4q**, but also the non-hydrolyzed enol ether **3q**, even after chromatographic purification. Just like norbornadiene itself, the tricyclic norbornadiene derivatives **3** must have a strong through-space electronic interaction,[4] which leads to an elevation of the HOMO energy. The enol ether moieties in **3** therefore undergo more facile hydrolysis than ordinary enol ethers. The phenylethynyl substituent in **4q**, however, exerts a stronger electron-withdrawing effect than others and thus probably causes a decrease of the hydrolysis rate.

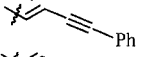
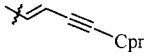
With the tungsten complex **1**-W, the same tricyclic compounds were formed, but in lower yields in most cases. In order to rationalize this difference, the transformation of the tungsten complex **1**-W in [D_5]pyridine at room temperature was monitored by NMR spectroscopy and found to proceed more slowly to **6** than that of **1**-Cr. This must be due to the enhanced bond strength between tungsten and the carbene carbon. The conversion of **1**-W to **6** was not complete within 2 days, yet during the whole period only the signals of the complex **1**-W and the cyclization product **6** were observed. Unfortunately, the highly labile molybdenum analogue **1**-Mo could not be isolated, therefore a complete comparison of the transition metal effect in this transformation for all of the group VI metals cannot be made.

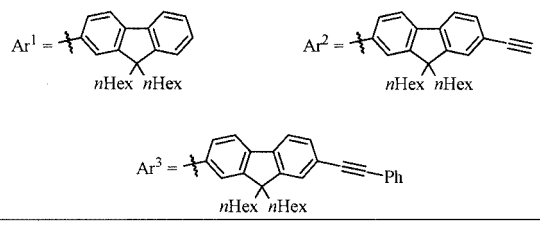
It is well-known that electronic as well as steric effects of substituents on both dienes and dienophiles play important roles in the Diels–Alder reaction.[5] The cyclopentadiene **7** with its two strong electron-donating groups is a particularly reactive diene. The arylacetylene **2j** with its methoxycarbonyl group afforded a much higher yield than **2h** with the electron-donating 4-ethoxy group (cf. entries 12 and 14 in Table 1). Apparently, alkynes containing electron-withdrawing groups are more suitable reaction partners for the cyclopentadiene **7**. Whereas the symmetric diphenylethyne did not react with **7**, ethyl 4-phenylethynylbenzoate (**2k**) gave the cycloadduct **4k** in 66% yield (entry 15 in Table 1).

Steric encumbrance in the applied alkynes may cause another limitation in this cycloaddition. In the reactions of the complex **1**-Cr with *o*-, *m*- and *p*-(trifluoromethyl)ethynylbenzene (entries 16–18 in Table 1), the *ortho*-isomer gave a much lower yield than the *m*- and the *p*-isomer. The cycloaddition of 1-phenyl-4-(trimethylsilyl)buta-1,3-diyne (**2p**) onto **7** is an example for a high regioselectivity furnishing **4p** as the sole product, probably due to electronic as well as steric reasons. The cycloaddition modes **B** and **D** (see Figure 1) should be disfavored due to the stronger electron-withdrawing ability of the phenylethynyl substituent as compared to that of the trimethylsilyl and (trimethylsilyl)-ethynyl group. In addition, the steric demand of the trimethylsilyl substituent disfavors the cycloaddition modes **C** and **D**. This steric influence is also supported by the observation that 3-(trimethylsilylethynyl)benzotrifluoride as a dienophile did not afford any tricyclic product in this reaction, whereas the cycloaddition product **4m** was obtained in 84% yield from the unsilylated 3-ethynylbenzotrifluoride **2m** (entry 17 in Table 1).

Styrene and substituted styrenes **8** also underwent cycloaddition with the diene **7** in situ formed from the complexes **1**-M to yield the cyclohexane-annelated ethoxy(dimethylamino)norbornene derivatives **9** (Scheme 2). These enol ethers did not undergo rapid subsequent hydrolysis, such as all but one of the norbornadienes **3** do (see above). The yields of compounds **9** were consistently lower than those of products **4** from alkynes. Since the LUMO energy of styrene is ca. 0.5 eV higher than that of phenylethyne (**2e**),

Table 1. One-pot synthesis of 7-(dimethylamino)tricyclo-[5.2.2.0^{1,6}]undec-10-en-9-ones **4** (see Scheme 1)

Entry	1-M	Alkyne	R^1	R^2	Product	Yield (%)
1	**1**-Cr	**2a**	1-cyclopentenyl	H	**4a**	43[a]
2	**1**-W	**2a**			**4a**	35
3	**1**-Cr	**2b**	1-cyclohexenyl	H	**4b**	40[a]
4	**1**-W	**2b**			**4b**	24
5	**1**-Cr	**2c**	1-cycloheptenyl	H	**4c**	26[a]
6	**1**-Cr	**2d**	2-isopropenyl	H	**4d**	73[a]
7	**1**-W	**2d**			**4d**	44
8	**1**-Cr	**2e**	Ph	H	**4e**	88[a]
9	**1**-W	**2e**			**4e**	58
10	**1**-Cr	**2f**	2-thienyl	H	**4f**	34
11	**1**-Cr	**2g**	4-*n*Pr-C_6H_4	H	**4g**	87[a]
12	**1**-Cr	**2h**	4-EtO-C_6H_4	H	**4h**	50[a]
13	**1**-Cr	**2i**	4-*n*Pr-C_6H_4-C_6H_4	H	**4i**	15[a]
14	**1**-Cr	**2j**	4-MeO_2C-C_6H_4	H	**4j**	91
15	**1**-Cr	**2k**	4-EtO_2C-C_6H_4	H	**4k**	66[a]
16	**1**-Cr	**2l**	2-CF_3-C_6H_4	H	**4l**	44
17	**1**-Cr	**2m**	3-CF_3-C_6H_4	H	**4m**	84
18	**1**-Cr	**2n**	4-CF_3-C_6H_4	H	**4n**	85
19	**1**-W	**2n**			**4n**	58
20	**1**-Cr	**2o**	1-naphthyl	H	**4o**	52
21	**1**-W	**2o**			**4o**	52
22	**1**-Cr	**2p**	—≡—$SiMe_3$	Ph	**4p**	49
23	**1**-Cr	**2q**	—≡—Ph	Ph	**4q**	60[a]
24	**1**-Cr	**2r**		Ph	**4r**	48[a]
25	**1**-Cr	**2s**		*c*Pr	**4s**	46[a,b]
26	**1**-Cr	**2t**	4-ethynyl-Ph	H	**4t**	69
27	**1**-W	**2t**			**4t**	62
28	**1**-Cr	**2u**	3,5-diethynyl-Ph	H	**4u**	65
29	**1**-Cr	**2v**	Ar^1	H	**4v**	51
30	**1**-Cr	**2w**	≡—Ar^1	Ar^1	**4w**	57
31	**1**-Cr	**2x**	Ar^2	H	**4x**	60
32	**1**-Cr	**2y**	≡—Ar^3	Ar^3	**4y**	34



[a] See ref.[2] [b] 2.2 equiv. of complex **1a** was used for this reaction.

its reaction with the same diene **7** probably proceeds more slowly.[6] The constitution and the *endo* configuration of **9a** were rigorously proved by an X-ray crystal structure analysis (Figure 2).[7]

Generally speaking, the alkynes and alkenes used above are considered as being unreactive dienophiles in the Diels–Alder reaction. However, more reactive dienophiles such as methyl propiolate, dimethyl acetylenedicarboxylate, maleic anhydride etc. could not be employed in this trans-

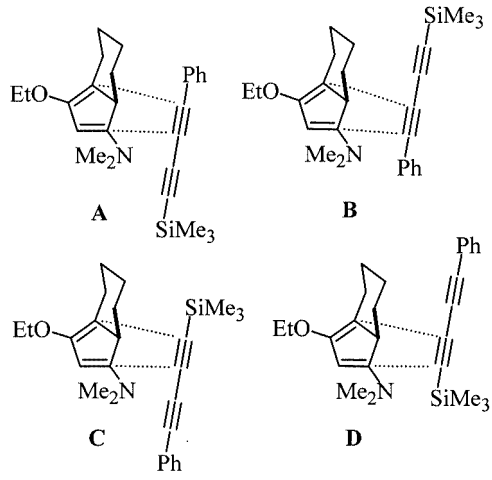
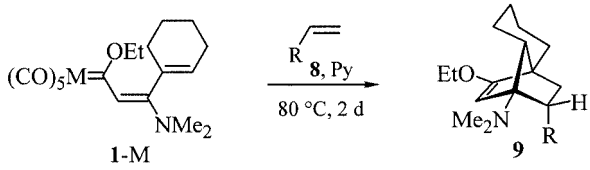


Figure 1. Four conceivable reaction modes of the intermediate cyclohexane-annelated (dimethylamino)ethoxycyclopentadiene **7** with phenyl(trimethylsilyl)butadiyne **2q**



1-M	Alkene	R	Product	Yield (%)
1-Cr	**8a**	C_6H_5	**9a**	59
1-Cr	**8b**	3-Me-C_6H_4	**9b**	54
1-Cr	**8c**	4-Me-C_6H_4	**9c**	57
1-W	**8c**		**9c**	19

Scheme 2. Synthesis of 7-(dimethylamino)-9-ethoxytricyclo-[5.2.2.0^{1,6}]undec-8-enes **9** from the complexes **1**-M and styrenes **8**

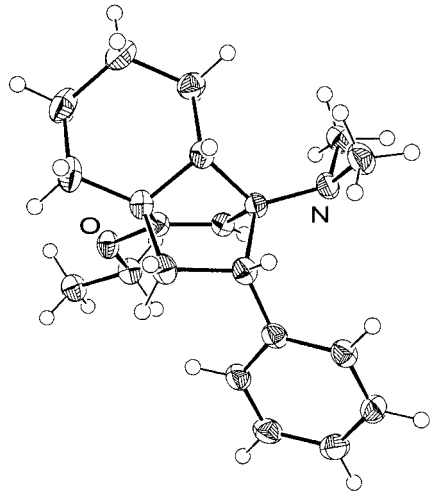
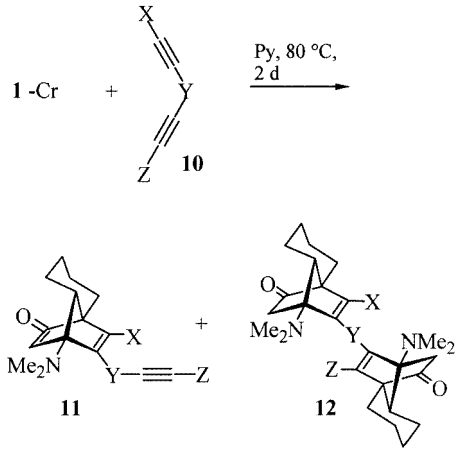


Figure 2. Structure of the cyclohexane-annelated ethoxy(dimethylamino)norbornene **9a** in the crystal[7]

formation, since they reacted with the solvent, pyridine, and produced dark-colored complicated mixtures.[8]

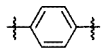
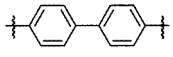
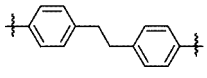
In all of the [4+2] cycloadditions of a variety of diynes, enediynes and oligoynes used, only the monoadducts **4** were

obtained, even when a 2.2-fold excess of complex **1**-Cr was employed (entry 25 in Table 1). In view of this result, the possibilities of forming bisadducts **12** from not directly conjugated diynes were investigated. Since phenyl-substituted monoalkynes consistently gave the highest yields, a number of diynes of type **10** were employed for the reaction (Scheme 3). Indeed, twofold adducts were obtained when more than 1.5 equivalents of the complex **1**-Cr per triple bond was employed, otherwise mainly the monoadducts of type **4** were isolated. However, with 1,4-diethynylbenzene **10a** (≡ **2t**) the bisadduct **12a** was obtained in 8% yield, and none of the monoadduct was observed (entry 1 in Table 2). This unsatisfactory result could arise from the much lower solubility of **12a** in organic solvents. The directly conjugated bis-dienophile, 1,4-diphenyl-1,3-butadiyne (**2q**), yielded only the monoadduct **11d** (≡ **4q**), even when 3.5 equiv. of the complex **1**-Cr was employed.



Scheme 3. Synthesis of twofold cycloadducts **12** from the complex **1**-Cr and diynes **10**; for details see Table 2

Table 2. Synthesis of twofold cycloadducts **12** (see Scheme 4)

Entry	1-Cr (equiv.)	Alkyne	X	Y	Z	Product	Yield (%)[a]	
1	3.1	**10a** (≡ **2t**)	H		H	**11a** (≡ **4t**)	0	8
						12a	8	
2	3.4	**10b**	H		H	**11b**	0	50
						12b	50	
3	2.2	**10c**	H		H	**11c**	33	47
						12c	14	
4	3.5	**10d** (≡ **2q**)	Ph	—	Ph	**11d** (≡ **4q**)	83	83
						12d	0	

[a] All reactions were carried out at 80 °C for 2 d.

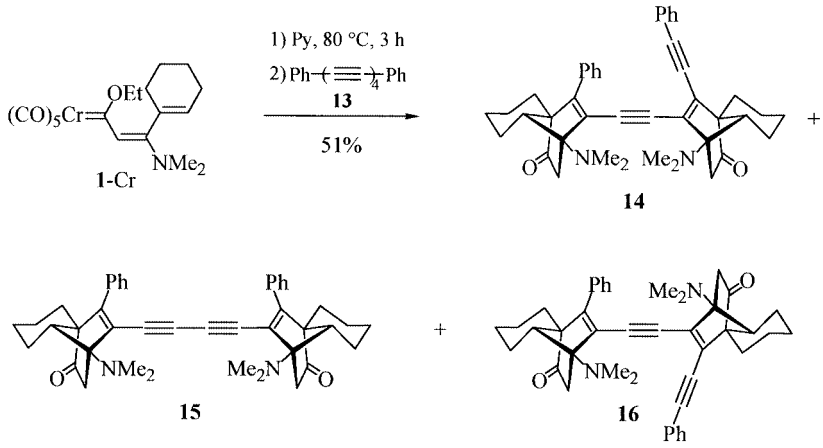
In view of the thermal instability of the highly reactive 1,8-diphenyl-1,3,5,7-octatetrayne (**13**), the cyclopentadiene **6** was first generated by heating the complex **1**-Cr in pyridine at 80 °C for 3 h. Then, the tetrayne **13** was introduced into the reaction medium, and the mixture was stirred at ambient temperature for 3 days. After purification, only bisadducts could be detected in the mass spectrum. Their ^{1}H- and ^{13}C-NMR spectra each show five sets of signals with an approximate intensity ratio of 2:1:1:1:1 for the signals of dimethylamino as well as the carbonyl groups. According to these observations, the mixture of bisadducts consisted of the three regioisomers **14**, **15** and **16** in a ratio of 1:1:1 (Scheme 4). Hence, the degree to which bisadducts are formed, greatly depends upon the nature of the linkage Y in **10**, and it appears that they are only formed from alkynyl- and phenyl-substituted diynes.

Recently, oligo-(9,9-di-*n*-hexyl-2,7-fluorenethynylene)s were reported as potential candidates for light-emitting diodes (LEDs), the fluorescence of which would possibly be shifted towards blue light by way of an appropriate variation of the length of their conjugated systems.[9]

With this information in mind, the electronic absorption and fluorescence spectra (Figure 3) as well as the fluorence decay times (Table 3) of the fluorenyl-substituted tricyclic compounds **4w** and **4y** and their corresponding dienophilic precursors **2w** and **2y** were measured.

The fluorescence spectra of **2w** and **2y** in diethyl ether are structured and show only a small decrease in energy between the lowest-energy absorption and the highest-energy fluorescence bands (small Stokes-shift), comparable to that found for an alternating aromatic hydrocarbon such as anthracene. This observation indicates that there is not an appreciable change in molecular structure when going from the electronic ground state S_0 via the Franck-Condon excited state reached in absorption to the equilibrated fluorescing lowest singlet excited state S_1. For **4w** and **4y** in acetonitrile, in contrast, the Stokes shift is considerably larger than that observed with **2w** and **2y**, similar to that found e.g. with an aromatic amine such as aniline, which means that the change in molecular structure of **4w** and **4y** between S_0 and S_1 is larger than for the compounds **2w** and **2y**.

The fluorescence spectrum of **4w** in acetonitrile consists of two emission bands (Figure 3, c). The structureless fluorescence band at lower energies is obtained by subtracting from the total fluorescence spectrum that of **4w** in *n*-hexane, for which only a single fluorescence band is observed (Table 4). The excitation spectrum of **4w** in acetonitrile, measured at 610 nm (low-energy emission band) is similar to that determined at 460 nm, see part c in Figure 3, which shows that both emission bands originate from **4w**. This dual fluorescence is due to an intramolecular charge transfer (ICT) process, giving rise to an ICT band red-shifted with respect to the locally excited (LE) emission.[10] This conclusion is based on the observation that the ICT/LE fluorescence quantum yield ratio Φ_{ICT}/Φ_{LE} increases when the solvent polarity becomes larger (see Table 4). In the nonpolar solvent *n*-hexane, dual fluorescence is not observed, as mentioned above, whereas the second band is clearly present in the more polar diethyl ether ($\Phi_{ICT}/\Phi_{LE} = 0.24$) and dual emission becomes progressively more important when the solvent polarity increases (Table 4), with a value for Φ_{ICT}/Φ_{LE} of 0.40 (tetrahydrofuran), 0.82 (*n*-propyl cyanide) and 1.15 (acetonitrile).



Scheme 4. Synthesis of twofold cycloadducts **14**, **15** and **16**

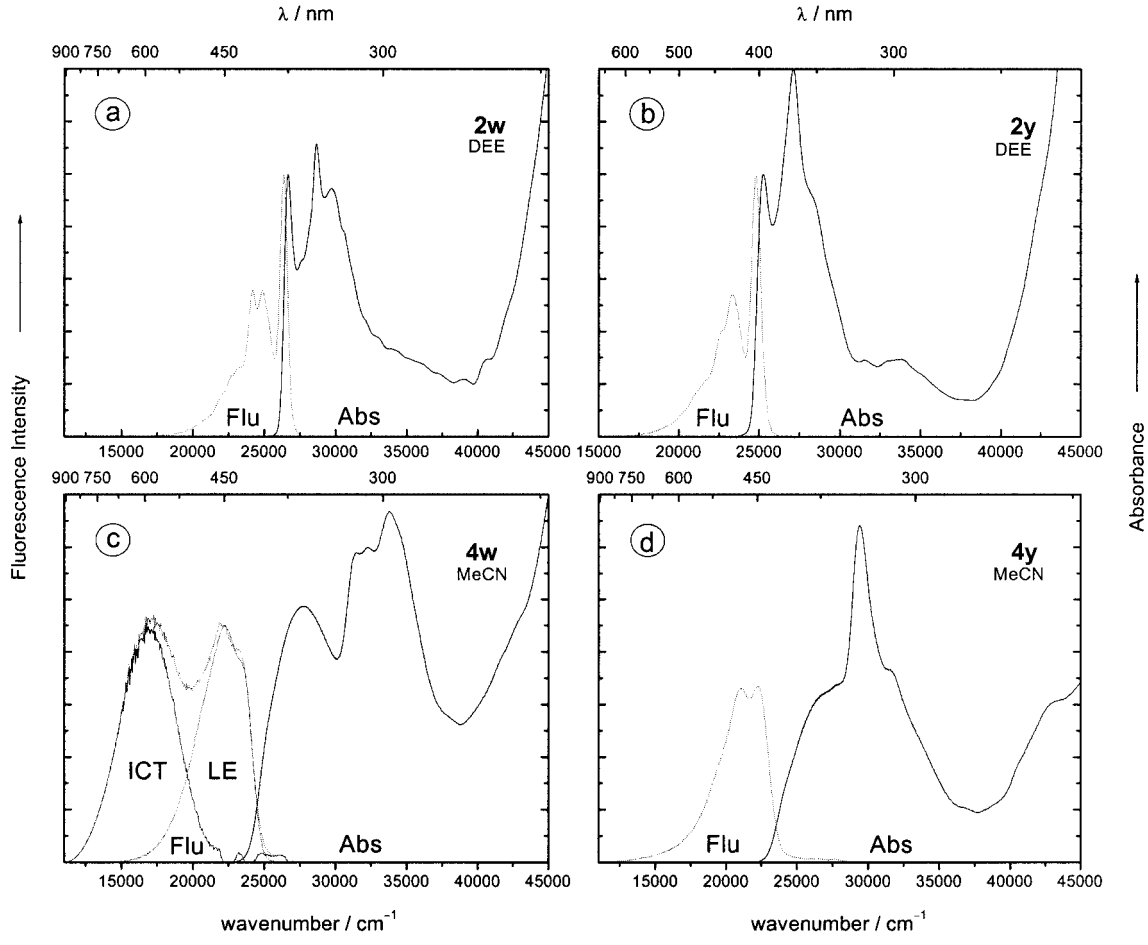


Figure 3. Absorption and fluorescence spectra (at 25 °C) of the alkynes **2w** and **2y** and their cycloadducts **4w** and **4y** in diethyl ether (DEE) and in acetonitrile (MeCN)

The maximum of the ICT fluorescence band $\tilde{\nu}^{max}$(ICT) of **4w** undergoes a red-shift with increasing solvent polarity, from 20080 cm^{-1} (diethyl ether) to 17000 cm^{-1} (acetonitrile, see Table 4). From these data, an ICT dipole moment μ_e(ICT) of 32 D is estimated (Equations 1 and 2),[11] employing a calculated (Hyperchem, PM3) ground state dipole moment μ_g of 3.4 D and assuming that **4w** has a molecular density of 1.0.[12] The fact that an ICT process does not occur in the case of **4y**, may be caused by the presence in this molecule of the phenylethynyl substituent which ap-

Table 3. Absorption and fluorescence data (at 25 °C) of the alkynes **2w** and **2y** and their cycloadducts **4w** and **4y** in diethyl ether (DEE) and in acetonitrile (MeCN)

	Solvent	Extinction coefficient (ε) [$M^{-1}cm^{-1}$][a]	Fluorescence Quantum yield (Φ)	Fluorescence decay Time (τ) [ns]	Radiative rate constant[b] (k_f) [10^8 s^{-1}]
2w	DEE	10000 (375 nm)	0.19	0.23	8.2
2y	DEE	66070 (369 nm),	0.60	0.46	13
4w	MeCN	17780 (361 nm)	0.013 (Φ)[c]	1.84 (430, 560 nm)[d]	
4y	MeCN	112200 (340 nm), 380 (376 nm)	0.138	1.69	0.8

[a] At selected wavelengths in the absorption spectrum above 340 nm, see Figure 3. [b] $k_f = \Phi/\tau$. [c] See Table 4. [d] See Figure 3, c.

Table 4. ICT and LE fluorescence quantum yields Φ_{ICT} and Φ_{LE} and the energy $\tilde{\nu}^{max}$(ICT) of the ICT emission band maximum of **4w** at 25 °C in five solvents of different polarity

Solvent	ε	*n*	$f - 1/2f'$[a]	Φ_{ICT}/Φ_{LE}	Φ_{ICT}	Φ_{LE}	$\tilde{\nu}^{max}$(ICT)/ cm^{-1}
n-hexane	1.88	1.372	0.092	0	0	0.48	
diethyl ether	4.27	1.361	0.252	0.24	0.03	0.13	20080
tetrahydrofuran	7.39	1.405	0.307	0.40	0.013	0.03	18520
n-propyl cyanide	24.2	1.382	0.375	0.82	0.006	0.008	17570
acetonitrile	36.1	1.342	0.393	1.15	0.007	0.006	17000

[a] $f = (\varepsilon - 1)/(2\varepsilon + 1)$, $f' = (n^2 - 1)/(2n^2 + 1)$, see Equation (2).

parently reduces the electron-donor character of the fluorenyl moieties.

$$\tilde{\nu}^{max}(\mathrm{ICT}) = -\frac{2}{hc\rho^3}\mu_e(\mu_e - \mu_g)(f - \frac{1}{2}f') + const. \quad (1)$$

$$\text{in which} \quad f - \frac{1}{2}f' = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{1}{2}\frac{(n^2 - 1)}{(2n^2 + 1)} \quad (2)$$

In Equation (1), ρ is the Onsager radius of the solute, *h* is the Planck constant, and *c* is the speed of light, whereas ε and *n* are the dielectric constant and refractive index of the solvent, respectively.

The fluorescence decays of all four compounds are single exponential (Table 3). For **4w** this means that the ICT process leading to the appearance of the second red-shifted emission band is faster than the time resolution (around 3 ps) of the SPC laser equipment used in the present experiments.[13]

It is of interest to note that the radiative rate constant k_f of **2y**, in particular, is exceptionally large, with a value of 13.0×10^8 s^{-1} (Table 3). For comparison, the highly fluorescent molecule *p*-terphenyl, as an example, has a clearly smaller k_f of 9.8×10^8 s^{-1}.[14]

Conclusion

The in situ generated cyclohexane-annelated cyclopentadiene **7** shows a remarkably high Diels–Alder reactivity even towards moderately activated alkynes which act as dienophiles. The donor-acceptor substituted norbornadienes **3** thus formed exhibit strong through-space electronic interactions and therefore undergo rapid hydrolysis at their enol ether moieties to yield acceptor-substituted norbornenones **4**. With **4w** in sufficiently polar solvents (diethyl ether to acetonitrile) dual fluorescence is observed. The red-shifted new emission band originates from intramolecular charge transfer in **4w**, leading to an ICT state with a dipole moment of 32 D. In the case of **2y**, especially, an exceptionally large radiative rate constant is found.

Experimental Section

General: ^1H and ^{13}C NMR: Bruker AM 250 (250 and 62.9 MHz). IR: Bruker IFS 66 (FT-IR). Low-resolution EI-MS: Varian MAT CH 7, MAT 731, ionizing voltage 70 eV. High-resolution EI-MS (HR EI-MS): Varian MAT 311 A. X-ray crystal structure determination: The data were collected on a Stoe–Siemens-AED diffractometer. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analysis: Mikroanalytisches Laboratorium der Georg-August-Universität Göttingen. Chromatography: ICN neutral alumina (Super I, activity II). Solvents for chromatography were technical grade and freshly distilled before use. Tetrahydrofuran was distilled from sodium benzophenone ketyl, and pyridine was distilled from calcium hydride. Pentacarbonyl[(2*E*)-3-cyclohexenyl-3-(dimethylamino)-1-ethoxy-2-propen-1-ylidene]chromium (**1**-Cr),[2] 1-ethynyl-1-cyclopentene (**2a**),[15] 1-ethynyl-1-cyclohexene (**2b**),[15] methyl *p*-ethynylbenzoate (**2j**),[16] 2-ethynylthiophene (**2f**),[17] 2-ethynylbenzotrifluoride (**2l**),[17] 3-ethynylbenzotrifluoride (**2m**),[17] 4-ethynylbenzotrifluoride (**2n**),[17] 1-ethynylnaphthalene (**2o**),[17] 1-phenyl-4-(trimethylsilyl)-1,3-butadiyne (**2p**),[17,18] 1,4-diethynylbenzene (**2t**),[19] 1,3,5-triethy-

nylbenzene (**2u**),[19] 2-ethynyl-9,9-di-*n*-hexylfluorene (**2v**),[9] 2,7-diethynyl-9,9-di-*n*-hexylfluorene (**2 ×**),[9] 1,2-bis(4-ethynylphenyl)ethane (**10c**),[17,20] 1,8-diphenyl-1,3,5,7-octatetrayne (**13**),[21] 2-bromo-9,9-di-*n*-hexyl-7-(3′-hydroxy-3′-methylbut-1′-ynyl)fluorene[17,22] were prepared according to published procedures.

Pentacarbonyl[(*2E*)-3-cyclohexenyl-3-(dimethylamino)-1-ethoxy-2-propen-1-ylidene]tungsten (1-W): Following a previously published protocol,[2,23] (2.50 mL, 21.3 mmol) of 1-ethynyl-1-cyclohexene (**2b**) in THF (100 mL) was treated with *n*-butyllithium (9.00 mL, 2.36 M in *n*-hexane, 21.2 mmol), hexacarbonyltungsten (8.01 g, 22.8 mmol), Et_3OBF_4 (4.18 g, 22.0 mmol), and gaseous dimethylamine (1 equiv.). Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 10:1 to 4:1) gave 9.77 g (87%) of **1**-W [R_f — 0.53 (pentane/Et_2O, 1:1)] as a yellow solid, m.p. 92−94 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2938 cm^{-1} (C−H), 2054 (C=O), 1910 (C=O), 1888 (C=O), 1653, 1558, 1520, 1261. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.39 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.60−1.80 (m, 4 H, 4′,5′-H), 2.00−2.20 (m, 4 H, 3′,6′-H), 3.06 [s, 6 H, $N(CH_3)_2$], 4.54 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 5.58 (br. s, 1 H, 2′-H), 6.30 (s, 1 H, 2-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.8 (+, OCH_2CH_3), 21.3, 22.0, 24.7, 27.2 (−, C-3′,4′,5′,6′), 40.5 [+, $N(CH_3)_2$], 76.3 (−, OCH_2CH_3), 120.0 (+, C-2), 126.9 (+, C-2′), 134.9 (C_{quat}, C-1′), 161.1 (C_{quat}, C-3), 199.9 (C_{quat}, CO), 204.3 (C_{quat}, CO), 267.8 (C_{quat}, C-1). MS (70 eV), *m*/*z* (%) = 531 (1) [M^+], 475 [M^+ − CO], 443 (1) [M^+ − 2 CO], 369 (2) [M^+ − 5 CO], 207 (28), 179 (72), 150 (27), 124 (100), 69 (27), 43(28). $C_{18}H_{21}NO_6W$ (531.2): calcd. C 40.70, H 3.98; found C 40.72, H 3.82.

General Procedure for Cocyclizations of Complexes 1-M with Alkynes 2 or Alkenes 8 (GP): A thick-walled, screw-cap Pyrex bottle equipped with a magnetic stirring bar was charged with a 0.05 M solution of the complex **1** in anhydrous pyridine. Dry nitrogen was bubbled through the solution for 5 min, and 2 equiv. of the respective alkyne **2** (alkene **8** or diyne **10**) were immediately added. The sealed bottle was kept in an oil bath at 80 °C for 2−3 days. The solvent was removed under reduced pressure, the residue was diluted with Et_2O, and the solution exposed to air for 2 h. After filtration and removal of the solvents, the residue was purified by column chromatography on aluminum oxide (activity II).

7-(Dimethylamino)-11-(2′-thienyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (4f): According to GP, to a solution of (1.01 g, 2.53 mmol) of complex **1**-Cr in 45 mL of pyridine was added (412 mg, 3.81 mmol) of 2-ethynylthiophene (**2f**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 245 mg (34%) of **4f** [R_f = 0.67 (pentane/Et_2O, 3:1)] as a pale yellow solid, m.p. 104−105 °C. IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1} (C−H), 1728 (C=O), 1315, 850, 831. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.11−1.47 (m, 4 H, 2,3,4,5-H), 1.60−1.74 (m, 2 H, 3,4-H), 1.83−1.88 (m, 1 H, 5-H), 2.05 (ABM, dd, ^2J = 16.3, ^4J = 2.4 Hz, 1 H, 8-H), 2.24−2.31 (m, 1 H, 2-H), 2.40−2.43 (m, 1 H, 6-H), 2.46 [s, 6 H, $N(CH_3)_2$], 2.63 (AB, d, ^2J = 16.3 Hz, 1 H, 8-H), 5.91 (s, 1 H, 10-H), 6.98 (dd, ^3J = 5.1, ^3J = 3.5 Hz, 1 H, 4′-H), 7.24 (dd, ^3J = 5.1, ^4J = 1.0 Hz, 1 H, 3′-H), 7.45 (dd, ^3J = 3.5, ^4J = 1.0 Hz, 1 H, 5′-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 22.9, 24.2, 25.7 (−, C-2,3,4,5), 37.1 (−, C-8), 40.4 [+, $N(CH_3)_2$], 59.5 (+, C-6), 62.1 (C_{quat}, C-1), 74.0 (C_{quat}, C-7), 124.4, 125.0, 126.5, 126.8 (+, C-10,3′,4′,5′), 136.1 (C_{quat}, C-2′), 150.3 (C_{quat}, C-11), 211.0 (C_{quat}, C-9). EI MS (70 eV), *m*/*z* (%) = 287 (100) [M^+], 259 (39) [M^+ − CO], 245 (52) [M^+ − C_3H_6], 230 (12), 215 (19), 179 (17), 162 (34), 150 (14). $C_{17}H_{21}NOS$ (287.4): calcd. C 71.04, H 7.36; found C 70.78, H 7.23.

7-(Dimethylamino)-11-[4′-(methoxycarbonyl)phenyl]tricyclo-[5.2.2.0^{1,6}]undec-10-en-9-one (4j): According to GP, a solution of (1.04 g, 2.61 mmol) of complex **1**-Cr in pyridine (52 mL) was treated with (500 mg, 3.12 mmol) of methyl *p*-ethynylbenzoate (**2j**), and the mixture was stirred at 80 °C for 60 h. Chromatography on aluminum oxide (activity II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 805 mg (91%) of **4j** [R_f = 0.26 (pentane/Et_2O, 3:1)] as a colorless solid, m.p. 151−152 °C. IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1} (C−H), 1745 (C=O), 1715 (C=O), 1607, 1432, 1321, 1284, 1113, 765, 701. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.00−1.45 (m, 4 H, 2,3,4,5-H), 1.50−1.70 (m, 2 H, 3,4-H), 1.80−1.90 (m, 1 H, 5-H), 2.10−2.30 (m, 2 H, 2,8-H), 2.33 [s, 6 H, $N(CH_3)_2$], 2.41−2.57 (m, 1 H, 6-H), 2.76 (AB, d, ^2J = 14.4 Hz, 1 H, 8-H), 3.86 (s, 3 H, CO_2CH_3), 5.96 (s, 1 H, 10-H), 7.64 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 7.92 (d, ^3J = 8.0 Hz, 2 H, Ar-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 22.9, 24.3, 26.0 (−, C-2,3,4,5), 37.0 (−, C-8), 40.1 [+, $N(CH_3)_2$], 51.9 (+, CO_2CH_3), 59.7 (+, C-6), 62.5 (C_{quat}, C-1), 74.6 (C_{quat}, C-7), 125.1 (+, Ar-C), 128.8 (C_{quat}, Ar-C), 129.3 (+, Ar-C), 131.7 (+, C-10), 140.0 (C_{quat}, Ar-C), 155.6 (C_{quat}, C-11), 166.9 (C_{quat}, CO_2CH_3), 211.6 (C_{quat}, C-9). EI MS (70 eV), *m*/*z* (%) = 339 (100) [M^+], 311 (92) [M^+ − CO], 297 (84) [M^+ − C_3H_6], 282 (12), 268 (24), 242 (10), 179 (23), 162 (22), 150 (16), 59 (10). $C_{21}H_{25}NO_3$ (339.4): calcd. C 74.31, H 7.42; found C 74.62, H 7.13.

7-(Dimethylamino)-11-[2′-(trifluoromethyl)phenyl]tricyclo-[5.2.2.0^{1,6}]undec-10-en-9-one (4l): According to GP, to a solution of (840 mg, 2.10 mmol) of complex **1**-Cr in 42 mL of pyridine was added (537 mg, 3.16 mmol) of 2-ethynylbenzotrifluoride (**2l**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 320 mg (44%) of **4l** [R_f = 0.33 (pentane/Et_2O, 3:1)] as a colorless solid, m.p. 135−136 °C. IR (KBr): $\tilde{\nu}$ = 2935 cm^{-1} (C−H), 1741 (C=O), 1444, 1312, 1160, 1110, 1034, 770. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.12−1.47 (m, 4 H, 2,3,4,5-H), 1.59−1.72 (m, 2 H, 3,4-H), 1.80−1.88 (m, 1 H, 5-H), 2.24−2.30 (m, 1 H, 2-H), 2.30 [s, 6 H, $N(CH_3)_2$], 2.50 (ABM, dd, ^2J = 16.5, ^4J = 2.5 Hz, 1 H, 8-H), 2.57−2.62 (m, 1 H, 6-H), 2.74 (AB, d, ^2J = 16.5 Hz, 1 H, 8-H), 5.88 (s, 1 H, 10-H), 7.26−7.44 (m, 3 H, Ar-H), 7.66 (d, ^3J = 7.8 Hz, 1 H, Ar-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 22.9, 24.1, 25.4 (−, C-2,3,4,5), 39.0 (−, C-8), 40.1 [+, $N(CH_3)_2$], 61.3 (+, C-6), 63.5 (C_{quat}, C-1), 75.6 (C_{quat}, C-7), 126.5 (+, q, $^3J_{C,F}$ = 5.6 Hz, C-3′), 127.0, 127.1, 135.4 (+, C-4′,5′,6′), 127.5 (C_{quat}, q, $^2J_{C,F}$ = 29.6 Hz, C-2′), 130.2 (+, C-10), 134.2 (C_{quat}, q, ^3J = 4.2 Hz, C-1′), 152.7 (C_{quat}, C-11), 212.4 (C_{quat}, C-9). The signal of the CF_3 carbon was not detected. EI MS (70 eV), *m*/*z* (%) = 349 (100) [M^+], 321 (58) [M^+ − CO], 307 (64) [M^+ − C_3H_6], 292 (14), 278 (24), 252 (11), 179 (22), 162 (14). $C_{20}H_{22}NOF_3$ (349.4): calcd. C 68.75, H 6.35; found C 68.40, H 6.02.

7-(Dimethylamino)-11-[4′-(trifluoromethyl)phenyl]tricyclo-[5.2.2.0^{1,6}]undec-10-en-9-one (4n). Variant A: Following GP, to a solution of complex **1**-Cr (958 mg, 2.40 mmol) in 48 mL of pyridine was added (612 mg, 3.60 mmol) of 4-ethynylbenzotrifluoride (**2n**), and the mixture was stirred at 80 °C for 2 days. Chromatography on aluminum oxide (activity II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 714 mg (85%) of **4n** [R_f = 0.25 (pentane/Et_2O, 6:1)] as a colorless solid, m.p. 88−89 °C. IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (C−H), 1744 (C=O), 1616, 1327, 1162, 1126, 1068, 1017, 851, 819. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.10−1.45 (m, 4 H, 2,3,4,5-H), 1.57−1.72 (m, 2 H, 3,4-H), 1.84−1.91 (m, 1 H, 5-H), 2.14−2.35 (m, 2 H, 2,8-H), 2.34 [s, 6 H, $N(CH_3)_2$], 2.44−2.54 (m,

1 H, 6-H), 2.75 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 5.96 (s, 1 H, 10-H), 7.51 (m, ^3J = 8.2 Hz, 2 H, Ar-H), 7.70 (d, ^3J = 8.2 Hz, 2 H, Ar-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.1, 22.9, 24.3, 26.0 (−, C-2,3,4,5), 36.9 (−, C-8), 40.0 [+, $N(CH_3)_2$], 59.7 (+, C-6), 62.5 (C_{quat}, C-1), 74.5 (C_{quat}, C-7), 124.2 (C_{quat}, q, $^1J_{C,F}$ = 273.3 Hz, CF_3), 124.9 (+, q, $^3J_{C,F}$ = 3.7 Hz, C-3′,5′), 125.4 (+, C-2′,6′), 129.2 (C_{quat}, q, $^2J_{C,F}$ = 32.3 Hz, C-4′), 131.6 (+, C-10), 138.9 (C_{quat}, C-1′), 155.1 (C_{quat}, C-11), 211.6 (C_{quat}, C-9). EI MS (70 eV), *m/z* (%) = 349 (100) [M^+], 321 (79) [$M^+ - CO$], 307 (66) [$M^+ - C_3H_6$], 292 (12), 278 (24), 270 (38), 179 (14), 162 (17), 150 (7). $C_{20}H_{22}NOF_3$ (349.4): calcd. C 68.75, H 6.35; found C 68.43, H 6.28. **Variant B:** Following GP, to a solution of (531 mg, 1.00 mmol) of complex **1**-W in 20 mL of pyridine was added (255 mg, 1.50 mmol) of 4-ethynylbenzotrifluoride (**2n**), and the mixture was stirred at 80 °C for 2 days. After chromatography on aluminum oxide (activity II, 20 g), 204 mg (58%) of **4n** was obtained.

7-(Dimethylamino)-11-[2′-(trimethylsilyl)ethynyl]-10-phenyltricyclo-[5.2.2.0^{1,6}]undec-10-en-9-one (4p): Following GP, to a solution of complex **1**-Cr (1.38 g, 3.46 mmol) in pyridine (40 mL) was added (655 mg, 3.30 mmol) of 1-phenyl-4-(trimethylsilyl)-1,3-butadiyne (**2p**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity II, 60 g) eluting with pentane/Et_2O (from 1:0 to 3:1), gave 613 mg (49%) of **4p** [R_f = 0.26 (pentane/Et_2O, 3:1)] as a colorless solid, m.p. 92−94 °C. IR (KBr): $\tilde{\nu}$ = 2937 cm^{-1} (C−H), 2132 (C≡C), 1744 (C=O), 1248, 843, 761, 696. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 1.00−1.34 (m, 4 H, 2,3,4,5-H), 1.61−1.74 (m, 3 H, 3,4,5-H), 2.33−2.57 (m, 4 H, 2,6,8-H), 2.73 [s, 6 H, $N(CH_3)_2$], 7.19−7.39 (m, 5 H, Ph-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.52 ppm[+, $Si(CH_3)_3$], 22.6, 22.7, 23.57, 23.62 (−, C-2,3,4,5), 39.7 (−, C-8), 39.8 [+, $N(CH_3)_2$], 62.0 (+, C-6), 65.1 (C_{quat}, C-1), 73.8 (C_{quat}, C-7), 101.2, 107.3 (C_{quat}, C-1′,2′), 127.5, 127.7, 127.8 (+, Ph-C), 132.1, 133.5 (C_{quat}, C-10, Ph-C), 152.5 (C_{quat}, C-11), 211.9 (C_{quat}, C-9). EI MS (70 eV), *m/z* (%) = 377 (26) [M^+], 349 (7) [$M^+ - CO$], 335 (100) [$M^+ - C_3H_6$], 178 (11), 150 (6), 73 (10). $C_{24}H_{31}NOSi$ (377.6): calcd. C 76.34, H 8.28; found C 76.07, H 8.59.

7-(Dimethylamino)-11-(9′,9′-dihexyl-2′-fluorenyl)-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (4v): Following GP, to a solution of complex **1**-Cr (798 mg, 2.00 mmol) in pyridine (40 mL) was added (850 mg, 2.37 mmol) of 9,9-dihexyl-2-ethynylfluorene (**2v**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity II, 50 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 546 mg (51%) of **4v** [R_f = 0.46 (pentane/Et_2O, 9:1)] as a pale yellow oil. IR (oil): $\tilde{\nu}$ = 2930 cm^{-1} (C−H), 1742 (C=O), 1454, 1131, 1114, 817, 739. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70−0.84 (m, 10 H, hexyl-H), 1.00−1.49 [m, 16 H, 2,3,4,5-H (4 H), hexyl-H (12 H)], 1.64−1.78 (m, 2 H, 3,4-H), 1.89−2.02 [m, 5 H, 5-H (1 H), hexyl-H (4 H)], 2.43 (m, 2 H, 2,8-H), 2.43 [s, 6 H, $N(CH_3)_2$], 2.57−2.62 (m, 1 H, 6-H), 2.84 (d, ^2J = 16.4 Hz, 1 H, 8-H), 5.95 (s, 1 H, 10-H), 7.26−7.38 (m, 3 H, Ar-H), 7.57−7.71 (m, 4 H, Ar-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.86, 13.87 (+, hexyl CH_3), 22.2, 23.0, 24.3, 26.0 (−, C-2,3,4,5), 22.4, 22.5, 23.5, 23.6, 29.5, 29.7, 31.3, 31.4, 40.2 × 2 (−, C-hexyl), 37.2 (−, C-8), 40.0 [+, $N(CH_3)_2$], 54.8 (C_{quat}, C-9′), 59.7 (+, C-6), 62.0 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 119.1, 119.5, 119.6, 121.6, 124.1, 126.6, 126.8 (+, Ar-C), 128.4 (+, C-10), 134.2, 140.4, 140.7, 150.1, 150.8 (C_{quat}, Ar-C), 157.0 (C_{quat}, C-11), 211.8 (C_{quat}, C-9). EI MS (70 eV), *m/z* (%) = 537 (100) [M^+], 509 (37) [$M^+ - CO$], 495 (44) [$M^+ - C_3H_6$], 179 (12). HRMS (EI) calcd. for $C_{38}H_{51}NO$: 537.3971 (correct HRMS).

7-(Dimethylamino)-9-ethoxy-11-phenyltricyclo[5.2.2.0^{1,6}]undec-8-ene (9a): Following GP, to a solution of (813 mg, 2.04 mmol) of complex **1**-Cr in 40 mL of pyridine was added (0.47 mL, 4.06 mmol) of styrene (**8a**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity II, 40 g) eluting with pentane/Et_2O (from 1:0 to 3:1) gave 374 mg (59%) of **9a** [R_f = 0.60 (pentane/Et_2O, 3:1)] as a colorless solid, m.p. 57 °C. IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1} (C−H), 1621 (C=C), 1446, 1347, 1245, 1081, 1036, 754. ^{1}H NMR (250 MHz, $CDCl_3$, plus CH COSY and HH NOESY): δ = 0.95−1.36 (m, 3 H, 2,3,4-H), 1.45 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.47−1.72 (m, 5 H, 3,4,5,10-H), 1.87 (t, ^3J = 7.7 Hz, 1 H, 6-H), 2.02 (dd, ^2J = 11.9, ^3J = 9.5 Hz, 1 H, 10-H_{endo}), 2.16−2.22 (m, 1 H, 2-H), 2.43 [s, 6 H, $N(CH_3)_2$], 3.70 (dd, ^3J = 9.5, ^3J = 4.8 Hz, 1 H, 11-H), 3.94 (q, ^3J = 7.0 Hz, 2 H, CH_2CH_3), 4.46 (s, 1 H, 8-H), 7.13−7.28 (m, 5 H, Ph-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5 (+, CH_2CH_3), 23.4, 23.6, 24.5, 27.7 (−, C-2,3,4,5), 39.9 [+, $N(CH_3)_2$], 44.2 (−, C-10), 45.5 (+, C-11), 50.8 (C_{quat}, C-1), 59.9 (+, C-6), 64.1 (−, CH_2CH_3), 80.5 (C_{quat}, C-7), 93.3 (+, C-8), 125.4, 127.2, 129.1 (+, Ph-C), 144.9 (C_{quat}, Ph-C), 161.9 (C_{quat}, C-9). DCI MS (70 eV), *m/z* (%) = 329 (2) [$M + NH_4^+$], 312 (100) [$M + H^+$]. $C_{21}H_{29}NO$ (311.5): calcd. C 80.98, H 9.38; found C 80.92, H 9.09.

4,4′-Bis[7′′-(dimethylamino)-9"-oxotricyclo[5.2.2.0^{1,6}]undec-10′′-en-11′′-yl]biphenyl (12b): Following GP, a solution of (2.27 g, 5.68 mmol) of complex **1**-Cr in pyridine (40 mL) was treated with (344 mg, 1.70 mmol) of 4,4′-diethynylbiphenyl (**10b**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity II, 60 g) eluting with pentane/Et_2O (from 1:0 to 1:1) gave 476 mg (50%) of **12b** [R_f = 0.56 (pentane/Et_2O, 1:1)] as a colorless solid, m.p. >230 °C. IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1} (C−H), 1736 (C=O), 1492, 1305, 1114, 904, 810. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13−1.48 (m, 8 H, 2′′,3′′,4′′,5′′-H), 1.65−1.76 (m, 4 H, 3′′,4′′-H), 1.82−1.92 (m, 2 H, 5"-H), 2.27 (ABM, dd, ^2J = 16.3, ^4J = 2.3 Hz, 2 H, 8′′-H), 2.29−2.40 (m, 2 H, 2′′-H), 2.41 [s, 12 H, $N(CH_3)_2$], 2.52−2.70 (m, 2 H, 6′′-H), 2.77 (AB, d, ^2J = 16.3 Hz, 2 H, 8′′-H), 5.92 (s, 2 H, 10′′-H), 7.54 (d, ^3J = 8.5 Hz, 4 H, Ar-H), 7.77 (d, ^3J = 8.5 Hz, 4 H, Ar-H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 23.0, 24.4, 26.1 (−, C-2′′,3′′,4′′,5′′), 37.2 (−, C-8′′), 40.2 [+, $N(CH_3)_2$], 59.7 (+, C-6′′), 62.2 (C_{quat}, C-1′′), 74.5 (C_{quat}, C-7′′), 125.7, 126.4 (+, Ar-C), 129.3 (+, C-10"), 134.5, 139.7 (C_{quat}, Ar-C), 156.0 (C_{quat}, C-11"), 212.1 (C_{quat}, C-9"). EI MS (70 eV), *m/z* (%) = 560 (72) [M^+], 532 (50) [$M^+ - CO$], 518 (100) [$M^+ - C_3H_6$], 490 (17), 179 (24), 162 (24), 150 (32). $C_{38}H_{44}N_2O_2$ (560.8): calcd. C 81.39, H 7.91; found C 81.37, H 8.21.

Supporting Information: Preparation and full characterization of compounds **2w**, **2x**, **2y**, **4m**, **4o**, **4q**, **4t**, **4u**, **4w**, **4y**, **9b**, **9c**, **12a**, **12c**, **14**, **15**, **16** (see also the footnote on the first page of this article).

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[7] Compound **9a**: $C_{21}H_{29}NO$, triclinic crystals of space group *P*1, unit cell dimensions: a = 8.4438(8), b = 9.9685(9), c = 11.8828(11) Å, α = 97.698(7), β = 91.575(7), γ = 115.012(7)°, V = 894.28(14) Å^3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-239241. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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