CC-Coupling Reactions of Group 6 Allenylidenes with Ynamines: Formation of New Cyclobutenylidene and Pentatrienylidene Complexes

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The reaction of the diarylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(C_6H_4R\text{-}p)_2]$ (M = Cr (**1**), W (**2**); R = H (**a**), Me (**b**), OMe (**c**), NMe_2 (**d**)) with the ynamines $MeC{\equiv}CNEt_2$ and $PhC{\equiv}CNEt_2$ affords two products: alkenylallenylidene (**3**, **5**) and cyclobutenylidene complexes (**4**, **6**). The alkenylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(NEt_2)C(R'){=}C(C_6H_4R\text{-}p)_2]$ (R′ = Me, M = Cr (**3**), W (**5**), R = H (**a**), Me (**b**), OMe (**c**), NMe_2 (**d**); R′ = Ph, M = Cr (**3**), R = OMe (**e**), NMe_2 (**f**)) are formed *via* cycloaddition of the C≡C bond of the ynamine to the $C^2{=}C^3$ bond of **1** and **2**, respectively, and subsequent cycloreversion. The cyclobutenylidene complexes $[(CO)_5M{=}C{-}C(R'){=}C(NEt_2){-}C{=}C(C_6H_4R\text{-}p)_2]$ (R′ = Me, M = Cr (**4**), W (**6**), R = H (**a**), Me (**b**), OMe (**c**), NMe_2 (**d**); R′ = Ph, M = Cr (**4**), R = OMe (**e**), NMe_2 (**f**)) are formed by cycloaddition of the ynamines to the $C^1{=}C^2$ bond of **1** and **2**. The compounds **3**, **4a**−**c**, **5**, and **6a**−**c** are stable at room temperature. In contrast, **4d**−**f** and **6d** decompose on contact with air, light, or silica. Complex **3d** was characterized by an X-ray structural analysis. The product ratios **3**/**4** and **5**/**6** strongly depend on the solvent and the substitution pattern of both the allenylidene complexes **1** and **2** and the ynamine. In general, decreasing polarity of the solvent increasingly favors formation of cyclobutenylidene complexes. The solvent dependence indicates that the transition state for the formation of **4** and **6** is significantly less polar than that for the formation of **3** and **5**. The ratios **3**/**4** and **5**/**6** increase in the series **a** < **b** < **c** < **d**. Kinetic measurements of the reaction of **1c**,**d** with the ynamines $MeC{\equiv}CNEt_2$ and $PhC{\equiv}CNEt_2$ reveal that the complex pairs **3**,**4** and **5**,**6** are formed in parallel pathways with an associative rate-determining step for each. The reactions follow second-order kinetics, first-order in the concentrations of the allenylidene complexes **1**,**2** and of the ynamines. The activation enthalpies $\Delta H^{\ddagger}$ are small, and the activation entropies $\Delta S^{\ddagger}$ are strongly negative. $\Delta S^{\ddagger}$ is more negative for the formation of the alkenylallenylidene complexes than for the formation of the cyclobutenylidene complexes.

Introduction

Terminal allenylidene complexes of the general type $[L_nM{=}C{=}C{=}CR_2]$ have been known since 1976.[1] Like other systems with an unsaturated carbon chain σ-coordinated to a transition metal, these cumulenylidenes are expected to possess interesting new chemical and physicochemical properties. Significant second-harmonic generation efficiencies of allenylidene complexes have been reported recently.[2] Surprisingly, the chemical reactivity of metal allenylidenes has only been sparingly investigated during the past two decades.[3] However, there is ample evidence for the highly electrophilic character of the metal-bound C^1 atom and the terminal C^3 atom of allenylidene complexes (structures **B** and **C**, Scheme 1). Thus, simple heteroatom nucleophiles such as alcohols, thiols, phosphines, and amines either add exclusively to C^1 *or* C^3 or they attack both of these centers.[3,4] As a consequence, heteroatom substrates with two nucleophilic centers such as hydrazines[5] or hydroxylamines[6] can be added to group 6 allenylidenes to give heterocyclic carbene complexes.

Mostly in the past few years, the reactivity of allenylidene complexes toward carbon nucleophiles has also been investigated.[3,4l−m,w−x,7] Such CC-coupling reactions are especially valuable with respect to the synthetic application of metal allenylidenes. Usually, carbanions attack cationic allenylidene complexes at the terminal C^3 atom to give neutral alkynyl complexes.[4l−m,w−x] Similarly, Me_3C^- adds to the C^3 atom of $[Cp'(CO)_2Mn{=}C{=}C{=}CPh_2]$. Subsequent alkylation affords a neutral vinylidene complex.[8] Only an intramolecular version for direct carbanion attack at the metal-bound C^1 atom of an allenylidene complex has been known until now.[4x] However, neutral carbon nucleophiles such as isonitrile[9] or diazomethane[7b] exclusively insert into the $M{=}C^1$ bond of allenylidene complexes via attack at the metal-bound C^1 atom.

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(2) (a) Tamm, M.; Jentzsch, T.; Werncke, W. *Organometallics* **1997**, *16*, 1418. (b) Roth, G.; Fischer, H.; Meyer-Friederichsen, T.; Heck, J. *Organometallics*, in press.

(3) Recent reviews: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 693. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Le Bozec, H.; Dixneuf, P. H. *Izv. Akad. Nauk, Ser. Khim.* **1995**, 827; *Russ. Chem. Bull.* **1995**, *44*, 801. (e) Werner, H. *Chem. Commun.* **1997**, 903.

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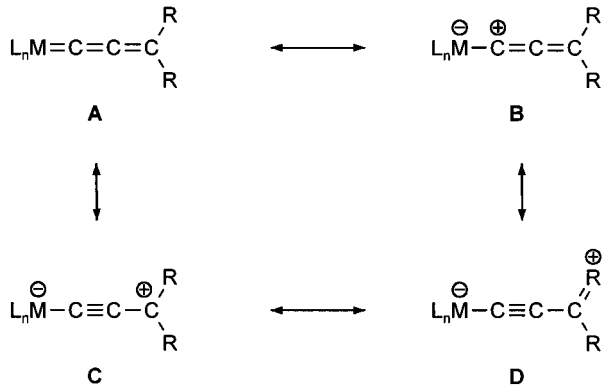
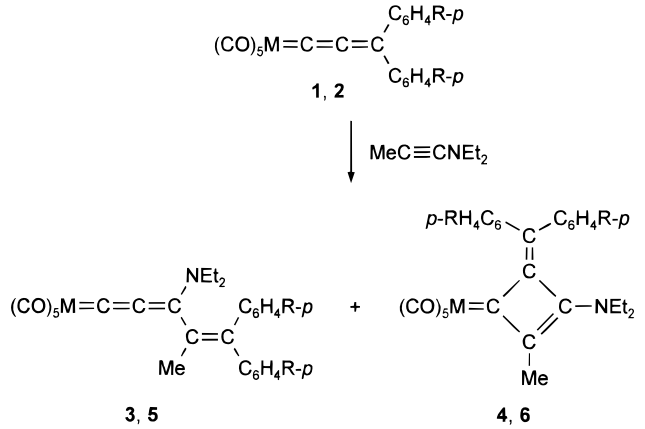
Scheme 1



Studies on coupling reactions of transition metal allenylidenes with CC multiple bond systems are very scarce. $[Cl(P^iPr_3)_2Rh{=}C{=}C{=}CPh_2]$ reacts with $BrMgCH{=}CH_2$ or $PhC{\equiv}CH$ to give π-allylic rhodium complexes.[7a,c] Up to now, a cycloaddition-type reaction of allenylidene complexes has been observed only once. Recently, we showed that alkynyl complexes $[L_n MC{\equiv}CR]$ exclusively undergo a regioselective (2 + 2) cycloaddition to the $C^1{=}C^2$ bond of diarylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(C_6H_4R\text{-}p)_2]$ providing 1,3-dimetalated cyclobutenylidene complexes in high yield.[7d] We now report our results on the reaction of the ynamines $MeC{\equiv}CNEt_2$ and $PhC{\equiv}CNEt_2$ with diaryl-substituted group 6 allenylidenes.

Scheme 2



M = Cr (**1**, **3**, **4**), W (**2**, **5**, **6**)
R = H (**a**), Me (**b**), OMe (**c**), NMe_2 (**d**)

Results and Discussion

Reaction of Diarylallenylidene Complexes with $MeC{\equiv}CNEt_2$. The diarylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(C_6H_4R\text{-}p)_2]$ (M = Cr (**1**), W (**2**); R = H (**a**), Me (**b**), OMe (**c**), NMe_2 (**d**)) are accessible in high yield by reaction of $[(CO)_5M(THF)]$ with the dianion of propargyl alcohols $[C{\equiv}CC(Aryl)_2O]^{2-}$ and subsequent deoxygenation with phosgene.[10] As a solid, **1d** and **2d** are stable in air at room temperature while **1a**−**c** and **2a**−**c** are rather thermolabile. The stability decreases in the series **c** (R = OMe) > **b** (R = Me) > **a** (R = H). Therefore, the deep blue complexes **1a**−**c** and **2a**−**c** were generated in CH_2Cl_2 in situ and the solutions immediately used for the subsequent reaction at −20 °C with the highly nucleophilic ynamine $MeC{\equiv}CNEt_2$ (Scheme 2). On addition of a slight excess of the ynamine, the color of the solutions instantaneously changed to brownish-red. Similarly, the addition of $MeC{\equiv}CNEt_2$ to the blue allenylidene complexes **1d** and **2d** in CH_2Cl_2 at room temperature gave red-brown reaction mixtures within a few seconds (Scheme 2).

IR spectroscopy indicated that two reaction products (**3**,**4** and **5**,**6**) were formed in each case. It was not possible to separate the complex pairs **3**,**4** and **5**,**6** by chromatography. However, since **4d** and **6d** decomposed on contact with silica, chromatographic workup afforded pure fractions of dark red **3d** and **5d** from the reaction of **1d** and **2d** with $MeC{\equiv}CNEt_2$. Red **3a**−**c** and yellow **4a**−**c** as well as red **5a**−**c** and yellow-orange **6a**−**c** were obtained separately by fractional crystallization. In general, the red complexes **3** and **5** are significantly more soluble in pentane or pentane/CH_2Cl_2 mixtures than the yellow compounds **4** and **6**. Thus, **4d** and **6d** could also be obtained in pure form. Stirring a suspension of **1d** or **2d** in pentane with an excess of $MeC{\equiv}CNEt_2$ for 3 days resulted in the formation of a brownish-yellow precipitate of **4d** or **6d**. Purification of the precipitate was performed by extraction with pentane. The total yields (**3** + **4** and **5** + **6**) range from 46% to 87%. All complexes **3** and **5** as well as **4a**−**c** and **6a**−**c** are stable at room temperature. In contrast,

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(10) Fischer, H.; Reindl, D.; Roth, G. *Z. Naturforsch.* **1994**, *49b*, 1207.

4d and **6d** decompose in solution and even in the solid state when exposed to air or light for several hours.

The cyclobutenylidene complexes **4** and **6** show a ν(CO) band pattern, as expected for octahedral pentacarbonyl transition metal complexes. As already discussed for other 3-aminocyclobutenylidene complexes,[11] the E and A_1(trans) ν(CO) absorptions of **4** and **6** are at lower energy than those of simple amino-substituted carbene complexes, indicating an enhanced electron transfer from the cyclic carbene ligand to the metal. Surprisingly and in contrast to **1**, **2**,[10] **4**, and **6**, complexes **3** and **5** show no distinct A_1(cis) ν(CO) absorption in the region between 2040 and 2100 cm^{-1}. The E and A_1(trans) ν(CO) absorptions of **3** and **5** are shifted to higher energy by $\Delta\tilde{\nu} \approx 10-15$ cm^{-1} when compared to **4** and **6**. This indicates that the electron transfer from the cumulenylidene ligand to the metal is less pronounced than that of the cyclobutenylidene ligand to the metal. As expected,[12] the amino(alkenyl)allenylidene complexes **3** and **5** exhibit a characteristic ν(CCC) absorption at 1990 cm^{-1}. The strong mesomeric interaction of the $(CO)_5M$ moiety with the C^3 amino substituent in **3** and **5** leads to a high-energy shift of the ν(CCC) band when compared to the diaryl-substituted allenylidene complexes **1** and **2**.[10] This reflects the enhanced importance of dipolar alkynyl structures for **3** and **5**, as discussed earlier for diaminoallenylidene complexes (structure **C** and **D**, Scheme 1).[12d] The slight shift to higher energy in the series **a** < **b** < **c** < **d** is consistent with the Hammett σ_p coefficients of the *para*-aryl substituents of **3** and **5**.

At room temperature, the ^{1}H NMR spectra of **3** and **5** as well as those of **4** and **6** exhibit two sets of signals for the NEt_2 substituent. This indicates a significant double-bond character of the C^3-N bond in complexes **3**−**6** due to mesomeric interaction of the nitrogen atom with the metal center. Moreover, in **3** and **5**, the methylene protons of the NEt_2 substituent are diastereotopic. Thus, four cleanly separated multiplets with the relative intensity of one proton each are observed for all derivatives of **3** and **5**. As a consequence, atropisomerism[13] for **3** and **5** by steric repulsion has to be assumed due to a hindered rotation of the C(R)═C-$(Aryl)_2$ moiety around the C^3-C^4 bond.

The ^{13}C NMR resonance of the metal-bound C^1 atom (δ 268 (**4**), 248 (**6**)) in the cyclobutenylidene complexes **4** and **6** is comparable to that of aminocarbene complexes. The corresponding signal of dicarbon-substituted carbene complexes with a $(CO)_5M$ fragment is usually observed at considerably lower field.[14,15] The resonance of the allenylidene C^1 carbon atom in the alkenylallenylidene complexes **3** and **5** is at rather high field (δ 220 (**3**), 200 (**5**)). In contrast to **4** and **6**, the ^{13}C resonance of the metal-bound C^1 atom in **3** and **5** is directly affected by the *para*-aryl substituent. To a lesser extent, this is also true for the resonance of the C^2 atom. In the series **a** (H) > **b** (Me) > **c** (OMe) > **d** (NMe_2), the C^1 and C^2 signals shift to higher field, indicating an enhanced electron density in the cumulenylidene ligand with increasing donor capacity of the *para*-substituent. The positions of the signals correlate well with the Hammett σ_p coefficients.

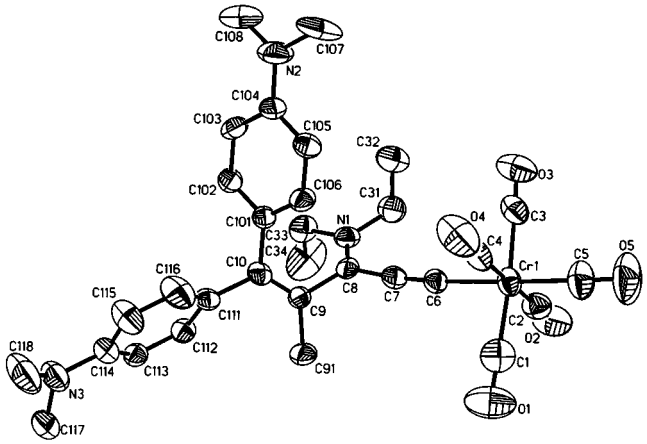


Figure 1. ORTEP plot of complex **3d** (ellipsoids drawn at 50% level, hydrogens omitted).

Table 1. Selected Bond Distances and Angles for 3d

Bond Distances (Å)			
Cr1−C6	2.019(5)	C6−C7	1.221(7)
C7−C8	1.392(7)	C8−N1	1.318(8)
N1−C31	1.480(7)	N1−C33	1.481(7)
C8−C9	1.492(7)	C9−C10	1.339(7)
C10−C101	1.502(7)	C10−C111	1.485(6)
C9−C91	1.510(7)		
Bond Angles (deg)			
Cr1−C6−C7	175.5(5)	C6−C7−C8	173.8(5)
C7−C8−N1	119.7(4)	C8−N1−C31	121.0(4)
C8−N1−C33	123.6(4)	C31−N1−C33	115.4(4)
C7−C8−C9	120.0(5)	C8−C9−C10	120.2(4)
N1−C8−C9	120.2(4)	C9−C10−C101	120.6(4)
C9−C10−C111	123.9(4)	C101−C10−C111	115.5(4)
C8−C9−C91	113.5(4)	C91−C9−C10	126.0(4)

The structure of the new alkenylallenylidene complex **3d** was also established by X-ray structural analysis. In the crystal (Figure 1, Table 1), the CrC_3 fragment of **3d** is nearly linear with a short C6−C7 (1.221(7) Å) and a long C7−C8 (1.392(7) Å) bond similar to other amino-substituted allenylidene complexes.[1a,4i,12d,16] Together with the short C8−N1 bond (1.318(8) Å) and the trigonal-planar coordination of the allenylidene amino substituent (sum of angles at N1 360°), these observations indicate a strong mesomeric interaction of the NEt_2 group with the metal center in **3d**. In contrast, there is no electronic interaction between the alkenyl moiety and the $(CO)_5Cr$ fragment in the solid state. The alkenyl plane of **3d** adopts an upright conformation with respect to the allenylidene plane (torsion angle N1−C8−C9−C10 74.9(6)°), and the C8−C9 (1.492(7) Å) and C9−C10 (1.339(7) Å) bonds are comparable to other conjugated $C(sp^2)-C(sp^2)$ single (1.455 Å) and double

(11) (a) Fischer, H.; Podschadly, O.; Früh, A.; Troll, C.; Stumpf, R.; Schlageter, A. *Chem. Ber.* **1992**, *125*, 2667. (b) Fischer, H.; Volkland, H.-P.; Früh, A.; Stumpf, R. *J. Organomet. Chem.* **1995**, *491*, 267. (c) Fischer, H.; Podschadly, O.; Roth, G.; Herminghaus, S.; Klewitz, S.; Heck, J.; Houbrechts, S.; Meyer, T. *J. Organomet. Chem.* **1997**, *541*, 321.

(12) (a) Peron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497. (b) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157. (c) Péron, D.; Romero, A.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 3319. (d) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139.

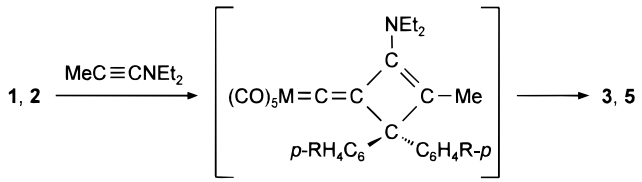
(13) Dötz, K. H. *Chem. Ber.* **1977**, *110*, 78.

(14) For example δ 399 (M = Cr), 358 (M = W) in $(CO)_5M$═CPh_2.

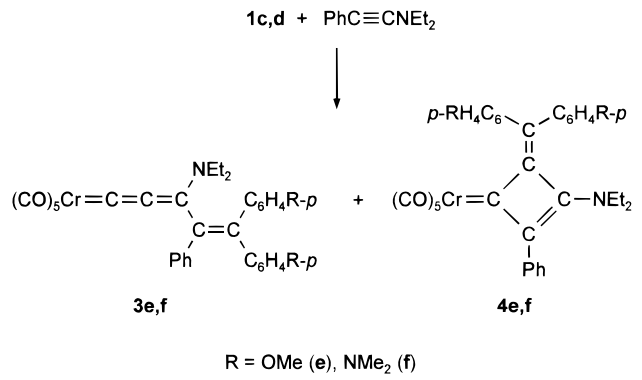
(15) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, U.K., 1981.

(16) (a) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 3173. (b) Bruce, M. I.; Hinterding, P.; Low, P. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1996**, 1009. (c) Winter, R. F.; Hornung, F. M. *Organometallics* **1997**, *16*, 4248.

Scheme 3



Scheme 4



(1.330 Å) bonds.[17] In addition, the aryl substituents and the alkenyl plane of **3d** are not coplanar (angle between the C101−C10−C111 plane and the aryl rings 59.3° and 42.3°). Unfortunately, due to the poor quality of crystals of **4b**, **4d**, and **6a**, a detailed discussion of the structure of these new cyclobutenylidene complexes is not feasible.

Very likely, the alkenylallenylidene complexes **3** and **5** and the cyclobutenylidene complexes **4** and **6** are formed independently in the reaction of the diarylallenylidene complexes **1** and **2** with the ynamine $MeC{\equiv}CNEt_2$. The regioselective formal (2 + 2) cycloaddition of $MeC{\equiv}CNEt_2$ to the $C^1{=}C^2$ bond of **1** and **2** affords **4** and **6** (Scheme 2). The formation of the "insertion products" **3** and **5** presumably proceeds via addition of $MeC{\equiv}CNEt_2$ to the $C^2{=}C^3$ bond of **1** and **2** and a subsequently fast cycloreversion (Scheme 3). However, neither NMR nor IR signals corresponding to any intermediates were observed during the reaction of **1** and **2** with $MeC{\equiv}CNEt_2$.

The product ratios **3**/**5** and **4**/**6** are strongly influenced by the *para*-aryl substituents of the reacting allenylidene complexes **1** and **2**. With the increasing donor capacity of the *para*-substituent, the relative yield of the insertion products **3** and **5** increases: **3**/**4** = 1.6 (**a**), 3.2 (**b**), 7.1 (**c**), 12.4 (**d**); **5**/**6** = 1.8 (**a**), 3.4 (**b**), 7.2 (**c**), 15.0 (**d**). From these trends, it follows that either only one of the two competing reactions (insertion *or* cycloaddition) is affected by electronic factors or both of them are affected in a different way.

Kinetic Investigations. To elucidate the difference between the two reaction mechanisms, kinetic investigations were performed of the reactions of **1c** and **1d** with $MeC{\equiv}CNEt_2$ (DEAP) (Scheme 2) and with $PhC{\equiv}CNEt_2$ (APA) (Scheme 4) using stopped-flow techniques and pseudo-first-order conditions. Similarly to the reaction of **1**,**2** with $MeC{\equiv}CNEt_2$, treatment of **1c**,**d** with $PhC{\equiv}CNEt_2$ also results in the formation of two reaction products (**3e**,**f** and **4e**,**f**, respectively) (Scheme 4).

(17) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

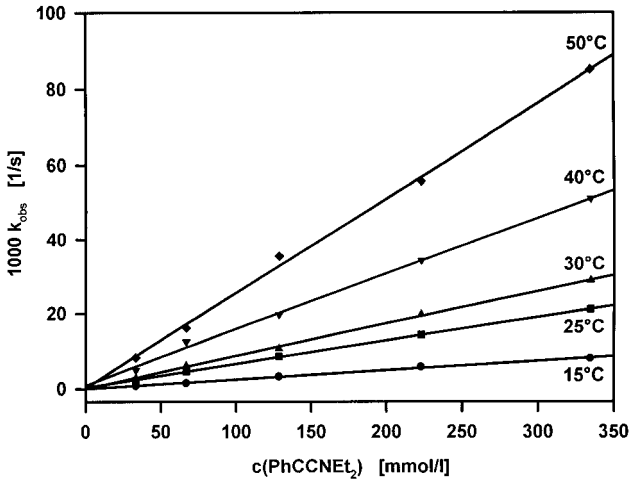


Figure 2. Plot of k_{obs} vs ynamine concentration for the reaction of **1d** with $PhC{\equiv}CNEt_2$ (APA) in 1,1,2-trichloroethane/*n*-heptane (1:4) at 25 °C.

Table 2. Second-Order Rate Constants (L/mol·s) for the Insertion (k_2^{ins}) and Cycloaddition (k_2^{ca}) Reactions of 1c,d with $MeC{\equiv}CNEt_2$ (DEAP) and $PhC{\equiv}CNEt_2$ (APA)[a]

complex	ynamine	solvent	k_2^{ins}	k_2^{ca}	k_2^{ins}/k_2^{ca}
1c	DEAP	TCE	64(1)	43(1)	1.49
1c	DEAP	TCE/H	10.3(5)	35(1)	0.29
1c	APA	TCE	8.7(4)	2.5(2)	3.48
1c	APA	TCE/H	1.7(2)	4.0(2)	0.42
1d	DEAP	TCE	0.57(6)	0.11(1)	5.18
1d	DEAP	TCE/H	0.34(3)	0.55(5)	0.62
1d	APA	TCE	0.013(1)	0.013(1)	1.00
1d	APA	TCE/H	0.014(1)	0.047(3)	0.30

[a] At 25 °C in 1,1,2-trichloroethane (TCE) and 1,1,2-trichloroethane/*n*-heptane (1:4) (TCE/H).

With ynamines in large excess, all reactions are uniform. The product ratios **3**/**5** remain constant throughout the reaction, as indicated by time-resolved UV−vis spectroscopy in CH_2Cl_2 solution. Three isosbestic points are observed for the reaction of **1c** with $MeC{\equiv}CNEt_2$ (at λ = 354, 440, and 520 nm) and $PhC{\equiv}CNEt_2$ (at λ = 356, 438, and 524 nm) and one for the reaction of **1d** with $MeC{\equiv}CNEt_2$ (at λ = 504 nm) and $PhC{\equiv}CNEt_2$ (at λ = 508 nm). Extinction−extinction graphs show a good linear correlation. There is no indication for the formation of any intermediate. Obviously, the alkenylallenylidene complexes **3** as well as the cyclobutenylidene complexes **4** are formed by parallel pathways.

The reactions of **1** with DEAP and APA follow a second-order rate law, first-order in the concentrations of **1** and the ynamine: $-d[\mathbf{1}]/dt = k_2[\mathbf{1}][\text{ynamine}]$.

Representative plots of k_{obs} ($k_{obs} = k_2$[ynamine]) vs ynamine concentration are shown in Figure 2.

Since **3** and **4** are formed by parallel pathways, the product ratio [**3**]/[**4**] reflects the ratio of the rate constants for the formation of **3** (k_2^{ins}) and **4** (k_2^{ca}). From k_2 ($k_2 = k_2^{ins} + k_2^{ca}$) and [**3**]/[**4**] = k_2^{ins}/k_2^{ca}, the constants k_2^{ins} and k_2^{ca} can be calculated. The values of the constants at 25 °C are summarized in Table 2 (for the data at 15, 30, 40, and 50 °C, see Supporting Information).

The overall reaction rate increases (a) with increasing nucleophilicity of the ynamine (by a factor between 8 and 26) and (b) with decreasing π-donor capacity of the

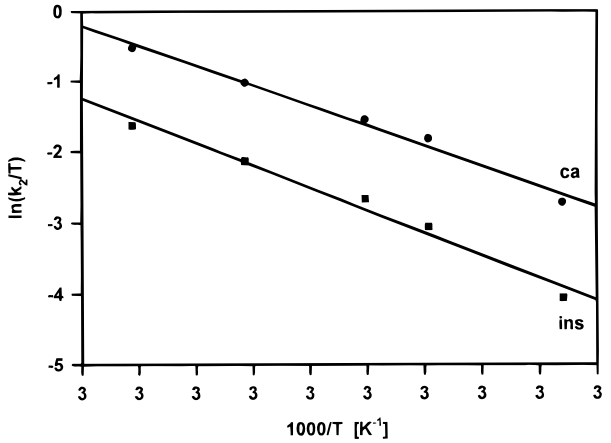


Figure 3. Plot of $\ln(k_2/T)$ vs $1/T$ for the reaction of **1d** with $PhC{\equiv}CNEt_2$ (APA) in 1,1,2-trichloroethane/*n*-heptane (1:4).

Table 3. Activation Enthalpies $\Delta H^{\ddagger}$ (kJ/mol), and Entropies $\Delta S^{\ddagger}$ (J/mol·K) for the Insertion and Cycloaddition Reactions of 1c,d with $MeC{\equiv}CNEt_2$ (DEAP) and $PhC{\equiv}CNEt_2$ (APA)[a]

			insertion		cycloaddition	
complex	ynamine	solvent	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
1c	DEAP	TCE	21(1)	−140(4)	30(1)	−113(5)
1c	DEAP	TCE/H	23(2)	−147(15)	28(1)	−121(6)
1c	APA	TCE/H	26(3)	−152(32)	38(1)	−107(9)
1d	DEAP	TCE	39(1)	−118(5)	60(3)	−61(5)
1d	DEAP	TCE/H	39(1)	−122(5)	46(1)	−93(5)
1d	APA	TCE	34(3)	−147(5)	37(5)	−136(13)
1d	APA	TCE/H	51(7)	−91(10)	48(5)	−91(9)

[a] In 1,1,2-trichloroethane (TCE) and 1,1,2-trichloroethane/*n*-heptane (1:4) (TCE/H).

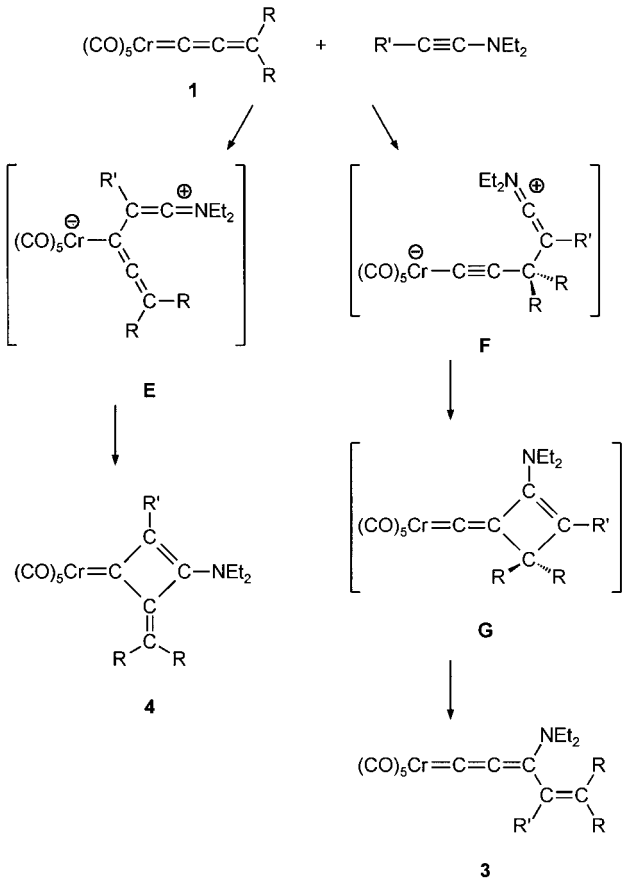
para-substituent in **1** (**1c** → **1d**). The polarity of the solvent influences the overall reaction rates k_2 only slightly, although those of **1c** and **1d** are influenced differently. When the solvent mixture 1,1,2-trichloroethane/*n*-heptane (1:4) is replaced by the more polar 1,1,2-trichloroethane, k_2 for the reaction of **1c** increases and that of **1d** decreases.

However, the individual rate constants k_2^{ins} and k_2^{ca} are strongly affected by a change of the solvent polarity. In 1,1,2-trichloroethane/*n*-heptane (1:4), cycloaddition dominates ($k_2^{ins}/k_2^{ca} \approx 0.3-0.6$) and complexes **4** are the major products. In 1,1,2-trichloroethane, the insertion is favored ($k_2^{ins}/k_2^{ca} \approx 1-5$) and complexes **3** are the main products. Opposing effects are also observed when the nucleophilicity of the ynamine and the π-donor capacity of the *para*-aryl substituent change. Substitution of DEAP for APA in the reaction with **1c**,**d** results in a decrease of k_2^{ins}/k_2^{ca} for **1c** and an increase for **1d**. When **1c** is replaced by **1d**, k_2^{ins}/k_2^{ca} increases for the reaction with DEAP and decreases for the reaction with APA. Both effects are more pronounced in polar 1,1,2-trichloroethane than in the solvent mixture 1,1,2-trichloroethane/*n*-heptane (Table 2).

The activation parameters calculated from plots of $\ln(k_2/T)$ vs $1/T$ (a representative plot is shown in Figure 3) are summarized in Table 3.

The activation enthalpies $\Delta H^{\ddagger}$ are small, and the activation entropies $\Delta S^{\ddagger}$ are strongly negative. These data are in the range usually observed for related reactions. For the insertion reaction of the C≡C bond of DEAP into the M=C bond of the $(CO)_5M$ carbene complexes $[(CO)_5M{=}C(OMe)C_6H_4R\text{-}p]$ (M = Cr, W; R = OMe, Me, H, Br, CF_3), $\Delta S^{\ddagger}$ was reported to lie between −129 and −145 kJ/mol.[18] With the exception of the reaction of **1d** with APA in 1,1,2-trichloroethane/*n*-heptane, $\Delta S^{\ddagger}$ of the insertion reaction is more negative than that of the cycloaddition reaction. As expected from the rate constants, all $\Delta S^{\ddagger}$ values for the reactions of **1c** are more negative than those of **1d**.

Scheme 5

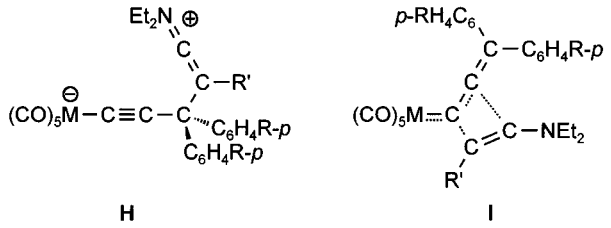


For the initiating reaction steps, essentially two different pathways have to be taken into account. Competing nucleophilic attacks of the ynamine via the C-substituted end of the C≡C bond occur at the most electrophilic allenylidene centers, as shown in Scheme 1. Thus, addition at C^1 (Scheme 5, pathway a) and C^3 of the allenylidene fragment (pathway b) gives **E** and **F**, respectively. A regioselective ring closure involving the allenylidene C^2 atom gives the (2 + 2) cycloadducts **4** and **G**. A subsequent ring closure of **E** involving the metal (i.e., cycloaddition of the C≡C bond across the M=C bond) and cycloreversion would yield amino(butatrienyl)carbene complexes. Products of this type which correspond to a formal insertion of the C≡C bond into the M=C bond have not been observed.

Alternatively, **4** and **G** are also obtained by an electrophilic attack of the ynamine at the allenylidene C^2 atom and subsequent ring closures involving C^1 or C^3. However, since the reaction rate considerably drops (by a factor between 47 and 430) when the π-donor capacity of the *para*-substituent in **1** increases (**1c** → **1d**), this alternative pathway is unlikely.

(18) Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980**, *113*, 193.-

Scheme 6



H **I**

From the solvent dependence of the product ratio, it follows that the transition state for the cycloaddition to the $C^2{=}C^3$ bond of **1** (formation of the insertion product **3** via **G**) is more polar than for the cycloaddition to the $C^1{=}C^2$ bond of **1** (formation of **4**). Therefore, a dipolar transition state like **H** (Scheme 6) in the rate-determining step of the insertion pathway (formation of **3**) and a rather weakly polar transition state like **I** (Scheme 6) in that of the $C^1{=}C^2$-cycloaddition pathway (formation of **4**) is proposed. This proposal is also supported by the other kinetic data and their dependence on the change of the allenylidene and the ynamine substituents.

Concluding Remarks

The reaction of diaryl-substituted group 6 allenylidene complexes $[(CO)_5M{=}C{=}C{=}C(Aryl)_2]$ with ynamines, $RC{\equiv}CNEt_2$, affords two product complexes in each case, alkenylallenylidene complexes and cyclobutenylidene complexes. These results demonstrate the ambident character of the allenylidene ligand. The alkenylallenylidene complexes which are formally the products of an insertion of the C≡C bond into the $C^2{=}C^3$ bond of **1**,**2** are very likely formed via nucleophilic attack of the ynamine at the terminal allenylidene carbon atom C^3 of the allenylidene ligand and a subsequent cyclization−cycloreversion sequence. As a competing reaction, the regioselective cycloaddition of the ynamine to the $C^1{=}C^2$ allenylidene bond by attack at the metal-bound C^1 atom leads to cyclobutenylidene complexes. The rate ratio for the insertion and the cycloaddition depends on the polarity of the solvent, the substitution pattern of the diarylallenylidene complexes, and the nucleophilicity of the ynamine. Decreasing polarity of the solvent favors formation of the cycloadduct. Thus, it is possible to influence the product distribution by choice of the solvent and to predetermine the desired reaction product.

Experimental Section

All operations were performed under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, $Cl_2HC{-}CH_2Cl$) and sodium/benzophenone ketyl (pentane, heptane, Et_2O, THF). The reported yields refer to analytically pure substances. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC250 spectrometer in $CDCl_3$ at 293 K unless otherwise stated. Chemical shifts are relative to TMS. Assignment of the ^{13}C NMR signals is based on HMBC experiments with **4b** and **5c** (Bruker DRX600). Numbering schemes: $[(CO)_5M{=}C^1{=}C^2{=}C^3(NEt_2)C^4(R){=}C^5(Aryl)_2]$ (**3**, **5**) and $[(CO)_5M{=}C^1C^2(R){=}C^3(NEt_2)C^4{=}C^5(Aryl)_2]$ (**4**, **6**). Other analyses: IR, Biorad FTS 60; UV−vis, Hewlett-Packard 8452A diode array spectrophotometer; MS, Finnigan MAT 312; elemental analyses, Heraeus CHN-O-RAPID. The silica used for column chromatography (silica for flash chromatography, J. T. Baker) was dried in vacuo for 8 h before usage. The compounds **1c**, **1d**, and **2d**[10] and $MeC{\equiv}CNEt_2$ and $PhC{\equiv}CNEt_2$[19] were prepared by literature methods.

Reaction of 1a−c and 2a−c with $MeC{\equiv}CNEt_2$. The allenylidene complexes **1a**−**c** and **2a**−**c** were generated in situ according to a literature method[10] starting from 5.00 mmol (1.10 g) of $[Cr(CO)_6]$ or 5.00 mmol (1.76 g) of $[W(CO)_6]$. At −20 °C, to these deep blue (**1a**,**b** and **2a**,**b**) or deep green (**1c** and **2c**) solutions in CH_2Cl_2 was added a solution of 6.03 mmol (0.67 g) of $MeC{\equiv}CNEt_2$ in 5 mL of CH_2Cl_2. The color of the solutions instantaneously turned to brown-red. After the mixtures were warmed to room temperature, they were chromatographed at −20 °C on silica with pentane/CH_2Cl_2/Et_2O (7:2:1). A dark red band was eluted. The solvent was evaporated in vacuo, and the residue containing the complex pair **3**,**4** or **5**,**6** was extracted twice with 100 mL of pentane. The remaining brown-yellow powder (complex **4** or **6**) and the dark red residue obtained from the pentane extract (complex **3** or **5**) were recrystallized (solvent see below).

Pentacarbonyl[3-(diethylamino)-4-methyl-5,5-diphenyl-1,2,4-pentatrienylidene]chromium (3a): 0.96 g (39% based on $[Cr(CO)_6]$) of red crystals from pentane/CH_2Cl_2 (20:1), mp 72 °C. Anal. Calcd for $C_{27}H_{23}CrNO_5$ (493.5): C, 65.71; H, 4.70; N 2.84. Found: C, 65.50; H, 4.77; N, 2.96. IR (Et_2O): ν(CO) 1939 vs, 1921 m cm^{-1}; ν(CCC) 1986 m cm^{-1}. ^{1}H NMR: δ 0.97 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.10 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.15 (s, 3 H, $=CCH_3$), 3.05, 3.32, 3.81, 4.28 (4 × m$_c$, 4 × 1 H, CH_2CH_3) 7.16−7.40 (m, 10 H, aromatic). ^{13}C{^{1}H} NMR: δ 11.1, 13.3 (CH_2CH_3), 20.5 ($=CCH_3$), 45.6, 47.9 (CH_2CH_3), 121.3 (C^2), 129.4 (C^4), 128.1, 128.4, 129.5, 129.6, 139.9, 140.2 (aromatic), 143.4 (C^5), 155.5 (C^3), 217.8 (*cis*-CO), 223.9 (*trans*-CO), 224.3 (C^1). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 466 nm (4.294).

Pentacarbonyl[3-(diethylamino)-4-(diphenylmethylene)-2-methyl-2-cyclobutenylidene]chromium (4a): 0.59 g (24% based on $[Cr(CO)_6]$) of yellow needles from pentane/CH_2Cl_2 (4:1), mp 151 °C (dec). Anal. Calcd for $C_{27}H_{23}CrNO_5$ (493.5): C, 65.71; H, 4.70; N, 2.84. Found: C, 65.62; H, 4.86; N, 2.78. IR (Et_2O): ν(CO) 2046 m, 1967 w, 1927 s sh, 1922 vs, 1909 m sh cm^{-1}. ^{1}H NMR: δ 0.72 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.57 (s, 3 H, $=CCH_3$), 2.65 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.47 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 7.08−7.36 (m, 10 H, aromatic). ^{13}C-{^{1}H} NMR: δ 12.5, 13.9 (CH_2CH_3), 16.0 ($=CCH_3$), 43.3, 45.9 (CH_2CH_3), 123.8 (C^5), 127.8, 127.9, 128.3, 128.5, 129.6, 132.0, 139.8, 143.6 (aromatic), 149.2 (C^4), 162.7 (C^2), 163.2 (C^3), 218.3 (*cis*-CO), 225.4 (*trans*-CO), 268.0 (C^1). FAB MS (NBOH) *m*/*z*: 493 (16, [M$^+$]), 409 (100, [M$^+$ − 3CO]), 353 (78, [M$^+$ − 5CO]).

Pentacarbonyl[3-(diethylamino)-4-methyl-5,5-bis(*p*-tolyl)-1,2,4-pentatrienylidene]chromium (3b): 0.91 g (35% based on $[Cr(CO)_6]$) of red needles from pentane/CH_2Cl_2 (40:1), mp 110 °C. Anal. Calcd for $C_{29}H_{27}CrNO_5$ (521.5): C, 66.79; H, 5.22; N, 2.69. Found: C, 66.72; H, 5.42; N, 2.59. IR (Et_2O): ν(CO) 1938 vs, 1919 m cm^{-1}; ν(CCC) 1988 m cm^{-1}. ^{1}H NMR: δ 1.02 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3); 1.10 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.14 (s, 3 H, $=CCH_3$), 2.30, 2.36 (2 × s, 2 × 3 H, $C_6H_4CH_3$), 3.06, 3.37, 3.78, 4.25 (4 × m$_c$, 4 × 1 H, CH_2CH_3), 7.02−7.23 (m, 8 H, aromatic). ^{13}C{^{1}H} NMR: δ 11.1, 13.2 (CH_2CH_3), 20.6 ($=CCH_3$), 21.1, 21.2 ($C_6H_4CH_3$), 45.6, 48.0 (CH_2CH_3), 120.6 (C^2), 128.3 (C^4), 128.9, 129.5, 129.6, 137.1, 137.4, 138.0, 138.3 (aromatic), 143.6 (C^5), 156.1 (C^3), 217.8 (*cis*-CO), 221.5 (C^1), 223.9 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 462 nm (4.435).

Pentacarbonyl[4-(bis(*p*-tolyl)methylene)-3-(diethylamino)-2-methyl-2-cyclobutenylidene]chromium (4b): 0.29 g (11% based on $[Cr(CO)_6]$) of yellow needles from pentane/CH_2-

(19) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, Netherlands, 1988.

Cl_2 (4:1), mp 135 °C (dec). Anal. Calcd for $C_{29}H_{27}CrNO_5$ (521.5): C, 66.79; H, 5.22; N, 2.69. Found: C, 66.68; H, 5.40; N, 2.58. IR (Et_2O): ν(CO) 2046 m, 1968 vw, 1922 vs, 1908 m cm^{-1}. ^1H NMR: δ 0.74 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.33, 2.37 (2 × s, 2 × 3 H, $C_6H_4CH_3$), 2.55 (s, 3 H, =CCH_3), 2.66 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.46 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 6.95−7.26 (m, 8 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 12.5, 13.9 (CH_2CH_3), 15.9 (=CCH_3), 21.2, 21.3 ($C_6H_4CH_3$), 43.4, 45.9 (CH_2CH_3), 123.9 (C^5), 128.9, 129.1, 129.4, 131.8, 136.9, 137.5, 140.8 (aromatic), 148.4 (C^4), 162.0 (C^2), 163.8 (C^3), 218.3 (*cis*-CO), 225.6 (*trans*-CO), 267.2 (C^1).

Pentacarbonyl[3-(diethylamino)-5,5-bis(*p*-methoxyphenyl)-4-methyl-1,2,4-pentatrienylidene]chromium (3c): 1.57 g (57% based on $[Cr(CO)_6]$) of red crystals from pentane/Et_2O (15:1), mp 119 °C. Anal. Calcd for $C_{29}H_{27}CrNO_7$ (553.5): C, 62.92; H, 4.92; N, 2.53. Found: C, 62.89; H, 5.00; N, 2.69. IR (Et_2O): ν(CO) 1937 vs, 1920 m cm^{-1}; ν(CCC) 1988 m cm^{-1}. ^1H NMR (273 K): δ 1.04 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.11 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.18 (s, 3 H, =CCH_3), 3.00, 3.34 (2 × m_c, 2 × 1 H, CH_2CH_3), 3.80, 3.84 (2 × s, 2 × 3 H, OCH_3), 3.78, 4.32 (2 × m_c, 2 × 1 H, CH_2CH_3), 6.79−6.91, 7.08−7.23 (2 × m, 2 × 4 H, aromatic). $^{13}C\{^1H\}$ NMR (273 K): δ 11.2, 13.3 (CH_2CH_3), 20.9 (=CCH_3), 45.5, 48.1 (CH_2CH_3), 55.2 (OCH_3), 120.1 (C^2), 127.3 (C^4), 113.3, 113.4, 131.1, 131.3, 132.3, 132.8, 159.2, 159.4 (aromatic), 143.0 (C^5), 156.1 (C^3), 217.7 (*cis*-CO), 219.2 (C^1), 223.8 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 464 nm (4.285).

Pentacarbonyl[4-(bis(*p*-methoxyphenyl)methylene)-3-(diethylamino)-2-methyl-2-cyclobutenylidene]chromium (4c): 0.22 g (8% based on $[Cr(CO)_6]$) of yellow needles from pentane/Et_2O (10:1), mp 126 °C. Anal. Calcd for $C_{29}H_{27}CrNO_7$ (553.5): C, 62.92; H, 4.92; N, 2.53. Found: C, 62.63; H, 4.95; N, 2.82. IR (Et_2O): ν(CO) 2046 m, 1967 vw, 1921 vs, 1909 m cm^{-1}. ^1H NMR (273 K): δ 0.78 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.55 (s, 3 H, =CCH_3), 2.71 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.48 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.82, 3.86 (2 × s, 2 × 3 H, OCH_3), 6.81−7.04, 7.25−7.29 (2 × m, 6 and 2 H, aromatic). $^{13}C\{^1H\}$ NMR (273 K): δ 12.7, 14.0 (CH_2CH_3), 16.1 (=CCH_3), 43.3, 45.7 (CH_2CH_3), 55.3 (OCH_3), 123.4 (C^5), 113.5, 113.7, 130.8, 132.3, 133.2, 136.2, 159.0 (aromatic), 147.7 (C^4), 161.4 (C^2), 164.7 (C^3), 218.3 (*cis*-CO), 225.6 (*trans*-CO), 268.1 (C^1).

Pentacarbonyl[3-(diethylamino)-4-methyl-5,5-diphenyl-1,2,4-pentatrienylidene]tungsten (5a): 1.06 g (34% based on $[W(CO)_6]$) of red needles from pentane/CH_2Cl_2 (10:1), mp 84 °C. Anal. Calcd for $C_{27}H_{23}NO_5W$ (625.3): C, 51.86; H, 3.71; N, 2.24. Found: C, 51.87; H, 3.81; N, 2.25. IR (Et_2O): ν(CO) 1934 vs, 1914 m cm^{-1}; ν(CCC) 1988 m cm^{-1}. ^1H NMR: δ 0.98 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.12 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.14 (s, 3 H, =CCH_3), 3.05, 3.33, 3.81, 4.23 (4 × m_c, 4 × 1 H, CH_2CH_3), 7.15−7.41 (m, 10 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 11.0, 13.1 (CH_2CH_3), 20.2 (=CCH_3), 45.9, 48.1 (CH_2CH_3), 119.0 (C^2), 129.2 (C^4), 128.2, 128.3, 128.4, 129.4, 129.6, 139.7, 140.0 (aromatic), 143.6 (C^5), 157.4 (C^3), 197.2 (*cis*-CO, $^1J_{W,C}$ = 125 Hz), 200.4 (C^1); 203.7 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 456 nm (4.380). EI MS (70 eV) *m*/*z*: 625 (6, $[M^+]$), 470 (33, $[M^+ - 3CO - CH_3]$), 296 (39, $[(CO)_4W^+]$), 268 (100, $[(CO)_3W^+]$).

Pentacarbonyl[3-(diethylamino)-4-(diphenylmethylene)-2-methyl-2-cyclobutenylidene]tungsten (6a): 0.59 g (19% based on $[W(CO)_6]$) of yellow needles from pentane/CH_2Cl_2 (4:1), mp 150 °C (dec). Anal. Calcd for $C_{27}H_{23}NO_5W$ (625.3): C, 51.86; H, 3.71; N, 2.24. Found: C, 51.94; H, 3.73; N, 2.28. IR (Et_2O): ν(CO) 2055 w, 1965 vw, 1919 vs, 1907 m sh cm^{-1}. ^1H NMR: δ 0.74 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.32 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.50 (s, 3 H, =CCH_3), 2.65 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.49 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 7.09−7.35 (m, 10 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 12.5, 13.9 (CH_2CH_3), 17.3 (=CCH_3), 43.6, 46.1 (CH_2CH_3), 124.6 (C^5), 127.9, 128.2, 128.6, 129.7, 132.3, 139.3, 143.5 (aromatic), 148.7 (C^4), 162.9 (C^2), 167.0 (C^3), 198.6 (*cis*-CO, $^1J_{W,C}$ = 126 Hz), 205.2 (*trans*-CO), 247.8 (C^1). EI MS (70 eV) *m*/*z*: 625 (13, $[M^+]$), 541 (100, $[M^+ - 3CO]$), 513 (28, $[M^+ - 4CO]$).

Pentacarbonyl[3-(diethylamino)-4-methyl-5,5-bis(*p*-tolyl)-1,2,4-pentatrienylidene]tungsten (5b): 1.21 g (37% based on $[W(CO)_6]$) of red needles from pentane/CH_2Cl_2 (50:1), mp 130 °C. Anal. Calcd for $C_{29}H_{27}NO_5W$ (653.4): C, 53.31; H, 4.17; N, 2.14. Found: C, 53.40; H, 4.20; N, 2.25. IR (Et_2O): ν(CO) 1933 vs, 1914 m cm^{-1}; ν(CCC) 1990 m cm^{-1}. ^1H NMR: δ 1.02 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.11 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.14 (s, 3 H, =CCH_3), 2.31, 2.37 (2 × s, 2 × 3 H, $C_6H_4CH_3$), 3.01, 3.35, 3.79, 4.24 (4 × m_c, 4 × 1 H, CH_2CH_3), 7.03−7.19 (m, 8 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 11.1, 13.1 (CH_2CH_3), 20.4 (=CCH_3), 21.2, 21.3 ($C_6H_4CH_3$), 45.8, 48.2 (CH_2CH_3), 118.8 (C^2), 128.3 (C^4), 129.0, 129.5, 129.6, 137.1, 137.4, 138.1, 138.4 (aromatic), 143.8 (C^5), 157.9 (C^3), 197.2 (*cis*-CO, $^1J_{W,C}$ = 125 Hz), 199.5 (C^1), 203.7 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 454 nm (4.373).

Pentacarbonyl[4-(bis(*p*-tolyl)methylene)-3-(diethylamino)-2-methyl-2-cyclobutenylidene]tungsten (6b): 0.36 g (11% based on $[W(CO)_6]$) of yellow crystals from pentane/CH_2Cl_2 (4:1), mp 135 °C (dec). Anal. Calcd for $C_{29}H_{27}NO_5W$ (653.4): C, 53.31; H, 4.17; N, 2.14. Found: C, 53.25; H, 4.21; N, 2.17. IR (Et_2O): ν(CO) 2055 w, 1964 vw, 1919 vs, 1906 m sh cm^{-1}. ^1H NMR: δ 0.76 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.34, 2.37 (2 × s, 2 × 3 H, $C_6H_4CH_3$), 2.48 (s, 3 H, =CCH_3), 2.68 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.48 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 6.96−7.24 (m, 8 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 12.6, 14.0 (CH_2CH_3), 17.4 (=CCH_3), 21.2, 21.3 ($C_6H_4CH_3$), 43.6, 46.1 (CH_2CH_3), 124.7 (C^5), 128.9, 129.2, 129.7, 132.2, 136.3, 137.7, 137.8, 140.8 (aromatic), 147.9 (C^4), 162.2 (C^2), 167.4 (C^3), 198.6 (*cis*-CO, $^1J_{W,C}$ = 126 Hz), 205.5 (*trans*-CO), 248.5 (C^1).

Pentacarbonyl[3-(diethylamino)-5,5-bis(*p*-methoxyphenyl)-4-methyl-1,2,4-pentatrienylidene]tungsten (5c): 1.74 g (51% based on $[W(CO)_6]$) of red needles from pentane/CH_2Cl_2 (10:1), mp 141 °C. Anal. Calcd for $C_{29}H_{27}NO_7W$ (685.4): C, 50.82; H, 3.97; N, 2.04. Found: C, 50.81; H, 4.14; N, 2.08. IR (Et_2O): ν(CO) 1933 vs, 1912 m cm^{-1}; ν(CCC) 1990 m cm^{-1}. ^1H NMR: δ 1.06 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.11 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_2CH_3), 2.16 (s, 3 H, =CCH_3), 3.01, 3.39 (2 × m_c, 2 × 1 H, CH_2CH_3), 3.79, 3.83 (2 × s, 2 × 3 H, OCH_3), 3.78, 4.26 (2 × m_c, 2 × 1 H, CH_2CH_3), 6.80−6.91, 7.08−7.22 (2 × m, 2 × 4 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 11.3, 13.1 (CH_2CH_3), 20.6 (=CCH_3), 45.8, 48.3 (CH_2CH_3), 55.3 (OCH_3), 118.5 (C^2, $^2J_{W,C}$ = 25 Hz), 127.4 (C^4), 113.6, 131.0, 131.2, 132.3, 132.8, 159.4, 159.7 (aromatic), 143.4 (C^5), 158.1 (C^3), 197.2 (*cis*-CO, $^1J_{W,C}$ = 125 Hz), 197.8 (C^1, $^1J_{W,C}$ not found), 203.6 (*trans*-CO, $^1J_{W,C}$ = 130 Hz). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 454 nm (4.386).

Pentacarbonyl[4-(bis(*p*-methoxyphenyl)methylene)-3-(diethylamino)-2-methyl-2-cyclobutenylidene]tungsten (6c): 0.24 g (7% based on $[W(CO)_6]$) of yellow crystals from pentane/CH_2Cl_2 (4:1), mp 145 °C (dec). Anal. Calcd for $C_{29}H_{27}NO_7W$ (685.4): C, 50.82; H, 3.97; N, 2.04. Found: C, 50.71; H, 4.03; N, 2.00. IR (Et_2O): ν(CO) 2054 m, 1963 vw, 1921 vs sh, 1917 vs, 1905 m sh cm^{-1}. ^1H NMR: δ 0.81 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.32 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.47 (s, 3 H, =CCH_3), 2.72 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.49 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.81, 3.84 (2 × s, 2 × 3 H, OCH_3), 6.81−6.90, 7.00−7.04, 7.24−7.27 (3 × m, 4 and 2 × 2 H, aromatic). $^{13}C\{^1H\}$ NMR: δ 12.7, 14.0 (CH_2CH_3), 17.3 (=CCH_3), 43.6, 46.0 (CH_2CH_3), 55.3 (OCH_3), 124.1 (C^5), 113.6, 113.8, 130.9, 131.8, 133.5, 136.2, 159.3, 159.6 (aromatic), 147.2 (C^4), 161.8 (C^2), 168.1 (C^3), 198.7 (*cis*-CO, $^1J_{W,C}$ = 126 Hz), 205.5 (*trans*-CO, $^1J_{W,C}$ = 125 Hz), 248.4 (C^1, $^1J_{W,C}$ = 88 Hz).

Reaction of 1d and 2d with MeC≡CNEt$_2$ in CH$_2$Cl$_2$. At room temperature, to a blue solution of 0.32 mmol of **1d** (0.15 g) or **2d** (0.19 g) in 20 mL of CH_2Cl_2 was added a solution of 0.99 mmol (0.11 g) of MeC≡$CNEt_2$ in 5 mL of CH_2Cl_2. Within a few seconds the reaction mixture turned brown-red. After

removal of the solvent, the brown residue was chromatographed on silica at −20 °C. Elution with Et_2O afforded a dark red solution containing **3d** or **5d**.

Pentacarbonyl[3-(diethylamino)-5,5-bis(*p*-(dimethylamino)phenyl)-4-methyl-1,2,4-pentatrienylidene]chromium (3d): 0.16 g (87% based on **1d**) of red crystals from pentane/Et_2O (2:1), mp 150 °C. Anal. Calcd for $C_{31}H_{33}CrN_3O_5$ (579.6): C, 64.24; H, 5.74; N, 7.25. Found: C, 64.21; H, 5.80; N, 7.31. IR (Et_2O): ν(CO) 1936 vs, 1915 m cm^{-1}; ν(CCC) 1990 m cm^{-1}. ^{1}H NMR: δ 1.06 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.08 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 2.20 (s, 3 H, =CCH_3), 2.94, 2.99 (2 × s, 2 × 6 H, NCH_3), 2.95, 3.38, 3.75, 4.29 (4 × m_c, 4 × 1 H, CH_2CH_3), 6.55−6.68, 7.00−7.14 (2 × m, 2 × 4 H, aromatic). ^{13}C{^{1}H} NMR (273 K): δ 11.6, 13.3 (CH_2CH_3), 21.5 (=CCH_3), 40.3 (NCH_3), 45.5, 48.3 (CH_2CH_3), 119.4 (C^2), 124.4 (C^4), 111.1, 111.2, 128.1, 128.5, 131.1, 131.3, 149.8, 150.0 (aromatic), 145.1 (C^5), 157.5 (C^3), 214.1 (C^1), 217.8 (*cis*-CO), 223.8 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 466 nm (4.355). FAB MS (NBOH) *m/z*: 580 (14, [MH$^+$]), 495 (17, [M$^+$ − 3CO]), 467 (27, [M$^+$ − 4CO]), 439 (100, [M$^+$ − 5CO]).

Pentacarbonyl[3-(diethylamino)-5,5-bis(*p*-(dimethylamino)phenyl)-4-methyl-1,2,4-pentatrienylidene]tungsten (5d): 0.12 g (53% based on **2d**) of dark red crystals from pentane/Et_2O (2:1), mp 166 °C (dec). Anal. Calcd for $C_{31}H_{33}N_3O_5W$ (711.4): C, 52.33; H, 4.68; N, 5.91. Found: C, 52.46; H, 4.72; N, 5.89. IR (Et_2O): ν(CO) 1931 vs, 1909 m cm^{-1}; ν(CCC) 1992 m cm^{-1}. ^{1}H NMR: δ 1.07 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.09 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 2.19 (s, 3 H, =CCH_3), 2.94, 2.99 (2 × s, 2 × 6 H, NCH_3), 2.93, 3.41, 3.76, 4.26 (4 × m_c, 4 × 1 H, CH_2CH_3), 6.56−6.69, 7.00−7.13 (2 × m, 2 × 4 H, aromatic). ^{13}C{^{1}H} NMR: δ 11.6, 13.1 (CH_2CH_3), 21.2 (=CCH_3), 40.2 (NCH_3), 45.8, 48.5 (CH_2CH_3), 117.8 (C^2), 124.5 (C^4), 111.3, 111.4, 128.2, 128.6, 131.1, 131.3, 150.1, 150.4 (aromatic), 145.7 (C^5), 159.5 (C^3), 193.1 (C^1), 197.4 (*cis*-CO, $^1J_{W,C}$ = 125 Hz), 203.7 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 456 nm (4.398).

Reaction of 1d and 2d with MeC≡CNEt$_2$ in Pentane. At room temperature, 2.55 mmol (0.28 g) of MeC≡$CNEt_2$ was added to a suspension of 0.86 mmol of **1d** (0.40 g) or **2d** (0.51 g) in 100 mL of pentane and stirred for 72 h in the dark. The resulting brownish precipitate was filtered off, extracted 4 times with 100 mL of pentane/CH_2Cl_2 (9:1) each in order to remove a small amount of byproduct (**3d** or **5d**), and finally recrystallized.

Pentacarbonyl[4-(bis(*p*-(dimethylamino)phenyl)methylene)-3-(diethylamino)-2-methyl-2-cyclobutenylidene]chromium (4d): 0.38 g (76% based on **1d**) of a brown-yellow powder from pentane/CH_2Cl_2 (1:5), mp 194 °C. Anal. Calcd for $C_{31}H_{33}CrN_3O_5$ (579.6): C, 64.24; H, 5.75; N, 7.25. Found: C, 64.22; H, 5.74; N, 7.22. IR (Et_2O): ν(CO) 2046 w, 1966 vw, 1922 vs, 1904 m cm^{-1}. ^{1}H NMR: δ 0.81 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_2CH_3), 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.53 (s, 3 H, =CCH_3), 2.75 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 2.95, 2.98 (2 × s, 2 × 6 H, NCH_3), 3.46 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 6.60−7.30 (m, 8 H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 12.9, 14.1 (CH_2CH_3), 16.0 (=CCH_3), 40.4, 40.6 (NCH_3), 43.5, 45.7 (CH_2CH_3), 125.2 (C^5), 111.8, 112.2, 128.4, 130.6, 132.2, 133.0, 149.9, 150.5 (aromatic), 146.3 (C^4), 160.0 (C^2), 166.0 (C^3), 218.6 (*cis*-CO), 226.0 (*trans*-CO), 268.8 (C^1).

Pentacarbonyl[4-(bis(*p*-(dimethylamino)phenyl)methylene)-3-(diethylamino)-2-methyl-2-cyclobutenylidene]tungsten (6d): 0.26 g (42% based on **2d**) of a brown-yellow powder from pentane/CH_2Cl_2 (1:5), mp 211 °C (dec). Anal. Calcd for $C_{31}H_{33}N_3O_5W{\cdot}CH_2Cl_2$ (711.4 + 84.9): C, 48.26; H, 4.43; N, 5.28. Found: C, 48.54; H, 4.66; N, 5.31. IR (Et_2O): ν(CO) 2052 w, 1963 vw, 1915 vs, 1899 m cm^{-1}. ^{1}H NMR: δ 0.83 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.45 (s, 3 H, =CCH_3), 2.74 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 2.96, 2.98 (2 × s, 2 × 6 H, NCH_3), 3.48 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 6.60−6.72, 6.95−6.98, 7.18−7.22 (3 × m, 4 and 2 × 2 H, aromatic). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 13.1, 14.3 (CH_2CH_3), 17.6 (=CCH_3), 40.6, 40.8 (NCH_3), 44.3, 46.5 (CH_2CH_3), 126.2 (C^5), 112.3, 112.5, 128.3, 131.0, 132.2, 133.7, 150.7, 151.0 (aromatic), 146.0 (C^4), 161.2 (C^2), 170.2 (C^3), 199.5 (*cis*-CO, $^1J_{W,C}$ = 126 Hz), 206.2 (*trans*-CO, $^1J_{W,C}$ = 124 Hz), 247.1 (C^1).

Reaction of 1c and 1d with PhC≡CNEt$_2$. In addition to the kinetic investigations, complexes **3e**,**f** and **4e**,**f** were also synthesized on a preparative scale.

Pentacarbonyl[3-(diethylamino)-5,5-bis(*p*-methoxyphenyl)-4-phenyl-1,2,4-pentatrienylidene]chromium (3e): $C_{34}H_{29}CrNO_7$ (615.6). IR (Et_2O): ν(CO) 1939 vs, 1918 m cm^{-1}; ν(CCC) 1987 m cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 480 nm (4.048).

Pentacarbonyl[4-(bis(*p*-methoxyphenyl)methylene)-3-(diethylamino)-2-phenyl-2-cyclobutenylidene]chromium (4e): At room temperature, 1.50 mmol (0.26 g) of PhC≡$CNEt_2$ was added to a suspension of 0.50 mmol (0.22 g) of **1c** in 100 mL of pentane and stirred for 24 h. The resulting brownish-orange precipitate was filtered off, extracted 4 times with 100 mL of pentane/CH_2Cl_2 (9:1) each in order to remove a small amount of byproduct (**3e**), and finally recrystallized: 0.13 g (42% based on **1c**) of a yellow powder from pentane/CH_2Cl_2 (1:3), mp 134 °C. Anal. Calcd for $C_{34}H_{29}CrNO_7{\cdot}^1/_4CH_2Cl_2$ (615.6 + 21.2): C, 64.60; H, 4.67; N, 2.20. Found: C, 64.37; H, 5.02; N, 1.97. IR (Et_2O): ν(CO) 2046 w, 1967 vw, 1926 vs, 1908 m cm^{-1}. ^{1}H NMR: δ 0.82 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 0.96 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 2.69 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.12 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.82, 3.85 (2 × s, 2 × 3 H, OCH_3), 6.84−6.92, 7.07−7.11, 7.31−7.54 (3 × m, 4 and 2 and 7 H, aromatic). ^{13}C{^{1}H} NMR: δ 12.7, 12.8 (CH_2CH_3), 43.3, 45.4 (CH_2CH_3), 55.4 (OCH_3), 126.6 (C^5), 113.7, 113.9, 128.3, 128.5, 129.7, 131.1, 132.2, 133.5, 134.8, 136.4, 159.5, 159.8 (aromatic), 148.5 (C^4), 165.0 (C^2), 166.1 (C^3), 218.2 (*cis*-CO), 225.6 (*trans*-CO), 276.3 (C^1).

Pentacarbonyl[3-(diethylamino)-5,5-bis(*p*-(dimethylamino)phenyl)-4-phenyl-1,2,4-pentatrienylidene]chromium (3f): At room temperature, a solution of 1.50 mmol (0.26 g) of PhC≡$CNEt_2$ in 5 mL of CH_2Cl_2 was added to a blue solution of 0.32 mmol (0.15 g) of **1d** in 20 mL of CH_2Cl_2. Within a few seconds, the reaction mixture turned brown-red. After removal of the solvent, the brown residue was chromatographed on silica at −20 °C. Elution with CH_2Cl_2/pentane (1:3) afforded a dark red solution containing **3f**: 0.13 g (63% based on **1d**) of red crystals from pentane/Et_2O (4:1), mp 156 °C. Anal. Calcd for $C_{36}H_{35}CrN_3O_5$ (641.7): C, 67.38; H, 5.50; N 6.55. Found: C, 66.98; H, 5.63; N, 6.61. IR (Et_2O): ν(CO) 1936 vs, 1912 m cm^{-1}; ν(CCC) 1987 m cm^{-1}. ^{1}H NMR: δ 0.72 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 1.23 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3), 2.91, 2.96 (2 × s, 2 × 6 H, NCH_3), 3.28, 3.46, 3.97, 4.19 (4 × m_c, 4 × 1 H, CH_2CH_3), 6.42−6.45, 6.59−6.63, 6.88−6.92, 7.01−7.05, 7.14−7.24 (5 × m, 4 × 2 and 5 H, aromatic). ^{13}C{^{1}H} NMR: δ 11.4, 11.8 (CH_2CH_3), 40.1, 40.2 (NCH_3), 46.0, 47.0 (CH_2CH_3), 122.9 (C^2), 128.0 (C^4), 111.0, 111.4, 127.1, 128.5, 128.8, 129.8, 130.2, 131.3, 132.9, 139.6, 149.9, 151.0 (aromatic), 148.6 (C^5), 155.7 (C^3), 217.9 (*cis*-CO), 220.6 (C^1), 224.6 (*trans*-CO). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 482 nm (4.241).

Pentacarbonyl[4-(bis(*p*-(dimethylamino)phenyl)methylene)-3-(diethylamino)-2-phenyl-2-cyclobutenylidene]chromium (4f): At room temperature, 3.30 mmol (0.57 g) of PhC≡$CNEt_2$ was added to a suspension of 1.10 mmol (0.52 g) of **1d** in 100 mL of pentane and stirred for 72 h in the dark. The resulting brownish precipitate was filtered off, extracted 4 times with 100 mL of pentane/CH_2Cl_2 (9:1) each in order to remove a small amount of byproduct (**3f**), and finally recrystallized: 0.47 g (68% based on **1d**) of a brown-yellow powder from pentane/CH_2Cl_2 (1:4), mp 120 °C (dec). Anal. Calcd for $C_{36}H_{35}CrN_3O_5{\cdot}^1/_4CH_2Cl_2$ (641.7 + 21.2): C, 65.68; H, 5.40; N, 6.34. Found: C, 65.46; H, 5.66; N, 6.45. IR (Et_2O): ν(CO) 2045 w, 1968 vw, 1924 vs, 1904 m cm^{-1}. ^{1}H NMR: δ 0.84 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 0.97 (t, $^3J_{H,H}$ = 7.2 Hz,

3 H, CH_2CH_3), 2.72 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 2.97, 3.00 (2 × s, 2 × 6 H, NCH_3), 3.11 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2CH_3), 6.62−6.74, 7.01−7.05, 7.26−7.29, 7.37−7.54 (4 × m, 4 and 2 × 2 and 5 H, aromatic). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.0, 13.1 (CH_2CH_3), 40.5, 40.7 (NCH_3), 43.9, 45.9 (CH_2CH_3), 128.6 (C^5), 112.2, 112.3, 128.5, 130.4, 131.2, 132.2, 133.7, 135.9, 150.8, 151.0 (aromatic), 147.0 (C^4), 164.1 (C^2), 168.8 (C^3), 218.9 (*cis*-CO), 226.3 (*trans*-CO), 274.5 (C^1).

X-ray Structural Analysis of 3d. $C_{31}H_{33}CrN_3O_5$, M_r = 579.6, monoclinic, space group $P2_1/n$, a = 13.552(7) Å, b = 12.206(6) Å, c = 18.902(11) Å, β = 95.47(4)°, V = 3113(3) Å^3, Z = 4, d_c = 1.237 g cm^{-3}, $F(000)$ = 1216, μ = 0.396 mm^{-1}, R (R_w) = 0.072 (0.060) for 3343 observed reflections [$F > 3.0\sigma(F)$], largest difference peak/hole +0.43/−0.36 e Å^{-3}. A single crystal was grown from pentane/Et_2O (2:1) and mounted in a glass capillary. All crystal data were collected on a Siemens R3m/V diffractometer at −20 °C (Wyckoff scan, 4° < 2θ < 52°) with a graphite monochromator (Mo Kα, λ = 0.710 73 Å). The structure was solved with Patterson methods and refined by full-matrix least-squares techniques (Siemens SHELXTL PLUS). The positions of the hydrogen atoms were calculated in ideal geometry (d_{CH} = 0.960 Å) and refined in the "riding model". All other atoms were refined anisotropically.

Kinetic Investigations. Kinetic measurements were performed with a stopped-flow apparatus SFA-11 (HI-TECH) by using a thermostated UV−vis cuvette (d = 0.2 cm) as the reaction cell. Air and moisture were carefully excluded. The reactions were followed by UV−vis spectroscopy (Lambda 15, Perkin-Elmer). For all reactions, pseudo-first-order conditions were employed (ratio $[ynamine]_0/[\mathbf{1}]_0 > 10$). The disappearance of the educt complexes **1c**,**d** was monitored continuously at λ = 684 (**1c**) and 686 (**1d**) nm in 1,1,2-trichloroethane and λ = 678 (**1c**) and 708 (**1d**) nm in 1,1,2-trichloroethane/*n*-heptane (1:4) for at least 5−7 half-lives. Plots of $\ln(A - A_\infty)$ vs time were linear for more than 3 half-lives (usually 4−5 half-lives). The rate constant k_{obs} was determined from the slope of these lines by the least-squares method using the data for the first 3 half-lives. The rate constants k_{obs} for different kinetic runs under identical conditions were reproducible to at least 6%. The accuracy of the temperature measurements was ±0.1 °C. The second-order rate constants k_2 given in Table 2 were calculated from plots of k_{obs} vs $[\mathbf{1}]_0$. The averages of k_{obs} of at least 3 runs under identical conditions were employed. The activation parameters given in Table 3 were determined from second-order rate constants at 5 temperatures between 15 and 50 °C (15, 20, 25, 30, 40, and 50 °C) each. After completion of the kinetic runs, the reaction solutions were transferred into a Schlenk tube. The solvent was evaporated in vacuo, the residue dissolved in 1 mL of CH_2Cl_2, and the product ratio determined by IR spectroscopy.

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Supporting Information Available: Tables of crystal data and refinement details, positional and thermal parameters, and bond distances and angles for compound **3d** and kinetic data for the reactions of **1c**,**d** with ynamines (17 pages). Ordering information is given on any current masthead page.

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