Bidentate Alkene–Aminocarbene Complexes of Chromium. Synthesis and Reactivity toward Alkynes

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The reaction of the aminocarbene complex $(CO)_5Cr{=}C(CH_3)NHCH_2CH{=}CH_2$ (**2**) with lithium diisopropylamide (LDA) followed by methyl iodide led, at -60 °C, to $(CO)_5Cr{=}C(CH_3)N(CH_3)CH_2CH{=}CH_2$ (**7**) and, at 0 °C, to $(CO)_5Cr{=}C(CH_3)N(CH_3)CH{=}CH(CH_3)$ (**8**). Both complexes **7** and **8** gave upon coordination in refluxing toluene $(CO)_4Cr{=}C(CH_3)N(CH_3)(\eta^2\text{-}CH_2CH{=}CH_2)$ (**9**). Complex **9** reacted with diphenylacetylene to give the insertion–cyclopropanation (arene)chromium tricarbonyl complex **10**. In the case of the phenyl-substituted carbene complex $(CO)_4Cr{=}C(Ph)NHCH_2CH{=}CH_2$ (**6**) the reaction with alkynes led to the annulation products **11**, **12**, and **13** isolated as the (arene)chromium tricarbonyl complexes. The structures of complexes **8**, **9**, **10**, and **12** were determined by X-ray crystallography. Crystals of **8** are monoclinic, space group *Pn*, with unit cell dimensions a = 6.240 (2) Å, b = 10.787 (1) Å, c = 10.262 (2) Å, α = 90°, β = 95.96 (2)°, and γ = 90°. Crystals of **9** are triclinic, space group $P\bar{1}$, with a = 6.808 (3) Å, b = 6.952 (2) Å, c = 12.811 (2) Å, α = 93.73 (2)°, β = 100.05 (3)°, and γ = 102.45 (3)°. Crystals of **10** are monoclinic, space group $P2_1/n$, with a = 9.710 (2) Å, b = 19.278 (4) Å, c = 10.634 (4) Å, α = 90°, β = 103.24 (2)°, and γ = 90°. Crystals of **12** are monoclinic, space group $C2/c$, with a = 26.384 (14) Å, b = 6.398 (2) Å, c = 19.461 (4) Å, α = 90°, β = 115.27 (1)°, and γ = 90°. The structures were solved and refined to the following R and R_w values: **8**, R = 0.0313, R_w = 0.0357, on 997 observed ($I > 3\sigma(I)$) data; **9**, R = 0.0280, R_w = 0.0300, on 1666 data; **10**, R = 0.0413, R_w = 0.0357, on 1858 data; **12**, R = 0.0292, R_w = 0.0357, on 1858 data. The transformation of complex **8** into complex **9** provides the first example of the internal to terminal double-bond isomerization upon coordination of an alkene–carbene ligand.

Introduction

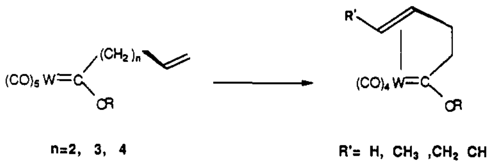
Two years ago,[1-3] we described the use of bidentate alkene–carbene complexes of tungsten both as initiators for the polymerization of alkynes and as synthons for the preparation of bicyclo[4.1.0]heptane derivatives. The high reactivity of these complexes was ascribed to the presence of a coordinated double bond in the γ-position with respect to the carbene function.[4] These alkene–carbene complexes were obtained by coordination of a double bond already in the γ-position or by isomerization of a terminal double bond toward an internal position, γ- with respect to the carbene function (Scheme I).[5-7]

In order to extend this insertion–cyclopropanation reaction to the preparation of heterocyclic compounds, we prepared complexes of tungsten and chromium bearing the 1-4 bidentate alkene–aminocarbene ligand[8,9] and studied their behavior toward alkynes. Such reactions are interesting from both a structural and a synthetic point of view. Here we report on the preparation and mechanistic and structural aspects of the starting compounds and also on their reaction with alkynes. The structures of an insertion–cyclopropanation product and of an insertion–annulation product established by X-ray analysis are reported.

Results and Discussion

Pentacarbonyl((*N*-2-propenyl-*N*-methylamino)methylcarbene)chromium(0) (7) and Pentacarbonyl((*N*-1-propenyl-*N*-methylamino)methylcarbene)chromium(0) (8). Complex **2** was prepared by aminolysis[7,10] of **1**, in ether at room temperature. According to the ^{1}H NMR spectrum, the isomer that is obtained in this reaction is **2E**, with only trace amounts of **2Z**: a signal due to the N–CH_2 group appears at 4.09 ppm whereas the presence of a free double bond is confirmed by signals at 5.87 ppm (1 H, m) and at 5.34 ppm (2 H, dd).

Scheme I



Methylation of complex **2** at nitrogen was performed according to a method described by Casey.[11] In a first attempt, the addition of an excess of lithium diisopropylamide (LDA) and methyl iodide at low temperature (-70 °C), gave complex **7**, as expected, as an orange oil.

According to the ^{1}H NMR spectrum, complex **7** exists as two *E* and *Z* isomers, in a 60:40 ratio. The signals could be assigned to each isomer according to the literature data on related compounds[7,11] and also by chemical means (vide infra): thus, the most abundant complex was assigned

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(1) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Organomet. Chem.* **1985**, *287*, C-8.

(2) Liaw, D. Y.; Soum, A.; Fontanille, M.; Rudler, H. *Makromol. Chem., Rapid. Commun.* **1985**, *6*, 309.

(3) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041.

(4) Alvarez, C.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1982**, *228*, C7.

(5) Alvarez, C.; Rudler, H.; Daran, J. C.; Parlier, A.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 576.

(6) Alvarez, C.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C.; Knobler, C.; Jeannin, Y. *J. Orgnomet. Chem.* **1987**, *328*, 357.

(7) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754.

(8) Parlier, A.; Rudler, H.; Alvarez, C.; Delgado-Reyes, F. *J. Organomet. Chem.* **1987**, *327*, 339.

(9) Parlier, A.; Rudler, H.; Daran, J. C.; Alvarez, C. *J. Organomet. Chem.* **1987**, *333*, 245.

(10) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578.

(11) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. T. *J. Am. Chem. Soc.* **1982**, *104*, 2417.

0276-7333/89/2308-2253$01.50/0

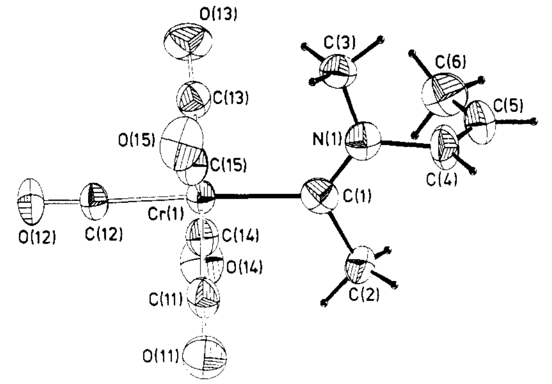
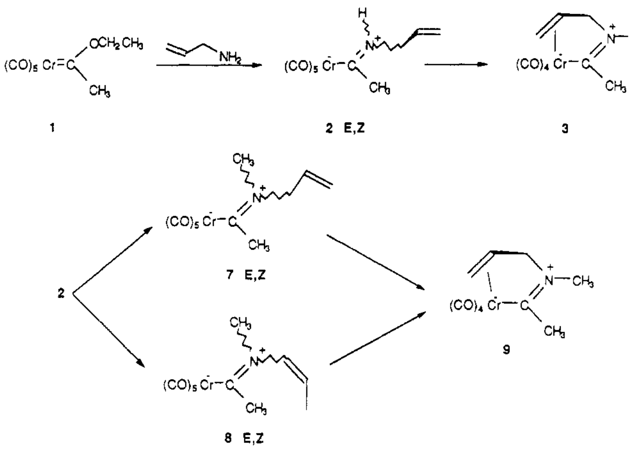


Figure 1. ORTEP drawing showing numbering scheme for 8.

structure **7E** with signals due to the N-CH_3 and N-CH_2 groups at 3.82 and 4.28 ppm, respectively, whereas the minor isomer **7Z** shows signals at 3.20 and 4.83 ppm, respectively.



When the reaction conditions were modified by carrying out the methyl iodide addition at 0 °C, a complex, different from 7(*E*,*Z*) was isolated in 86% yield. This complex is again a mixture of two isomers that could be partially separated into two fractions by silica gel chromatography: the first fraction contained only one isomer (mp 51 °C); the second fraction, a 20/80 mixture of the two isomers, enriched in the second one. According to the mass spectrum and to the elemental analysis, these new complexes are isomers of 7. The ^1H NMR spectrum clearly shows the absence of a terminal double bond: one observes for the pure isomer a doublet at 1.50 ppm (J = 6.6 Hz) due to a methyl group on a double bond, a doublet at 6.09 ppm (1 H, J = 8 Hz), and a doublet of quartets at 5.53 ppm (1 H, J = 8 and 6.6 Hz), both due to the protons associated with a cis-disubstituted double bond. The presence of a signal at 3.78 ppm for N-CH_3 is in agreement with that for structure **8E**.

An X-ray crystallographic study of **8E** confirmed its structure as a pentacarbonylchromium carbene–alkene complex. Interatomic distances and angles are listed in Table I. Figure 1 illustrates the octahedral geometry of **8E** with the cis C(4)–C(5) double bond. Three points must be noticed: the first one is the staggered geometry of the carbene function with respect to the four cis CO groups, the angle between the Cr(1)–C(15)–C(14)–C(12) plane and the Cr(1)–C(1)–N(1)–C(2) plane being equal to 45.5°; the second one is the geometry of the planes containing respectively C(1)–C(2)–N(1)–C(3) and C(4)–C(5)–C(6) which are almost perpendicular (88.9°); the third point concerns the C(1)–N(1) bond distance (1.279 Å) which, like other carbon–nitrogen bond distances of aminocarbene complexes,[7,8,9,12] is very close to the value for a carbon–nitrogen double bond (1.28–1.38 Å in iminium salts).[14]

Table I. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound 8

Bond Distances			
Cr(1)–C(1)	2.116 (6)	C(4)–C(5)	1.314 (9)
C(1)–C(2)	1.549 (9)	C(4)–N(1)	1.466 (6)
C(1)–N(1)	1.279 (7)	C(5)–C(6)	1.47 (1)
C(3)–N(1)	1.445 (7)		
Bond Angles			
C(11)–Cr(1)–C(1)	89.1 (2)	N(1)–C(4)–C(5)	122.2 (5)
C(12)–Cr(1)–C(1)	177.2 (2)	C(6)–C(5)–C(4)	125.9 (6)
C(13)–Cr(1)–C(1)	93.1 (2)	C(3)–N(1)–C(1)	124.3 (5)
C(14)–Cr(1)–C(1)	89.5 (2)	C(4)–N(1)–C(3)	114.2 (5)
C(15)–Cr(1)–C(1)	94.6 (2)	C(4)–N(1)–C(1)	121.4 (5)
N(1)–C(1)–C(2)	114.0 (5)		

Table II. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound 9

Bond Distances			
Cr(1)–C(1)	2.070 (2)	N(1)–C(3)	1.469 (3)
Cr(1)–C(5)	2.272 (2)	N(1)–C(4)	1.462 (3)
Cr(1)–C(6)	2.296 (2)	C(4)–C(5)	1.502 (3)
C(1)–C(2)	1.488 (3)	C(5)–C(6)	1.364 (3)
C(1)–N(1)	1.301 (3)		
Bond Angles			
C(2)–C(1)–Cr(1)	125.1 (2)	C(4)–N(1)–C(1)	119.3 (2)
N(1)–C(1)–Cr(1)	118.7 (1)	C(4)–N(1)–C(3)	114.3 (2)
N(1)–C(1)–C(2)	116.2 (2)	C(5)–C(4)–N(1)	111.0 (2)
C(3)–N(1)–C(1)	126.1 (2)	C(6)–C(5)–C(4)	122.2 (2)

As far as the formation of complexes 8(*E*,*Z*) is concerned, they probably result from a base-catalyzed isomerization of the double bond of 7(*E*,*Z*); since LDA is used in a slight excess and since it is known[11,15] that anions can be generated at a carbon α to the nitrogen in aminocarbene complexes, it is likely that the hydrogen on C(4), which is in the α-position of both the double bond and the positively charge nitrogen, is selectively abstracted, giving a crotyl anion and finally, upon protonation, the azadiene system 8. The observation that the cis isomer around the C(5)–C(6) double bond is formed could be assigned to the fact that, in general, a crotyl anion favors a cis skeleton.[16]

Coordination of the Double Bond of 7: Formation of *cis*-Tetracarbonyl(((*Z*)-η^2-*N*-methyl-*N*-2-propenylamino)methylcarbene)chromium(0) (9). When a mixture of complexes 7(*E*,*Z*) was heated in refluxing hexane, only the **7Z** isomer underwent the coordination of its double bond to the metal center, giving complex 9. **7E** and 9 could be separated easily by silica gel chromatography. More polar 9 was isolated as orange crystals (mp 103–104 °C): this result means that at 65 °C, no interconversion between **7E** and **7Z** took place. However, a complete conversion of 7(*E*,*Z*) into complex 9 could be observed at higher temperature, in refluxing toluene. The fact that in 9 the double bond is coordinated to the metal is readily apparent from the ^1H NMR spectrum, the three protons associated with the double bond being shifted to higher field at 3.86 ppm for C(5)–H and at 3.39 and 2.79 ppm for C(6)–H_2. The structure of 9 was determined, in an X-ray study. The most important bond

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(12) Guy, J. T.; Bennett, D. W. *Transition Met. Chem. (Weinheim, Ger.)* **1984**, *9*, 43.

(13) Dötz, K. H.; Popall, M.; Müller, G. *J. Organomet. Chem.* **1987**, *334*, 57.

(14) Merenyi, R. *Adv. Org. Chem.*, **1976**, *9*, 90.

(15) Casey, C. P.; Hornung, N. L.; Vollendorf, N. W. *J. Organomet. Chem.* **1986**, *303*, 375.

(16) Schleyer, P. v. R.; Diu, J. D.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497.

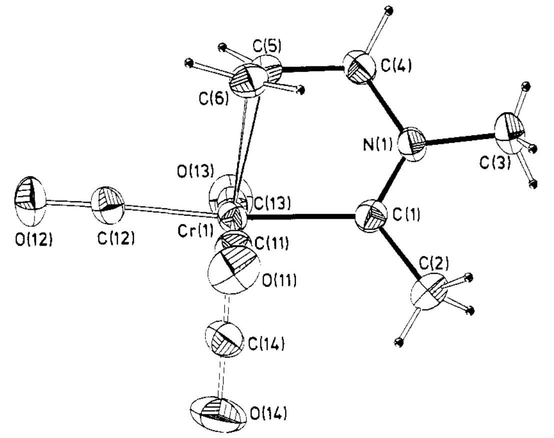


Figure 2. ORTEP drawing showing numbering scheme for **10**.

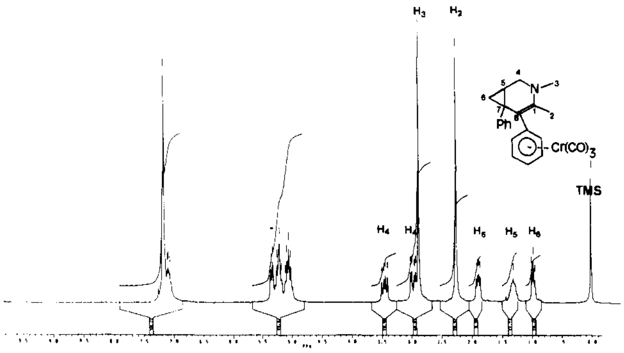


Figure 3. ^1H NMR spectrum of complex **10** at 200 MHz, in $CDCl_3$.

distances and angles are given in Table II. An ORTEP drawing (Figure 2) shows a slightly distorted octahedral geometry with an almost perpendicular orientation of the carbene and the alkene ligands, a feature common to related structures of the literature;[4-6,9,11-13] the angle between the C(4)–C(5)–C(6) and the Cr(1)–C(1)–N(1)–C(2) planes equals 117 (3)°.

Coordination of the Double Bond of 8 by an Internal to Terminal Double-Bond Isomerization. One of the most striking results of this study is the coordination of the double bond of **8**, after isomerization toward a terminal position. Thus, when a solution of **8E** was refluxed in toluene for 5 h, complex **9** was isolated in 79% yield. The same result was observed in the case of complex **8Z**.

Isomerization of terminal double bonds to internal double bonds have often been observed during coordination of the double bond of alkene–carbene complexes of tungsten and of chromium. To our knowledge, the reverse isomerization had never been observed. Terminal to internal double-bond isomerization reaction has been explained in terms of an intermolecular W(0)- or Cr(0)-promoted hydrogen migration via π-allyl complexes,[6,7] giving the more stable 1,4-chelate system. Such a mechanism could also account for the isomerization observed in the above case.

***cis*-Tetracarbonyl(((*Z*)-η^2-2-propenylamino)-phenylcarbene)chromium(0) (6).** The preparation of **6** was straightforward starting from the phenylethoxycarbene complex **4**: treatment with allylamine at room temperature, led to a mixture of isomers **5**(*E*,*Z*), which could not be separated. Heating of this mixture in refluxing toluene gave complex **6** in 51% yield (mp 103 °C). The presence of a coordinated double bond is again evident from the ^1H NMR and ^{13}C NMR spectra with signals due to the atoms associated with the double bond at respectively 5.3 (1 H, m), 4.40 (2 H, m), and 77.8 and 65.6 ppm.

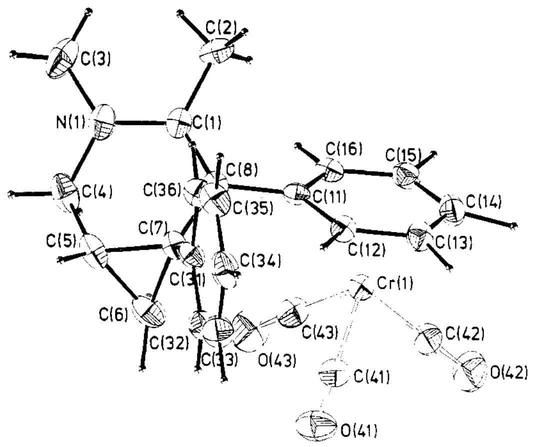
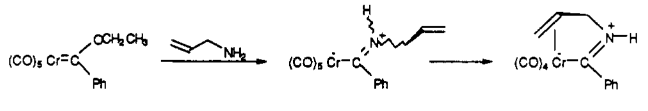
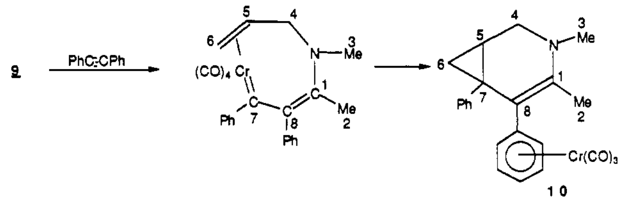


Figure 4. ORTEP drawing showing numbering scheme for **10**.



4 5 E,Z 6

Reactivity of Complexes 9 and 6 toward Alkynes. Complex 9: Insertion–Cyclopropanation Reaction. When **9** was heated for 12 h in refluxing benzene in the presence of diphenylacetylene, a new complex could be isolated in 51% yield after silica gel chromatography, as yellow crystals (mp 129–130 °C).



Structure **10** was established on the following grounds: the ^1H NMR spectrum (Figure 3) clearly shows the presence of two phenyl groups, thus confirming the insertion of one molecule of diphenylacetylene into the starting complex **9**. The first one gives signals at 7.15 ppm, as a multiplet; the second one, around 5.2 ppm, is typical for an (arene)chromium tricarbonyl group. All other hydrogens are magnetically inequivalent and give multiplets. Thus $C(6)–H_2$ gives signals at 0.96 (t) and 1.88 (q) ppm, C(5)H at 1.30 (m) ppm, and $C(4)H_2$ at 2.96 (dd) and 3.44 (qq) ppm. The two singlets at 2.24 and 2.86 ppm can be assigned to the methyl groups on the double bond and on the nitrogen, respectively. The ^{13}C NMR spectrum is also in agreement with such a structure: the (arene)chromium tricarbonyl group shows signals at 234.4 ppm (CO's) and between 97 and 90.9 ppm (Ar). The carbon atoms of the double bond C(1)–C(8) give two signals at 116 and 104 ppm.

Structure **10** was confirmed by an X-ray analysis. The ORTEP drawing (Figure 4) confirms all the structural features and especially the presence of a cyclopropane ring, the bond distances and bond angles (Table III) being classical for a substituted three-membered ring system.[17] The six-membered ring of **10** adopts a twisted geometry with a N(1)–C(4)–C(5)–C(7) torsion angle of 34.4°; the angle between the cyclopropane ring C(5)–C(6)–C(7) and the N(1)–C(1)–C(8)–C(7)–C(2)–C(11) plane is equal to

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[17] Tinant, B.; De Block, I.; Declercq, J. P.; Germain, G.; Van Meersch, M.; Leroy, G.; Weiler, J. *Bull. Soc. Chim. Belg.* **1982**, *91*, 629.

Table III. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound 10

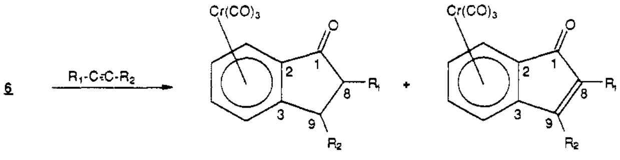
Bond Distances			
C(1)–C(2)	1.496 (7)	C(5)–C(6)	1.519 (9)
C(1)–C(8)	1.359 (7)	C(5)–C(7)	1.513 (7)
C(1)–N(1)	1.386 (7)	C(6)–C(7)	1.506 (7)
C(3)–N(1)	1.475 (8)	C(7)–C(8)	1.507 (7)
C(4)–C(5)	1.511 (9)	C(7)–C(31)	1.511 (7)
C(4)–N(1)	1.453 (8)	C(8)–C(11)	1.486 (7)
Bond Angles			
C(7)–C(5)–C(6)	89.6 (4)	N(1)–C(1)–C(2)	116.5 (5)
C(7)–C(6)–C(5)	60.0 (3)	N(1)–C(1)–C(8)	120.1 (5)
C(6)–C(7)–C(5)	60.4 (4)	N(1)–C(4)–C(5)	112.0 (4)
C(8)–C(7)–C(5)	114.6 (4)	C(6)–C(5)–C(4)	121.6 (5)
C(8)–C(7)–C(6)	118.1 (4)	C(7)–C(5)–C(4)	115.0 (4)
C(31)–C(7)–C(5)	115.4 (4)	C(12)–C(11)–C(8)	123.0 (4)
C(31)–C(7)–C(6)	119.7 (4)	C(16)–C(11)–C(8)	119.9 (4)
C(31)–C(7)–C(8)	116.3 (4)	C(32)–C(31)–C(7)	122.0 (4)
C(7)–C(8)–C(1)	119.4 (4)	C(36)–C(31)–C(7)	119.2 (4)
C(11)–C(8)–C(1)	122.2 (4)	C(3)–N(1)–C(1)	119.9 (5)
C(11)–C(8)–C(7)	118.3 (4)	C(4)–N(1)–C(1)	116.0 (5)
C(8)–C(1)–C(2)	123.4 (4)	C(4)–N(1)–C(3)	113.2 (5)

55.2°. As far as the phenyl groups are concerned, the one that is free is almost perpendicular to both the N(1)–C(1)–C(8)–C(7)–C(2)–C(11) plane (84.8°) and the more electron-rich phenyl ring, bearing the chromium tricarbonyl group (84.1°).

The formation of complex **10** from complex **9** is thus in agreement with our earlier results in the field of tungsten complexes bearing a 1–4 bidentate alkene–carbene ligand, which, in all cases, gave the insertion–cyclopropanation reaction.[3] A last point that has to be mentioned is the stability of the enamine function of **10** toward air oxidation. This was not the case for the enamines obtained from complex **3** which underwent an easy air oxidation of the double bond to form a cyclopropanic keto amide.[18]

Complex 6: Insertion–Annulation Reaction. It has been shown by Dötz[19] and more recently by Yamashita[20] that carbene complexes of chromium bearing a phenyl group on the carbene carbon atom undergo the annulation reaction. It was therefore of interest to see whether complex **6** would undergo either the insertion–cyclopropanation reaction or the insertion–annulation reaction.

When **6** was refluxed in benzene for 10 h, in the presence of a sixfold excess of 3-hexyne, a new complex could be isolated as bright orange crystals from hexane/CH_2Cl_2 (71% yield; mp 77 °C). The ^1H and ^{13}C NMR and IR spectra are in agreement with those for structure **12** in which diethylindanone is coordinated to $Cr(CO)_3$. The ^1H NMR spectrum shows multiplets between 5.3 and 6.0 ppm due to the 4 H's of the coordinated aromatic ring, two multiplets at 3 and 2.5 ppm, due to C(8)–H and C(9)–H, two multiplets centered at 2.15 and 1.85 ppm, due to the two methylene groups of CH_2CH_3, and finally two triplets at 1.05 and 1.30 ppm for the two methyl groups. The ^{13}C NMR spectrum shows signals at 231 (CO's), 205.6 (ketone), and 97.3, 93.5, 91.1, 87.9, and 86.4 ppm ($Ar(Cr(CO)_3)$).



12 $R_1 = R_2 = CH_2\ CH_3$
13 $R_1 = CH_3$, R_2 = Ph
15 $R_1 = R_2 = CH_3$

11 $R_1 = R_2 = CH_2\ CH_3$
14 $R_1 = CH_3$, R_2 = Ph

Table IV. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound 12

Bond Distances			
Cr(1)–C(2)	2.203 (2)	C(2)–C(7)	1.403 (3)
Cr(1)–C(3)	2.250 (2)	C(3)–C(13)	1.397 (3)
Cr(1)–C(4)	2.234 (2)	C(3)–C(9)	1.518 (3)
Cr(1)–C(5)	2.201 (2)	C(4)–C(5)	1.413 (4)
Cr(1)–C(6)	2.206 (2)	C(5)–C(6)	1.392 (4)
Cr(1)–C(7)	2.209 (2)	C(6)–C(7)	1.407 (4)
C(1)–C(2)	1.482 (3)	C(8)–C(9)	1.549 (3)
C(1)–C(8)	1.519 (3)	C(8)–C(81)	1.528 (3)
C(1)–O(1)	1.215 (3)	C(9)–C(91)	1.531 (4)
C(2)–C(3)	1.420 (3)	C(91)–C(92)	1.512 (4)
C(81)–C(82)	1.508 (4)		
Bond Angles			
C(8)–C(1)–C(2)	107.8 (2)	C(9)–C(3)–C(2)	111.1 (2)
O(1)–C(1)–C(2)	125.2 (2)	C(9)–C(3)–C(13)	130.1 (2)
O(1)–C(1)–C(8)	127.1 (2)	C(9)–C(8)–C(1)	105.5 (2)
C(1)–C(2)–Cr(1)	126.1 (2)	C(81)–C(8)–C(1)	113.1 (2)
C(7)–C(2)–C(1)	129.4 (2)	C(8)–C(9)–C(3)	103.6 (2)
C(7)–C(2)–C(3)	121.8 (2)	C(91)–C(9)–C(3)	114.3 (2)
C(13)–C(3)–C(2)	118.9 (2)	C(92)–C(91)–C(9)	114.3 (3)
C(9)–C(3)–Cr(1)	131.5 (1)	C(82)–C(81)–C(8)	115.3 (2)

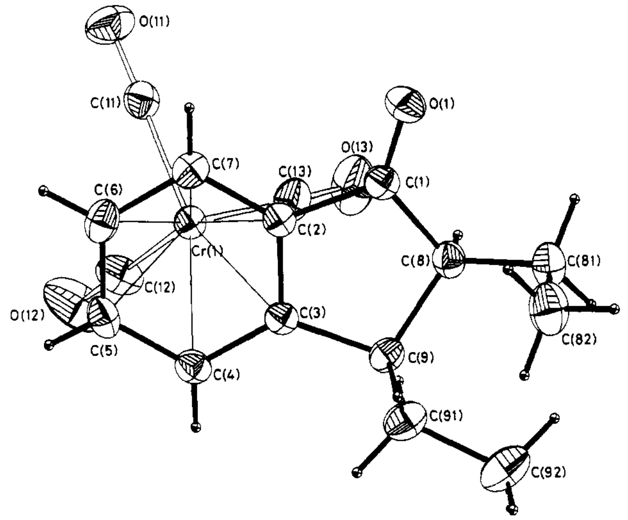


Figure 5. ORTEP drawing showing numbering scheme for **12**.

The structure of **12** was confirmed by an X-ray analysis. The important interatomic distances and angles are given in Table IV. An ORTEP drawing that confirms the annulation reaction appears in Figure 5. Such indanone chromium tricarbonyl complexes prepared directly from indanones and chromium hexacarbonyl[21] or from chromium carbene complexes[22] are well documented in the literature.

The nature of the alkyne seems to have little influence on the course of the reaction since 2-butyne and phenyl-2-propyne gave analogous results. Phenyl-2-propyne led to the expected complex **13** (30%; mp 170 °C), but a second compound could be isolated (21.7%, mp 102 °C) as purple crystals. The spectroscopic data, including the mass spectrum, are in agreement with those of an indenone coordinated to $Cr(CO)_3$: one observes a free phenyl group (5 H at 7 ppm), a coordinated aromatic ring (4 H between 6.5 and 5.3 ppm), and a methyl group at 1.95 ppm. The IR spectrum shows an absorption due to a ketone (ν(CO) = 1680 cm^{-1}), in addition to an absorption due to the terminal CO groups. In the case of 3-hexyne and 2-butyne, only trace amounts of the corresponding indenones could be detected. These results are thus in agreement with

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(18) Parlier, A.; Rudler, H.; Yefsah, R.; Alvarez, C. *J. Organomet. Chem.* **1987**, *328*, C21.

(19) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

(20) Yamashita, A. *Tetrahedron Lett.* **1986**, 5915.

(21) Debard, R.; Fournari, P.; Besançon, J. *C. R. Acad. Sci., Ser. C* **1965**, *260*, 2833.

(22) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059.

previous reports[19,20,22] and show that it is the annulation reaction which prevails over the intramolecular cyclopropanation reaction.

Conclusion

The work described herein was undertaken to demonstrate that the coupled alkyne insertion–double-bond cyclopropanation reactions are general reactions for complexes bearing the 1–4 alkene–carbene ligands, provided that no phenyl group is present on the carbene carbon atom. This reaction constitutes therefore a new entry into bicycloheptane derivatives, with or without heteroatoms.

During this study an interesting isomerization of a 1–3 alkene–carbene ligand to a 1–4 alkene–carbene ligand (internal to terminal double bond isomerization) was observed, for the first time, during the coordination of the double bond to the metal center.

Experimental Section

General Data. ^1H and ^{13}C NMR spectra were obtained on a Bruker WP 200 or a JEOL 90 spectrometer. IR spectra were measured on a Beckman 4240 spectrophotometer. Mass spectra were determined on a Kratos MS 3P. Melting points were determined on a Reichert Köfler block and are uncorrected. Air-sensitive materials were manipulated in an inert atmosphere by Schlenk techniques. Diethyl ether, THF, and hexane were distilled from $LiAlH_4$; CH_2Cl_2 was distilled from CaH_2. Preparative column chromatography was performed with 70–230 mesh Merck silica gel by using mixtures of petroleum ether and ethyl acetate as eluent.

$(CO)_5Cr{=}C(CH_3)OCH_3$ (1). A solution of methyllithium (17.6 mL, 1.6 N) in Et_2O was added to a suspension of $Cr(CO)_6$ (6.27 g, 28.5 mmol) in Et_2O (75 mL). After 10 min, the solvent was evaporated under vacuum. Distilled water (100 mL) was added to the residue and then triethyloxonium tetrafluoroborate (5.4 g).

The yellow suspension was extracted with petroleum ether; the organic phase was washed with $NaHCO_3$ and then dried over Na_2SO_4. After evaporation of most of the solvent under vacuum, the residue was chromatographed over a short column of silica gel with petroleum ether as eluent. Evaporation of the solvent under vacuum gave complex 1 as a yellow oil (6.45 g, 99%).

$(CO)_5Cr{=}C(CH)_3NHCH_2CH{=}CH_2$ (2). Anhydrous allylamine (5.76 mL, 75 mmol) was introduced into a solution of complex 1 (12.9 g, 50 mmol) in Et_2O (150 mL) at room temperature. After 5 min, the solvent was evaporated under vacuum and the residue chromatographed through a short column of silica gel (50 g of silica gel, 3-cm diameter column) using petroleum ether and ethyl acetate (95/5) as the eluent. The yellow band was collected and the solvent evaporated under vacuum to give complex **2** (13.6 g, 99%) as a yellow oil.

^1H NMR (200 MHz, $CDCl_3$): δ 8.83 (1 H, br s, NH), 5.87 (1 H, m, $CH{=}CH_2$), 5.34 (2 H, m, $CH{=}CH_2$), 4.09 (2 H, s, $N{-}CH_2$), 2.65 (3 H, s, CH_3). $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$) δ 283.14 (C1), 223.0, 217.8 (CO's), 130.4, 119.10 ($HC{=}CH_2$), 50.24 ($N{-}CH_2$), 35.3 (CH_3). MS: *m/z* 275 (M^+). Anal. Calcd for $C_{10}H_9NO_5Cr$: C, 43.63; H, 3.27; N, 5.09. Found: C, 43.79; H, 3.42; N, 5.22.

$(CO)_5Cr{=}C(CH_3)N(CH_3)CH_2CH{=}CH_2$ (7(*E,Z*)). A solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (2.88 mL) in THF (30 mL) and BuLi (12 mL, 1.6 N) was added at −70 °C, to a solution of complex **2** (5.5 g, 20 mmol) in THF (50 mL) at −70 °C. Then methyl iodide (1.44 mL, 20 mmol) was injected. The solution was then kept at room temperature for 1 h. Evaporation of the solent under vacuum followed by extraction with petroleum ether gave a dark oil which was chromatographed over a short column of silica gel. Elution with petroleum ether/ethyl acetate (90/10) gave an oil (5.6 g, 98.5%) containing **7**(*E,Z*) (60/40).

7E: ^1H NMR (200 MHz, $CDCl_3$) δ 5.76 (1 H, m, $-CH{=}CH_2$), 5.33 (1 H, d, J = 10 Hz, $CH{=}CHH$), 5.09 (1 H, d, J = 17 Hz, $CH{=}CHH$), 4.28 (2 H, m, NCH_2), 3.82 (3 H, s, $N{-}CH_3$), 2.72 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$) 275.9 (C1), 223.5, 218.0 (CO's), 129.3 ($CH{=}CH_2$), 118.2 ($CH{=}CH_2$), 57.4 (NCH_3), 51.1 ($N{-}CH_2$). **7Z**: ^1H NMR (200 MHz, $CDCl_3$) 5.85 (1 H, m, $CH{=}CH_2$), 5.42 (2 H, m, $CH{=}CH_2$), 4.83 (2 H, m, $N{-}CH_2$), 3.20 (3 H, s, $N{-}CH_3$), 2.72 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$) δ 275.9 (C1), 223, 219.0 (CO's), 131.9 ($CH{=}CH_2$), 116.5 ($CH{=}CH_2$), 57.7 (NCH_2), 51.1 (NCH_3), 40.6 (CH_3). MS: *m/z* 289 (M^+). Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.67; H, 3.80; N, 4.84. Found: C, 45.33; H, 3.93; N, 4.80.

$(CO)_5Cr{=}C(CH_3)N(CH_3)CH{=}CHCH_3$ (8(*E,Z*). A solution of LDA prepared from diisopropylamine (3.50 mL) in THF (30 mL) and BuLi (15 mL, 1.6 N) was added, at −70 °C, to a solution of complex **2** (5.5 g, 20 mmol) in THF (50 mL), at −70 °C. The temperature of the solution was allowed to rise to room temperature and kept at this temperature for 2 h. Then the solution was again cooled to −70 °C and methyl iodide (1.44 mL, 20 mmol) injected. The solution was then kept at room temperature for 1 h. Evaporation of the solvent under vacuum followed by extraction with petroleum ether gave a dark oil which was chromatographed over silica gel. Elution with petroleum ether/ethyl acetate (90/10) first gave complex **8E** as a yellow solid (1.5 g). Elution with petroleum ether/ethyl acetate (80/20) gave an oil (3.5 g) which, according to the ^1H NMR spectrum consisted of a mixture of **8E** (20%) and **8Z** (80%). Total yield: 86.3%.

8E: yellow mimosas like crystals; mp 51–52 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.09 (1 H, d, J = 8 Hz, $CH{=}CHCH_3$), 5.53 (1 H, dt, J = 8 and 6.6 Hz, $CH{=}CHCH_3$), 3.78 (3 H, s, $N{-}CH_3$), 2.59 (3 H, s, $=C(CH_3)N$), 1.50 (3 H, d, J = 6.6 Hz, $C(H)CH_3$); $^{13}C\{^1H\}$ NMR (51.1 MHz, CDC l_3) δ 278.3 (C1), 223.5, 219.0 (CO's), 133.5 ($CH{=}CH$), 124.4 ($CH{=}CH$), 50.4 ($N{-}CH_3$), 41.0 ($Cr{=}C(CH_3)$, 11.9 ($C{=}CHCH_3$). MS: *m/e* 289 (M^+). Anal. Calcd for $C_{11}H_{11}NO_5Cr$: Cr, 45.67; H, 3.80; N, 4.84. Found: C, 45.61; H, 3.78; N, 4.79.

8Z: yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ 6.77 (1 H, d, J = 8 Hz, $N{-}CH{=}$), 5.66 (1 H, dt, J = 8 and 6.8 Hz, $=CH(CH_3)$), 3.40 (3 H, s, NCH_3), 2.78 (3 H, s, $=C(CH_3)$), 1.68 (3 H, d, J = 6.8 Hz, =C(H)CH3). MS: *m/z* 289 (M^+). Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.67; H, 3.80; N, 4.84 Found: C, 46.20; H, 3.80; N, 4.89.

$(CO)_4Cr{=}C(CH_3)N(CH_3)(\eta^2\text{-}CH_2{=}CHCH_2)$ (9). (a) From 8(*E,Z*). A solution of complex **8E** (1.4 g) in toluene (50 mL) was refluxed for 5 h. Then the solvent was evaporated and the residue taken up in a small amount of benzene and chromatographed over a short column of silica gel. Elution with petroleum ether/ethyl acetate (80/20) gave complex **9** (1 g, 79%) as yellow crystals.

The reaction, carried out on complex **8Z** (containing 20% of complex **8E**), under the same conditions, gave complex **9** (84%).

(b) From Complexes 7E and 7Z. Complexes **7**(*E,Z*) (5.6 g) were refluxed in hexane for 10 h. After evaporation of the solvent under vacuum, the reaction mixture was chromatographed over silica gel. Elution with petroleum ether/ethyl acetate (80/10) gave complex **7E** (2.2 g); elution with petroleum ether/ethyl acetate (80/20) gave complex **9** (3 g) as a yellow solid.

9: yellow solid; mp 103–104 °C; ^1H NMR (200 MHz, C_6D_6) δ 3.86 (1 H, m, $=CH{=}CH_2$), 3.39 (1 H, dd, J = 13.6 and 4.6 Hz, $N{-}CHH$), 2.90 (1 H, d, J = 13.6 Hz, $N{-}CHH$), 2.79 (1 H, d, J = 8.9 Hz, $CH{=}CHH$), 2.52 (1 H, d, J = 12.9 Hz, $CH{=}CHH$), 1.69 (3 H, s, $N{-}CH_3$), 1.62 (3 H, s, $=C(CH_3)$ (decoupling of the secondary vinylic proton by irradiation at 3.86 ppm resulted in collapse of the doublets at 2.79 and 2.52 ppm to singlets and of the doublet of doublets at 3.39 ppm to a doublet); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$) δ 280.7 (C1), 233.2, 225.8, 225.4 (CO's), 73.5 ($CH{=}CH_2$), 64.4 ($CH_2{=}CH$), 64.0 ($N{-}CH_2$), 38.1 ($N{-}CH_3$), 33.2 ($C{-}CH_2$). MS: *m/z* 261 (M^+). Anal. Calcd for $C_{10}H_{11}NO_4Cr$: C, 45.97; H, 4.21; N, 5.3. Found: C, 46.30; H, 4.22; N, 4.85.

$(CO)_5Cr{=}C(Ph)NH(CH_2CH{=}CH_2)$ (5). Anhydrous allylamine (2.28 g, 40 mmol) was added at room temperature to a solution of $(CO)_5Cr{=}C(Ph)(OEt)$ (6 g, 20 mmol) in Et_2O (200 mL). After 3 h, the solvent was evaporated under vacuum and the residue taken up in a small amout of petroleum ether. Chromatography over a short column of silica gel gave with petroleum ether/ethyl acetate (80/20) complex **5** as an orange oil (5.7 g, 85%).

^1H NMR (200 MHz, $CDCl_3$): δ 8.57 (1 H, br s, $N{-}H$), 7.15 (5 H, m), 6.03 (1 H, m, $CH_2{=}CH$), 5.41 (2 H, m, $CH_2{=}CH$), 4.70 (2 H, m, $N{-}CH_2$). $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$); δ 280.5 (C1), 223.6, 217.1 (CO's), 155.0, 131.2, 128.5, 121.0 (Ar), 127.9, 120.5 ($C{=}C$), 55.8 ($N{-}CH_2$). MS: *m/z* 337 (M^+). Anal. Calcd for $C_{15}H_{11}O_5NCr$: C, 53.41; H, 3.26; N, 4.08. Found: C, 53.86; H, 3.47; N, 4.08.

Table V. Crystallographic Data Collection Parameters for 8, 9, 10, and 12

	8	9	10	12
formula	$C_{11}H_{11}O_5NCr$	$nC_{11}H_{11}O_4NCr$	$nC_{23}H_{21}O_3NCr$	$C_{16}H_{16}O_4Cr$
fw	289	261	411	324
cryst system	monoclinic	triclinic	monoclinic	monoclinic
space group	*Pn*	$P\bar{1}$	$P2_1/n$	$C2/c$
a, Å	6.240 (2)	6.808 (3)	9.710 (2)	26.384 (14)
b, Å	10.787 (1)	6.952 (2)	19.278 (4)	6.398 (2)
c, A	10.262 (2)	12.811 (2)	10.634 (4)	19.461 (4)
α, deg	90	93.73 (2)	90	90
β, deg	95.96 (2)	100.05 (3)	103.24 (2)	115.27 (1)
γ, deg	90	102.45 (3)	90	90
V, Å^3	687	580	1938	2970
Z	2	2	4	8
μ(Mo Kα), cm^{-1}	8.21	9.59	5.98	7.62
ρ(calcd), g·cm^{-3}	1.40	1.50	1.41	1.45
diffractometer	CAD4	CAD4	CAD4	PW1100
temp, °C	20	20	20	20
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
abs range	1.0–1.11	1.0–1.13	1.0–1.06	none
scan range θ, deg	$1.5 + 0.34 \tan \theta$	$1.8 + 0.34 \tan \theta$	$1.2 + 0.34 \tan \theta$	$0.9 + 0.34 \tan \theta$
2θ range, deg	2–50	2–50	3–50	4–50
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
reflctns collected	2574	2131	3738	2486
reflctns merged, R_m	1220 (2.99)	2032 (1.09)	3407 (3.74)	2311 (0.83)
reflctns used	997	1666	1655	1858
criteria	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R	0.0313	0.0280	0.0413	0.0292
R_w	0.0357	0.0300	0.0472	0.0357
coeff Ar	5.41, −0.42, 4.38	8.79, −3.32, 0.72	4.27, −1.85, 3.38	1.79, 0.28, 1.36
rms (shift/esd)	0.22	0.20	0.21	0.12
least-squares parameters	164	180	274	211
degrees of freedom	833	1486	1387	1647
GOF	1.28	0.94	1.31	0.90

$(CO)_4Cr{=}C(Ph)NH(\eta^2\text{-}CH_2{=}CHCH_2)$ (6). Complex **5** (5.7 g) was refluxed in toluene (150 mL) for 5 h. After evaporation of most of the solvent, the residue was chromatographed over silica gel. Elution with petroleum ether/ethyl acetate (80/10) gave complex **6** (2.9 g, 51%) as a solid which was recrystallized from petroleum ether/methylene chloride to give orange crystals, mp 103 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.63 (1 H, br s, N—H), 7.4 (5 H, m), 5.3 (1 H, m, $CH{=}CH_2$), 4.4 (2 H, m, $CH{=}CH_2$), 3.3 (2 H, m, N—CH_2). $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$): δ 283.0 (C1), 226.5, 225.6, 224.0 (CO's), 147.6, 130.0, 128.7, 123.6 (Ar), 77.8, 65.6 (*C*═*C*); 53.9 (N—CH_2). MS: *m*/*e* 309 (M^+). Anal. Calcd for $C_{14}H_{11}O_4NCr$: C, 54.36; H, 3.6; N, 4.3. Found: C, 53.61; H, 3.69; N, 4.82.

Reaction of Complex 9 with PhC≡CPh: Complex 10. A solution of complex **9** (1.5 g, 5 mmol) and PhC≡CPh in benzene (50 mL) was refluxed for 12 h. After evaporation of most of the benzene, the residue was chromatographed over silica gel. Elution with petroleum ether/acetone (85/15) gave complex **10** (1.2 g, 51%) as yellow crystals, mp 128 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.15 (5 H, m), 5.19 (5 H, m), 3.44 (1 H, dd), 2.96 (1 H, dd), 2.86 (3 H, s), 2.24 (3 H, s), 1.88 (1 H, dd), 1.30 (1 H, m), 0.96 (1 H, t). $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$): δ 234.4 (CO), 145.7, 145.4, 129.5, 127.4, 125.5, 116.7, 104.9 (Ph + C═C), 96.9, 95.5, 92.2, 92.0, 90.9 (Ph"bdCr), 52.6 (N—CH_2), 39.3 (N—CH_3), 26.2 (C—7), 24.8 (C—5), 19.9 (C—6), 17.6 (C—CH_3). Anal. Calcd for $C_{23}H_{21}O_3NCr$: C, 67.15, H, 5.1; N, 3.4. Found: C, 67.12; H, 5.19; N, 3.35.

Reaction of Complex 6 with 3-Hexyne: Complex 12. A solution of complex **6** (1 g, 3.2 mmol) in benzene (40 mL) was refluxed in the presence of 3-hexyne (1.30 g) for 6 h. After evaporation of most of the solvent, the residue was chromatographed over silica gel. Elution with petroleum ether/ethyl acetate (80/20) gave complex **12** as orange crystals (0.8 g, 71%), mp 77 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 5.7 (5 H, m), 3.0 (1 H, m), 2.5 (1 H, m), 2.15 (2 H, m), 1.85 (2 H, m), 1.3 (3 H, t), 1.05 (3 H, t). $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$): δ 231.0 (CO), 205.6 (CO ketone), 126.9, 97.3, 93.5, 91.1, 87.9, 86.4 (Ar—Cr), 54.0 (C2), 43.4 (C3), 28.3 (CH_2), 23.4 (CH_2), 13.6 (CH_3), 10.7 (CH_3). MS: *m*/*e* 314 (M^+).

Reaction of Complex 6 with 2-Butyne: Complex 15. A solution of complex **6** (1 g, 3.2 mmol) in benzene was refluxed for 12 h in the presence of 2-butyne (1.3 g, 16 mmol). After evaporation of most of the solvent, the residue was chromatographed over silica gel. Elution with petroleum ether/ethyl acetate (90/10) gave complex **15** (0.5 g, 52%) as orange crystals, mp 115 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 5.5 (5 H, m), 2.95 (1 H, q), 2.4 (1 H, q), 1.5 (3 H, d), 1.25 (3 H, d). $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$): δ 230.8 (CO), 204.9 (CO ketone), 126.9, 95.8, 94.4, 90.2, 87.4, 86.1 (Ar—Cr), 49.4 and 40.1 (C—CH_3), 15.9 and 13.0 (CH_3). MS: *m*/*z* 296 (M^+). Anal. Calcd for $C_{14}H_{12}O_4Cr$: C, 56.75; H, 4.03. Found: C, 56.88; H, 4.10.

Reaction of Complex 6 with Phenyl-2 propyne: Complexes 13 and 14. A solution of complex **6** (2.16 g, 7 mmol) in benzene (200 mL) was refluxed for 6 h in the presence of phenyl-2-propyne (4 g, 35 mmol). After evaporation of the solvent, the residue was chromatographed over silica gel. Elution with petroleum ether/ethyl acetate (95/5) gave complex **13** (0.75 g, 30%) as orange crystals, mp 170 °C. Elution with petroleum ether/ethyl acetate (90/10) gave complex **14** (0.54 g, 21.7%) as purple crystals, mp 102 °C.

Complex **13**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.34 (5 H, s), 5.7–5.30 (4 H, m), 4.05 (1 H d, J = 7 Hz), 3.18 (1 H, q), 1.25 (3 H, d); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$): δ 230.8 (CO's), 205.2 (CO ketone), 135.8, 129.1, 128.6, 128.3, 128.0 (Ar), 123.8, 96.0, 92.3, 88.5, 84.9 (Ar-Cr), 51.1 (CH), 47.4 (CH), 13.0 (CH_3). IR (cm^{-1}, $CHCl_3$): 1980, 1915, 1705 (CO). MS: *m*/*z* 358 (M^+). Anal. Calcd for $C_{19}H_{12}O_4Cr$: C, 63.68; H, 3.91. Found: C, 62.80; H, 3.90.

Complex **14**: ^{1}H NMR (200 MHz, C_6D_6): δ 7.5 (5 H, m), 6.2, 5.6, 5.35 (4 H, m), 1.95 (3 H, s); $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$): δ 231.4 (CO), 194.2 (CO ketone), 152.2 (C═C), 134.8, 131.5, 129.8, 129.2, 128.3 (Ar), 110.9 (C═C), 92.4, 90.7, 87.0, 86.9 (Ar-Cr), 9.21 (CH_3). IR (cm^{-1}; $CHCl_3$): 1980, 1920, 1680 (ν(CO)). MS: *m*/*z* 356 (M^+). Anal. Calcd for $C_{19}H_{10}O_4Cr$: C, 64.04; H, 3.37. Found: C, 63.91; H, 3.45.

Crystal Data. For all compounds, preliminary unit-cell dimensions and symmetry information were derived from precession photographs; selected crystals were then set up on an automatic four-circle diffractometer. Accurate unit-cell dimensions and crystal orientation matrices together with their estimated standard deviations were obained from least-squares refinements of the setting angles of 25 carefully centered reflections. Three standard reflections were monitored periodically; they showed no change during data collections. Crystallographic data and other pertinent information are summarized in Table V. Corrections were made for Lorentz and polarization effects. Absorption correction were applied via an empirical absorption technique.[24]

Computations were performed by using CRYSTALS[25] adapted on a VAX 11/725. Atomic form factors for neutral Cr, C, N, O, and H were taken from ref. 26; anomalous dispersion was taken into account. All structures were solved by interpretation of the Patterson maps that clearly indicated the position of Cr atoms. All remaining non-hydrogen atoms were found by seccessive electron density map calculations. Hydrogen atoms were located on difference electron density maps but were treated differently during refinements. In complex **8**, all methyl H were placed in calculated positions (C–H = 0.96 Å; H–C–H = 109.5°) and reset after each cycle; an overall isotropic thermal parameter was refined. Methyl H and phenyl H for phenyl not bound to Cr atom have been put in calculated positions in complex **10**, with a U(iso) set at 0.12 Å^2. In complex **12**, hydrogen for ethyl groups were given calculated positions with a fixed isotropic thermal parameter, U = 0.08 Å. The coordinates for all other hydrogen atoms were refined, and they were assigned refineable overall isotropic thermal parameters. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $w(|\mathrm{F_o}| - |F_c|)^2$, where F_o and f_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w(1 - (F/\sigma(F_o))^2)^2$ where $w = 1/1^3\mathrm{ArTr}(x)$ with three coefficients (Ar) for the Chebyshev polynomial ArTr(x) where x was $F_c/F_c(\mathrm{max})$.[27] The models converged to $R = (|F_o| - |F_c|)/|F_o|$ and $R_w = (w(|F_o| - |F_c|)^2/w(F_o)^2)^{1/2}$ having the values listed in Table V. The criteria for a satisfactory complete analysis were the ratio of the room-mean-square shift to standard deviation being less than 0.2 and no significant features in the final difference maps. Atomic coordinates are given in Tables VI–IX (supplementary material).

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Registry No. **1**, 20540-69-6; **2**, 111965-17-4; **5**, 121675-62-5; **6**, 121675-63-6; (*E*)-**7**, 121675-59-0; (*Z*)-**7**, 121784-58-5; (*E*)-**8**, 121784-57-4; (*Z*)-**8**, 121675-61-4; **9**, 121675-60-3; **10**, 121675-65-8; **12**, 121675-64-7; **13**, 121675-67-0; **14**, 121675-68-1; **15**, 121675-66-9; $Cr(CO)_6$, 13007-92-6; $(CO)_5Cr{=}C(Ph)(OEt)$, 26160-57-6; $PhC{\equiv}CCH_3$, 673-32-5; $PhC{\equiv}CPh$, 501-65-5; 3-hexyne, 928-49-4; 2-butyne, 503-17-3.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles, and least-squares planes for **8**, **9**, **10**, and **12** (14 pages); listings of structure factors for **8**, **9**, **10**, and **12** (41 pages). Ordering information is given on any current masthead page.

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(23) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

(24) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr, Ther. Gen. Crystallogr.* **1968**, *A24*, 351.

(25) Carruthers, J. R.; Watkin, D. J. CRYSTALS, Chemical Crystallography Laboratory; University of Oxford: Oxford, 1986.

(26) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(27) Prince, E. *Mathematical Techniques in Crystallography*; Springer-Verlag: Berlin, 1982.