Reaction of Aminocarbene Complexes of Chromium with Alkynes. 3. New Insights into the Mechanism of Formation and Rearrangement of Nitrogen Ylides

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The dissymmetrically N-substituted aminocarbene complexes $(CO)_5Cr{=}C(R_1)N(R_2)(R_3)$ **7** (R_1 = H, R_2 = CH_3, R_3 = Ph), **11** (R_1 = R_2 = CH_3, R_3 = Ph), **17** (R_1 = Ph, R_2 = CH_3, R_3 = cyclopropyl), **22** (R_1 = R_2 = CH_3, R_3 = *sec*-butyl), and **24** (R_1 = Ph, R_2 = CH_3, R_3 = *sec*-butyl) have been reacted with diphenylacetylene. Whereas complex **7** only led to the aminofuran complex **8**, which could be converted to the air-stable aminofuran **9**, complex **11** gave, besides the aminofuran complex **12**, the pyrrolinone **13** and the imine **15** as a result of respectively the insertion of the alkyne and CO, followed by the migration of the phenyl group from nitrogen to the γ-carbon, and the sole insertion of the alkyne followed by the migration of the phenyl group from nitrogen to the γ-carbon. However, **17** gave an intermediate (arene)-tricarbonylchromium nitrogen ylide complex $(CO)_3Cr(C_{29}H_{23}NO)$ (**18**). Upon heating of the sample in benzene, the cyclopropyl group, *cis* with respect to $Cr(CO)_3$ in **18**, migrates from nitrogen to the γ-carbon atom, to give a pyrrolinone $Cr(CO)_3$ complex **19** in which the cyclopropyl group is *trans* to $Cr(CO)_3$. **9**, **13**, **15**, **18**, and **19** were fully characterized by X-ray diffraction studies. Crystal data for **9**: $C_{23}H_{19}ON$, triclinic, space group $P\bar{1}$, a = 8.861(1) Å, b = 9.814(2) Å, c = 10.817(1) Å, α = 102.08(1)°, β = 94.67(1)°, γ = 105.93(1)°, V = 875(5) Å^3, d_{calc} = 1.24 g cm^{-3}, Z = 2. Data for **13**: $C_{24}H_{21}ON$, orthorhombic, space group $P2_12_12_1$, a = 9.957(6) Å, b = 9.767(4) Å, c = 19.244(19) Å, V = 1871(2) Å^3, d_{calc} = 1.20 g cm^{-3}, Z = 4. Data for **15**: $C_{23}H_{21}N$, monoclinic, space group $P2_1/c$, a = 9.290(2) Å, b = 22.324(3) Å, c = 9.630(1) Å, β = 116.14(1)°, V = 1793(13) Å^3, d_{calc} = 1.15 g cm^{-3}, Z = 4. Data for **18**: $C_{29}H_{23}O_4NCr$, orthorhombic, space group $Pc2_1n$, a = 12.763(11) Å, b = 13.854(14) Å, c = 13.577(26) Å, V = 2.401(6) Å^3, d_{calc} = 1.39 g cm^{-3}, Z = 4. Data for **19**: $C_{29}H_{23}O_4NCr$, monoclinic, space group $P2_1/a$, a = 4.044(5) Å, b = 9.664(2) Å, c = 18.035(3) Å, β = 97.93(2)°, V = 2424(7) Å^3, d_{calc} = 1.37 g cm^{-3}, Z = 4. A rearrangement without CO insertion could also be observed starting from complex **23a** which gave **25**. Finally, **24a,b** led, besides to the benzannulation products **28** and **29**, to the pyrrolinones **27a,b** resulting from the migration of the *sec*-butyl group; in the case of the optically active **24b**, no racemization of the migrating group is observed. The mechanisms of these transformations will be discussed.

Introduction

In preceding publications the reactivity of aminocarbene complexes toward alkynes has been discussed and the mechanism of their transformation analyzed.[1,2] Two types of reactions were observed: (1) those in which the transformation of the starting complexes into the final products took place without detectable intermediates; (2) those for which isolable intermediates, which could be transformed into the same type of end products, were fully characterized (Scheme 1). Although no doubt about the participation of the metal in the alkyne and the CO insertion reactions exists for both type of reactions, it is not clear whether they follow the same pathways involving the same intermediates. Especially questionable is the involvement of the metal in the rearrangement step of the ylides.

Since nitrogen ylides are known from organic chemistry to undergo rearrangements by concerted or radicalar routes,[3-5] without the participation of any metal, the same types of mechanisms might be suspected in the case of nitrogen ylide complexes **2**. However, two points are in contradiction with either a radical-involving or a concerted, non-metal-involving mechanism: (1) The cyclopropylcarbinyl group migrates without rearrangement, a result which is in agreement with a concerted reaction.[1] (2) Double CO insertions have been

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(1) Chelain, E.; Goumont, R.; Hamon, L.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* **1992**, *114*, 8088.

(2) Chelain, E.; Parlier, A.; Audouin, M.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* **1993**, *115*, 10568.

(3) Stevens, T. S.; Creighton, E. M.; Gordon, A. B.; MacNicol, M. *J. Chem. Soc.* **1928**, 3193.

(4) Jemison, W. R.; Mageswaran, S.; Ollis, W. D.; Sutherland, I. O.; Thebtaranonth, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1154.

(5) Ollis, W. D.; Rey, M.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1009, 1029, 1049.

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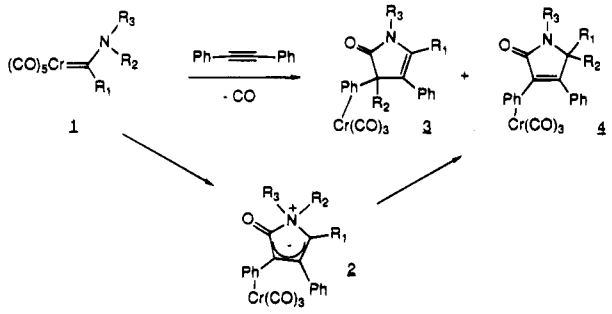
Scheme 1

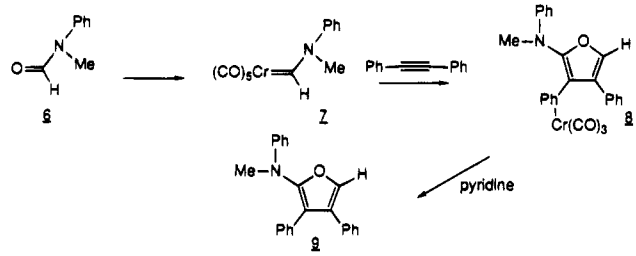


observed, the second one taking place at the very end of the reaction, a result which could imply the participation of the metal even in the migration step.[2] In order to shed some more light onto the mechanisms of these rearrangements, we have synthesized a series of aminocarbene complexes in which the nitrogen atom is dissymmetrically substituted and, in one instance, bears an optically active group likely to undergo the nitrogen to carbon migration and have subjected them to the alkyne insertion reaction.

Results and Discussion

Synthesis of the Aminocarbene Complexes. The starting aminocarbene complexes **7**, **11**, **17**, **22**, and **24** were obtained either from the corresponding (ethoxy) carbene complexes **5** (R_1 = Me, Ph) by aminolysis with the appropriate primary amine,[6] followed by alkylation at nitrogen (LDA, ICH_3),[7] or from the amide **6**, in the case of **7**.[8] It is noticed that the best way to obtain high yields of **10** is to add aniline at low temperature to an etheral solution of **5** and then to eliminate both the solvent and EtOH, *in vacuo* at room temperature. All the carbene complexes were characterized by elemental analysis or high-resolution mass spectrometry and by their ^1H and ^{13}C NMR spectra (for details, see the Experimental Section).

Case of Carbene Complexes 7 and 11: Direct Formation of Rearranged Products with and without CO Insertions. It is known from the chemistry of classical nitrogen ylides that phenyl groups do not easily migrate from nitrogen to carbon.[9,10] It was therefore interesting to follow the behavior of complexes such as **7** and **11** with respect to alkynes: Indeed, both might lead, on the one hand, to a dissymmetrically substituted ylide and, on a second hand, its rearrangement, in the event of its occurrence, might give complementary indications on the stereochemical course of the migration.



The reaction of **7** with diphenylacetylene in boiling benzene or cyclohexane gave neither the expected nitrogen ylide nor its rearrangement products: most of the starting material could be recovered after 12 h of reflux. However, such was not the case in refluxing toluene; after 12 h, complete disappearance of the starting material was observed. Silica gel chromatography allowed the isolation of a single complex, in 70% yield, to which structure **8** was assigned on the following grounds. The infrared and ^{13}C NMR spectra both confirmed the presence of a $Cr(CO)_3$ moiety and the absence of a non-metallic CO group. The ^1H NMR spectrum agreed with the presence of a NMe (δ, 3.09 ppm) and of eleven highly deshielded protons, one of them appearing, as a singlet, at δ 7.57 ppm. Signals at δ 152.1 and 148.0 ppm in the ^{13}C NMR spectrum were strong indications for a structure such as **8**, the $Cr(CO)_3$ complex of a 5-aminofuran. Refluxing **8** in pyridine gave quantitatively an organic compound the structure of which could finally be established as **9** by an X-ray analysis. Its ORTEP drawing appears in Figure 1, whereas the bond distances and bond angles are given in Table 1.

Under the same conditions as for **7**, complex **11** gave a mixture of four products which were separated by

(6) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147.
(7) Casey, C. P.; Vollendorf, W. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754.
(8) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.
(9) Heaney, H.; Ward, J. T. *J. Chem. Soc., Chem. Commun.* **1969**, 810.
(10) Truce, W. E.; Heuring, D. L. *J. Chem. Soc., Chem. Commun.* **1969**, *1499*.

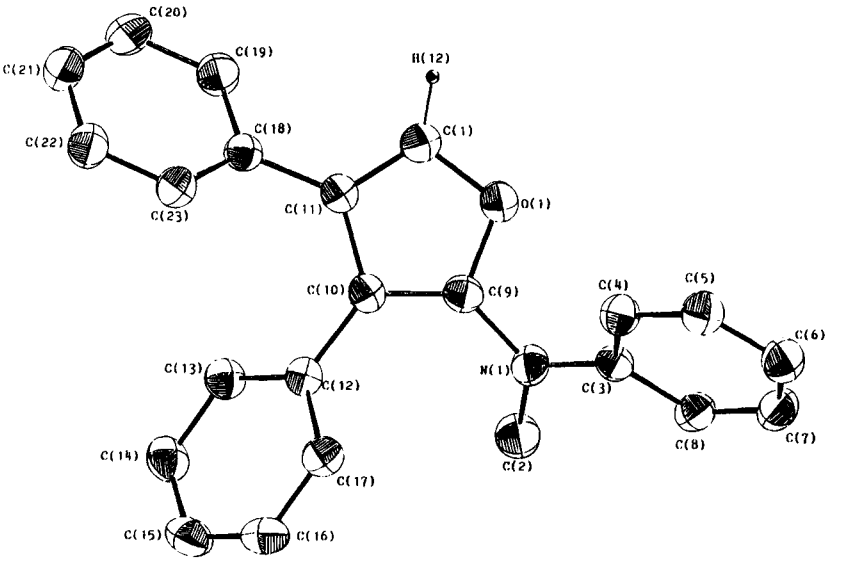
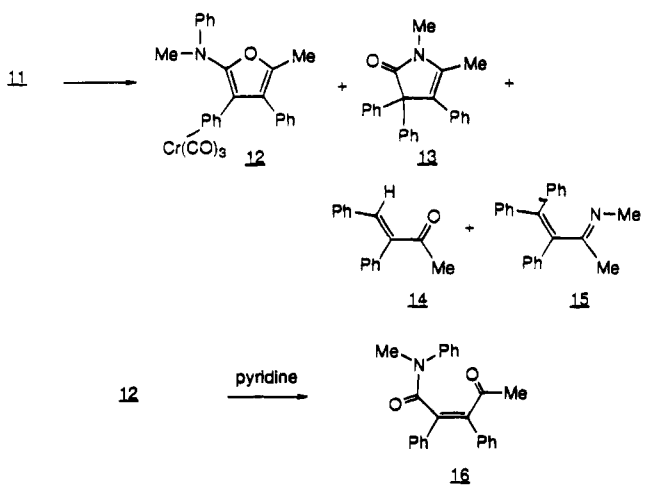


Figure 1. ORTEP drawing of complex **9**. Ellipsoids are shown at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 9

O(1)—C(1)	1.374(4)	O(1)—C(9)	1.381(3)
N(1)—C(2)	1.456(4)	N(1)—C(3)	1.404(4)
N(1)—C(9)	1.383(4)	C(1)—C(11)	1.336(4)
C(9)—C(10)	1.351(4)	C(10)—C(11)	1.447(4)
C(10)—C(12)	1.473(4)	C(11)—C(18)	1.476(4)
C(9)—O(1)—C(1)	105.7(2)	C(3)—N(1)—C(2)	120.1(3)
C(9)—N(1)—C(2)	118.3(3	C(9)—N(1)—C(3)	120.9(2)
C(11)—C(1)—O(1)	111.4(3)	C(4)—C(3)—N(1)	120.9(3)
N(1)—C(9)—O(1)	116.0(2)	C(10)—C(9)—O(1)	110.5(2)
C(10)—C(9)—N(1)	133.2(3)	C(11)—C(10)—C(9)	106.1(2)
C(12)—C(10)—C(9)	126.3(3)	C(12)—C(10)—C(11)	127.5(3)
C(10)—C(11)—C(1)	106.2(3)	C(18)—C(11)—C(1)	125.1(3)
C(18)—C(11)—C(10)	128.5(3)		

silica gel chromatography. The less polar compound, obtained as yellow crystals, was again a $Cr(CO)_3$ complex of an aminofuran: both the elemental analysis and the spectroscopic data agreed with structure **12**. However, heating **12** in pyridine did not lead to the expected metal-free aminofuran but to the keto amide **16**, the product of its air oxidation. Such a behavior of aminofurans of the same type was known from the literature.[11]



The structure of the second product, as established both by its elemental analysis, spectroscopic data, and

(11) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.

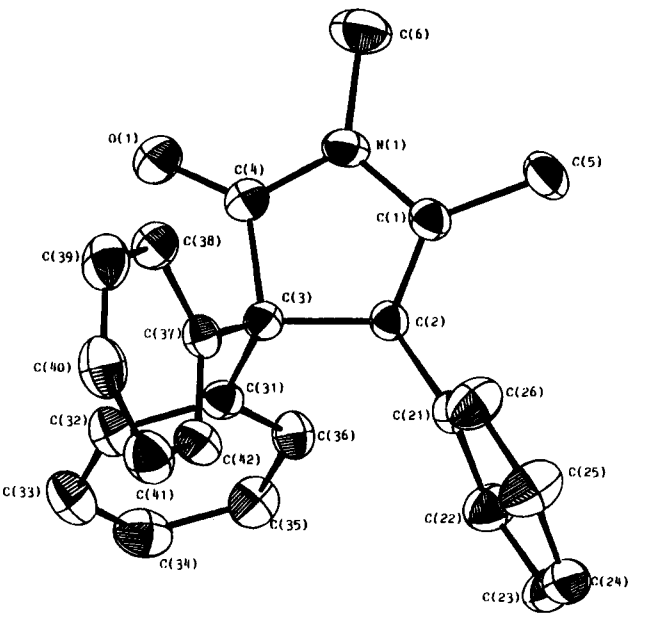


Figure 2. ORTEP drawing of complex **13**. Ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 13

O(1)—C(4)	1.230(5)	N(1)—C(1)	1.416(5)
N(1)—C(4)	1.341(5)	N(1)—C(6)	1.467(6)
C(1)—C(2)	1.329(5)	C(1)—C(5)	1.506(6)
C(2)—C(3)	1.531(6)	C(3)—C(4)	1.544(6)
C(4)—N(1)—C(1)	111.0(3)	C(6)—N(1)—C(1)	126.1(4)
C(6)—N(1)—C(4)	123.0(4)	C(2)—C(1)—N(1)	111.1(4)
C(5)—C(1)—N(1)	120.1(4)	C(5)—C(1)—C(2)	128.7(4)
C(3)—C(2)—C(1)	108.8(4)	C(21)—C(2)—C(1)	125.5(4)
C(4)—C(3)—C(2)	101.1(3)	N(1)—C(4)—O(1)	125.8(4)
C(3)—C(4)—O(1)	126.2(4)	C(3)—C(4)—N(1)	108.0(4)

X-ray analysis, was a metal-free pyrrolinone **13**, resulting from the insertion of the alkyne and CO and the migration of the phenyl group from nitrogen to the γ-carbon; the ORTEP projection appears in Figure 2, whereas the bond distances and bond angles are disclosed in Table 2. The third product, obtained in 10% yield, is the ketone **14**; its structure has been confirmed by comparison of its spectroscopic data with those of an

Scheme 2

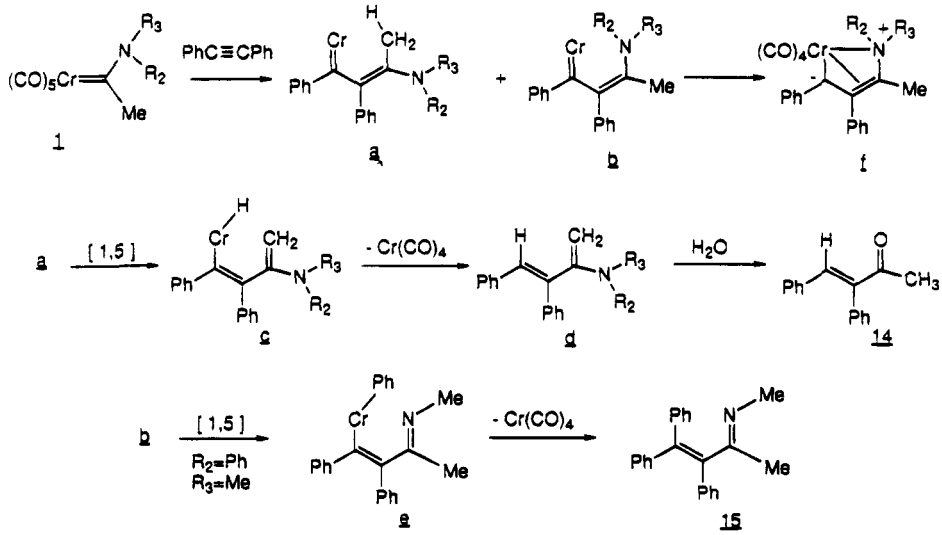


Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 15

N(1)–C(1)	1.261(7)	N(1)–C(2)	1.455(8)
C(1)–C(3)	1.508(8)	C(1)–C(6)	1.505(8)
C(4)–C(5)	1.499(8)	C(5)–C(6)	1.335(7)
C(5)–C(51)	1.501(8)	C(6)–C(61)	1.488(7)
C(2)–N(1)–C(1)	119.4(6)	C(5)–C(6)–C(1)	122.6(6)
C(6)–C(1)–N(1)	126.0(6)	C(3)–C(1)–N(1)	117.5(6)
C(6)–C(5)–C(4)	122.8(6)	C(6)–C(1)–C(3)	116.4(6)

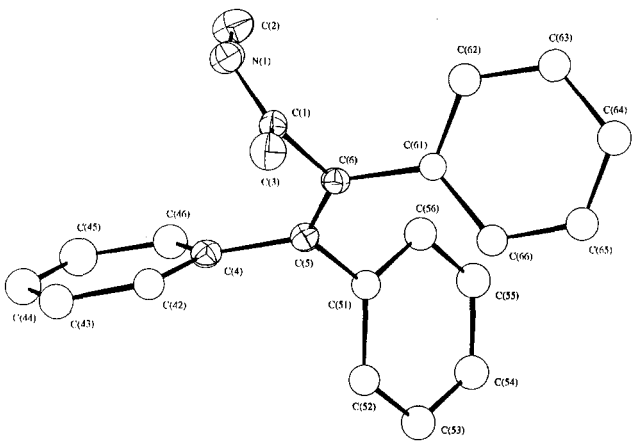


Figure 3. ORTEP drawing of complex **15**. Ellipsoids are shown at the 50% probability level.

authentic sample.[12] Finally structure **15**, a conjugated imine, has been assigned to the last product, both on grounds of its spectroscopic data and X-ray analysis. The absence of oxygen and the presence of a signal at δ 171.9 in the ^{13}C NMR spectrum agree with such a structure. Its ORTEP drawing is shown in Figure 3, whereas the bond distances and bond angles are collected in Table 3.

The formation of the various products from **11** could be explained according to Schemes 1 and 2. On the one hand, pyrrolinone **13** results from the insertion of the alkyne and of CO followed by the migration of the phenyl group (Scheme 1). On the other hand, the unexpected conjugated imine **15** and ketone **14** result from the sole insertion of the alkyne (Scheme 2).

The insertion of the alkyne can indeed lead to either of the two enaminocarbene complexes **a** or **b**; successive (1,5) migration and reductive elimination on **a** would give the enamine **d** via the hydride **c** and finally, upon hydrolysis, the ketone **14**. The same (1,5) migration on **b** might give complex **e** and, upon reductive elimination, the conjugated imine **15**. However, the formation of **15** might also be explained by a mechanism involving a N-ylide **f** resulting from the direct interaction of the nitrogen atom in **b** with the carbene complex followed by a (1,3) migration of the phenyl group on the carbon atom of the inserted alkyne. Such rearrangements via suspected N-ylides resulting from the interaction of a tertiary amine with a carbene complex are now common in reactions involving ω-amino diazo compounds and rhodium catalysts.[13,14]

Although lack of CO insertion into aminocarbene complexes, especially those bearing a phenyl group on the carbene carbon, is now well documented,[15] the migration without CO insertion had not been observed up to now.

Finally, the formation of aminofurans from carbene complexes **7** and **11** is another example of the diversity of the reaction pathways which can be followed during their interaction with alkynes; the overall transformation which took place was the migration of the disubstituted nitrogen atom from the carbene carbon to the carbon of the inserted carbonyl group. Aminofurans had already been observed by Semmelhack starting from aminocarbene complexes of iron.[11] In the case of alkoxycarbene complexes of chromium and molybdenum, the formation of alkoxyfurans had also been established by Dötz and by Wulff and its mechanism discussed.[16–18] This mechanism will be more thoroughly examined in a forthcoming paper.

Transformation of Carbene Complex 17 into 19 via 18. Heating of complex **17** in boiling hexane, in the

(12) Denise, B.; Dubost, P.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C.; Vaissermann, J.; Delgado, F.; Arevalo, A. R.; Toscano, R. A.; Alvarez, C. *J. Organomet. Chem.* **1991**, *418*, 377.

(13) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75 and references cited therein.

(14) West, F. G.; Naidu, B. N. *J. Am. Chem. Soc.* **1993**, *115*, 1177.

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

(16) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177.

(17) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

(18) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Shing Chan, K.; Gilbert, A. M.; Hsung, R. P. *Organometallics* **1994**, *13*, 102.

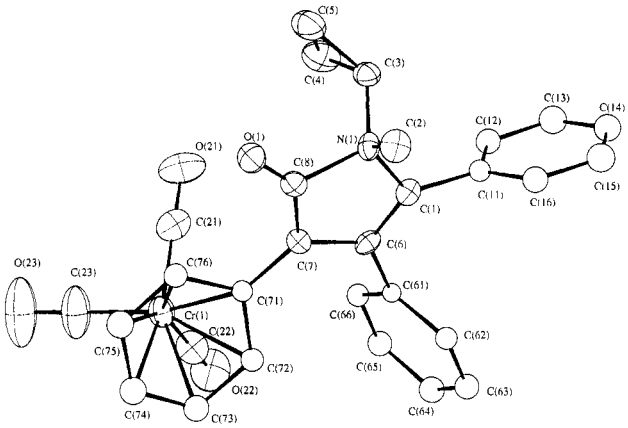
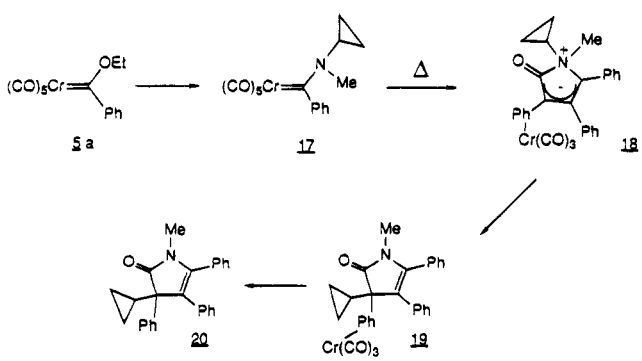


Figure 4. ORTEP drawing of complex **18**. Ellipsoids are shown at the 50% probability level.

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound 18

Cr(1)—C(21)	1.80(1)	C(21)—O(21)	1.17(1)
Cr(1)—C(22)	1.845(9)	C(22)—O(22)	1.16(1)
Cr(1)—C(23)	1.80(1)	C(23)—O(23)	1.16(1)
Cr(1)—C(71)	2.269(9)	Cr(1)—C(72)	2.245(8)
Cr(1)—C(73)	2.20(1)	Cr(1)—C(74)	2.18(1)
Cr(1)—C(75)	2.17(1)	Cr(1)—C(76)	2.179(9)
O(1)—C(8)	1.232(9)	N(1)—C(1)	1.49(1)
N(1)—C(2)	1.49(1)	N(1)—C(3)	1.49(1)
N(1)—C(8)	1.62(1)	C(1)—C(6)	1.32(1)
C(1)—C(11)	1.51(1)	C(3)—C(4)	1.45(1)
C(3)—C(5)	1.48(1)	C(4)—C(5)	1.47(1)
C(6)—C(7)	1.46(1)	C(7)—C(8)	1.39(1)
C(22)—Cr(1)—C(21)	88.1(4)	O(21)—C(21)—Cr(1)	177.6(8)
C(23)—Cr(1)—C(21)	88.3(5)	O(22)—C(22)—Cr(1)	178.7(10)
C(23)—Cr(1)—C(22)	87.1(5)	O(23)—C(23)—Cr(1)	179.1(11)
C(2)—N(1)—C(1)	114.3(6)	C(3)—N(1)—C(1)	109.9(6)
C(3)—N(1)—C(2)	110.2(6)	C(8)—N(1)—C(1)	102.6(6)
C(8)—N(1)—C(2)	106.2(6)	C(8)—N(1)—C(3)	113.5(6)
C(6)—C(1)—N(1)	109.8(7)	C(4)—C(3)—N(1)	121.1(7)
C(5)—C(3)—N(1)	124.3(7)	C(5)—C(3)—C(4)	60.2(7)
C(5)—C(4)—C(3)	60.9	C(4)—C(5)—C(3)	58.9(6)
C(7)—C(6)—C(1)	113.3(6)	C(8)—C(7)—C(6)	108.8(7)
N(1)—C(8)—O(1)	115.6(7)	C(7)—C(8)—O(1)	138.8(8)
C(7)—C(8)—N(1)	105.5(6)		

presence of diphenylacetylene, led after 12 h to a yellow, moisture-sensitive precipitate of the ylide complex **18**,



in 42% yield. In order to establish the geometry of the migrating group—the cyclopropyl group—with respect to the metal,[1] crystals suitable for an X-ray analysis were grown from dry mixtures of methylene chloride/hexane. The ORTEP drawing of **18** appears in Figure 4, whereas the bond distances and bond angles are listed in Table 4. Since, in general, the thermolysis of ylide complexes such as **18** took place in boiling toluene but led to the metal-free organic rearranged products,

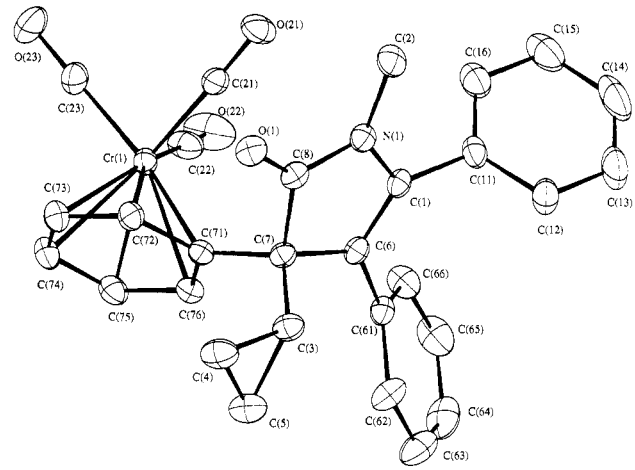


Figure 5. ORTEP drawing of complex **19**. Ellipsoids are shown at the 50% probability level.

Table 5. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound 19

Cr(1)—C(21)	1.822(3)	O(21)—C(21)	1.156(3)
Cr(1)—C(22)	1.819(3)	O(22)—C(22)	1.151(4)
Cr(1)—C(23)	1.830(3)	O(23)—C(23)	1.153(4)
Cr(1)—C(71)	2.238(3)	Cr(1)—C(72)	2.220(3)
Cr(1)—C(73)	2.214(3)	Cr(1)—C(74)	2.212(3)
Cr(1)—C(75)	2.211(3)	Cr(1)—C(76)	2.220(3)
O(1)—C(8)	1.223(3)	N(1)—C(1)	1.423(3)
N(1)—C(2)	1.457(4)	N(1)—C(8)	1.341(3)
C(1)—C(6)	1.333(4)	C(3)—C(4)	1.499(5)
C(3)—C(5)	1.492(5)	C(3)—C(7)	1.538(4)
C(4)—C(5)	1.481(5)	C(6)—C(7)	1.524(4)
C(7)—C(8)	1.563(4)		
C(22)—Cr(1)—C(21)	86.9(1)	O(21)—C(21)—Cr(1)	177.9(3)
C(23)—Cr(1)—C(21)	86.2(1)	O(22)—C(22)—Cr(1)	177.3(3)
C(23)—Cr(1)—C(22)	86.4(2)	O(23)—C(23)—Cr(1)	178.1(3)
C(2)—N(1)—C(1)	126.2(3)	C(8)—N(1)—C(1)	110.9(2)
C(8)—N(1)—C(2)	122.9(3)	C(6)—C(1)—N(1)	111.3(2)
C(5)—C(3)—C(4)	59.4(2)	C(7)—C(3)—C(4)	123.1(3)
C(7)—C(3)—C(5)	123.0(3)	C(5)—C(4)—C(3)	60.1(2)
C(4)—C(5)—C(3)	60.5(2)	C(7)—C(6)—C(1)	109.1(2)
C(6)—C(7)—C(3)	112.1(2)	C(8)—C(7)—C(3)	105.6(2)
C(8)—C(7)—C(6)	101.1(2)	N(1)—C(8)—O(1)	125.1(3)
C(7)—C(8)—O(1)	127.1(3)	C(7)—C(8)—N(1)	107.8(2)

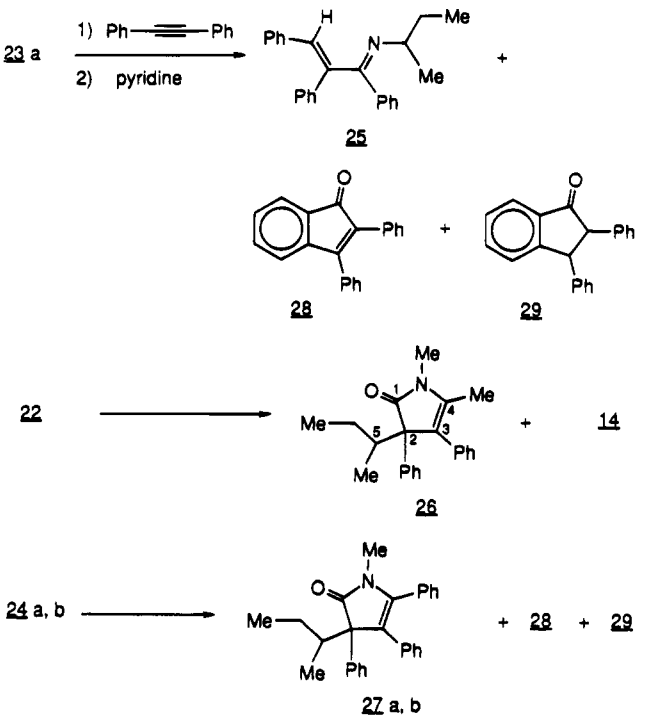
attempts were made to carry out the reaction under conditions such as to allow the isolation of the metal-coordinated, rearranged product **19**. This could be achieved partially in the case of **18** by using benzene instead of toluene: under such conditions, the expected complex **19** could be isolated in a low 11% yield. Its structure, which could be established by ^1H and ^{13}C NMR spectroscopies, was confirmed by an X-ray analysis. An ORTEP projection appears in Figure 5, the bond distances and bond angles being displayed in Table 5. As expected, complex **19** is a $Cr(CO)_3$ adduct of pyrrolinone **20** resulting from the migration of the cyclopropyl group from nitrogen to the γ-carbon atom.

Discussion of the Structure of 18. The structure of complex **18** clearly shows the presence of a nitrogen atom in a tetrahedral configuration, the angles around nitrogen being equal for C(1)—N(1)—C(2) to 114.3(6)°, for C(1)—N(1)—C(3) to 109.9(6)°, for C(2)—N(1)—C(3) to 110.2(6)°, and for C(2)—N(1)—C(8) to 106.2(6)°. Both the value of the N(1)—C(8) bond distance, 1.62(1) Å, and of the C(7)—C(8)—O(1) bond angle, 138.8(6)°, are in agreement with the existence of a bond between N(1) and C(8) as a result of the intramolecular interaction of the tertiary amine with the ketene function. Considered as a whole, the five-membered ylide and the

phenyl ring coordinated to $Cr(CO)_3$ are very nearly planar; the atoms which make the pyrrolinone ring all fall within 0.01 Å of their least squares plane. The two planes form an angle of 16.6° with each other. Lack of conjugation between the phenyl and the pyrrolinone rings is evidenced by the C(7)—C(71) bond distance of 1.45(1) Å which compares favorably with lengths for single bonds between sp^2 carbon atoms. It must nevertheless be pointed out that the Cr(1)—C(71) bond length of 2.269(9) Å and the Cr(1)—C(72) bond length of 2.245(8) Å compared to those of Cr(1)—C(74), 2.18(1) Å, and of Cr(1)—C(73), 2.20(1) Å, seem to indicate that delocalization of the negative charge from the benzylic position at C(7) to the chromium occurred to some extend as would be expected for such a system.[19,20] A similar observation had already been made on the first N-ylide complex derived from a piperidine-substituted carbene complex in which the length of the bond between the carbon vicinal to the benzylic position and the metal was of 2.313(4) Å. The length of 1.232(9) Å for the bond from C(8) to O is slightly longer than the generally accepted value of 1.215(5) Å for carbonyl bonds in a conjugated system. The five-membered ring is thus best described as a pyrrolium oxide, the C(7)—C(8), 1.39(1) Å, and C(6)—C(1), 1.32(1) Å, bond lengths being typical for double bonds and the C(6)—C(7) bond, 1.46(1) Å, for a single bond.

As far as the geometry of the cyclopropyl group with respect to the metal is concerned, it appears that in the solid state these two groups are cis but far away from each other. This geometry might be considered as a preferred conformation, but it appears that a preferred conformation exists also in solution since the hydrogen atoms of the coordinated aryl group show signals at different frequencies (δ 5.44, 1H, d; δ 5.34, 1H, d; δ 5.29, 2H, m; δ 4.89, 1H, t). Thus both in the solid state and in solution, no free rotation around the C(71)—C(7) bond takes place at room temperature. The reasons for this special geometry of the complex are not clear; one tentative explanation would be that as long as the metal is cis with respect to the cyclopropyl group, no migration, for steric reasons, can occur. Only after rotation around C(7)—C(71), which could be induced thermally, will the possibility for the migration exist. And indeed this seems to be the case; in the resulting pyrrolinone complex **19** the cyclopropyl group is trans to the $Cr(CO)_3$ group. That a preferred conformation exists for **19** both in the solid state and in solution appears again in the ^1H NMR spectrum: signals for the five hydrogen atoms of the coordinated phenyl group appear at δ 6.09 (d), 5.42 (d), 5.35 (t), 5.18 (t), and 5.03 (t) ppm.

Behavior of Carbene Complexes 23a and 24a,b Derived from *sec*-Butylamine: Migration of the *sec*-Butyl Group from 24b without Racemization. Under the same reaction conditions as above, complex **23a** led, after treatment of the crude product with pyridine and preparative silica gel chromatography, to **25**, a conjugated imine, in 32% yield, as a 50/50 mixture of isomers. The structure was confirmed both by the ^1H NMR spectroscopy with a multiplet at δ 3.53 for the N—CH proton, two doublets at δ 0.97 and 0.83 for the $CHCH_3$ proton, and two triplets at δ 0.60 and 0.63 ppm for the CH_2CH_3 groups of the two isomers and ^{13}C NMR spectroscopy with signals at δ 164.5 and 163.8 for the C—N carbons of the two isomers.



When a mixture of complex **22** and diphenylacetylene was refluxed in benzene for 12 h, complete disappearance of the starting product occurred. A pyridine treatment of the crude reaction product followed by silica gel chromatography gave, besides unreacted alkyne and ketone **14**, only trace amounts of pyrrolinone **26**. The mass (m/z = 319), and the ^1H NMR spectra were in agreement with such a structure; besides the signals for ten aromatic protons, a signal for the NMe group at δ 3.12 ppm, for the methyl on the double bond at δ 2.05 ppm, a multiplet due to one proton at δ 2.04 ppm, and a multiplet centered at δ 0.85 ppm (6H) were observed. Since the low yield of **26** was probably due to the presence of the methyl group on the carbene carbon (*vide supra*), we turned to the complexes **24a,b** (racemic and optically active) and carried out the same insertion reaction.

Thus, complex **24a** led after first heating in toluene for 12 h and then in pyridine for 6 h to a mixture of three products which could be separated by silica gel chromatography. Elution with light petroleum ether/methylene chloride (85/15) afforded diphenylindenone, a benzannulation product, as an orange solid, in 4% yield. Elution with the same solvents (70/30) gave diphenylindanone (cis/trans mixture), a second benzannulation product, as white crystals, in 27% yield. Finally elution with petroleum ether/ethyl acetate (95/5) gave the expected pyrrolinone **27a**, as an oil in 17% yield. Under the same conditions, the optically active carbene complex **24b** gave the same products, in respectively 11% yield for the diphenylindenone, 41% yield for the diphenylindanones, and 22.5% yield for the pyrrolinone which appeared to be optically active (α_D = −11°).

Since two asymmetric carbons are present in **27**, one might expect the formation of the four possible stereoisomers in the case of the racemic carbene complex **24a**,

(19) Ceccon, A.; Gambaro, A.; Romanin, A. M.; Venzo, A. *J. Organomet. Chem.* **1983**, *254*, 199.
(20) Rose-Munch, F.; Khourzoum, R.; Djukic, J. P.; Perrotey, A.; Rose, E. *J. Organomet. Chem.* **1994**, *467*, 195.

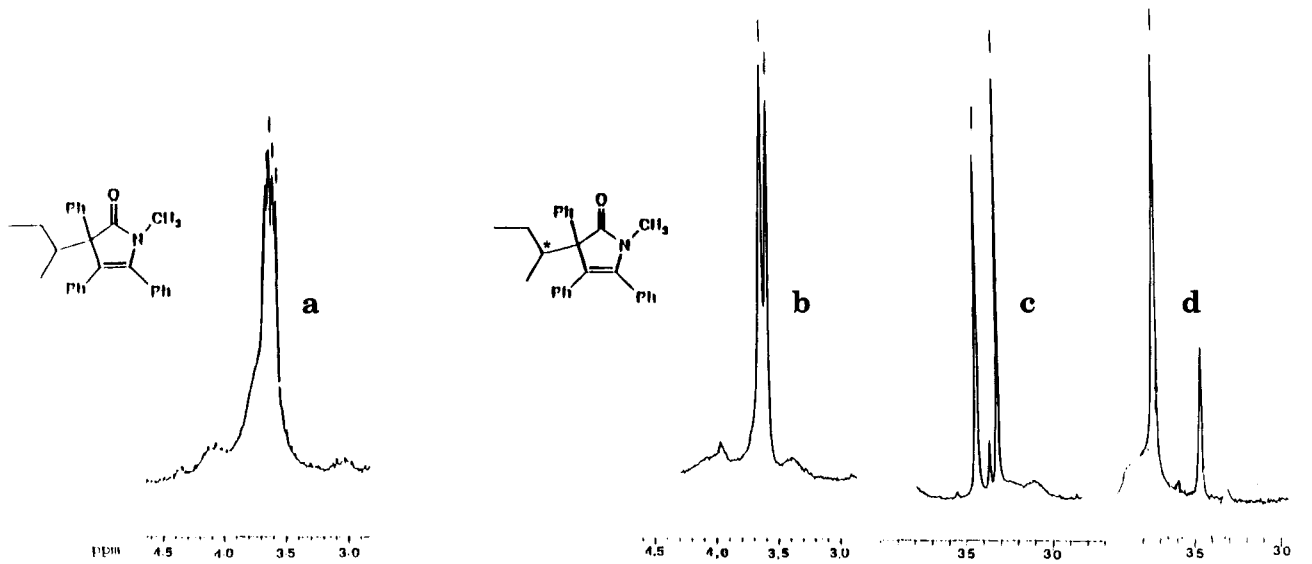


Figure 6. Partial ^1H NMR spectrum ($CDCl_3$, NMe region) of **27a** and **27b** in the presence of $Eu(tfc)_3$.

two of which are diastereoisomers, thus directly differentiable by NMR spectroscopy. In the case of the optically active complex **24b**, one could imagine two figures: (1) the first one in which partial or total racemization of the migrating group would occur, where in such an event four stereoisomers are expected showing optical activity in the case of partial racemization and no optical activity, as for the racemic carbene complex, in the case of complete racemization; (2) the second one in which no racemization (either retention or complete inversion of configuration) would take place, where only two diastereoisomers should be observed.

And indeed, as expected, identical spectroscopic data were observed, for both **27a** and **27b**. The IR and ^{13}C NMR spectra (ν(CO), 1690 cm^{-1}, δ(CO), 180.2 ppm) confirmed the presence of the pyrrolinone ring system. However both the ^1H and ^{13}C NMR spectra featured two signals for all of the characteristic resonances, at δ 2.97 and 2.96 ppm for the NMe group, at δ 180.25 and 180.18 ppm for the CO, at δ 65.69 and 65.61 for C(Ph), at δ 38.43 and 38.12 ppm for the NMe group, at δ 24.6 and 23.8 for the CH_2, and at δ 14.33, 13.16, 12.92, and 12.68 for the CH_3 groups. Thus, as expected two stereoisomers were formed during the migration. Although no difference in their R_f appeared on TLC, attempts were made to separate the pyrrolinones **27b** by silica gel chromatography. However, as reflected by the ^1H NMR spectrum of the first fractions of the chromatography, only partial (70/30; vide infra and see Figure 6d) separation could be achieved.

Differentiation between enantiomers by means of NMR spectroscopy can be achieved by use of chiral lanthanide chelates. In the case of **27a**, addition of successive amounts of (+)-$Eu(tfc)_3$ (tfc = 3-((trifluoromethyl)hydroxymethylene)-(+)-camphorato),[21] which is known to complex carbonyl groups, induced the appearance of two new signals of equal intensities for the NMe group (Figure 6a). However, in the case of **27b**, no splitting of the two signals could be observed upon addition of increasing amounts of the optically active shift reagents (Figure 6b). A better separation of the two signals could even be obtained by using instead (+)-$Eu(hfc)_3$, (hfc = 3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato)[22] (Figure 6c). Thus no (or less than 10%) racemization occurred during the insertion–rearrangement reaction carried out on **24b**. This result means that the migration of the *sec*-butyl group either took place with retention of configuration at carbon C(5) or with complete inversion at the same carbon. However, up to now, no conclusive arguments for one or the other proposal exist.

Conclusion

The key point of the present investigations is the lack of racemization during the migration of a chiral, racemizable alkyl group. Even though it had been established in the Stevens rearrangement of organic ylides that chirality could be retained even in radical involving migrations, the intermediacy of radicals in the reaction of alkynes with aminocarbene complexes can be excluded since the cyclopropylcarbinyl group migrates without rearrangement. The transformation could thus occur via two routes: (1) a concerted mechanism in which the metal is only involved in the insertion of the alkyne and of the carbonyl group and perhaps in the stabilization of the N-ylides which then undergo a concerted rearrangement (Scheme 3); (2) a mechanism in which the metal is involved in all the steps of the reaction leading via **a**, **b**, and **c** to **3** and **4**. Such a mechanism would easily account for the double CO insertions[2] which might occur via the intermediate **c** (Scheme 3). The first mechanism would hold for those reactions leading to isolable ylides; the second one would hold for those where no intermediates could be detected or where no phenyl-substituted alkynes are involved.

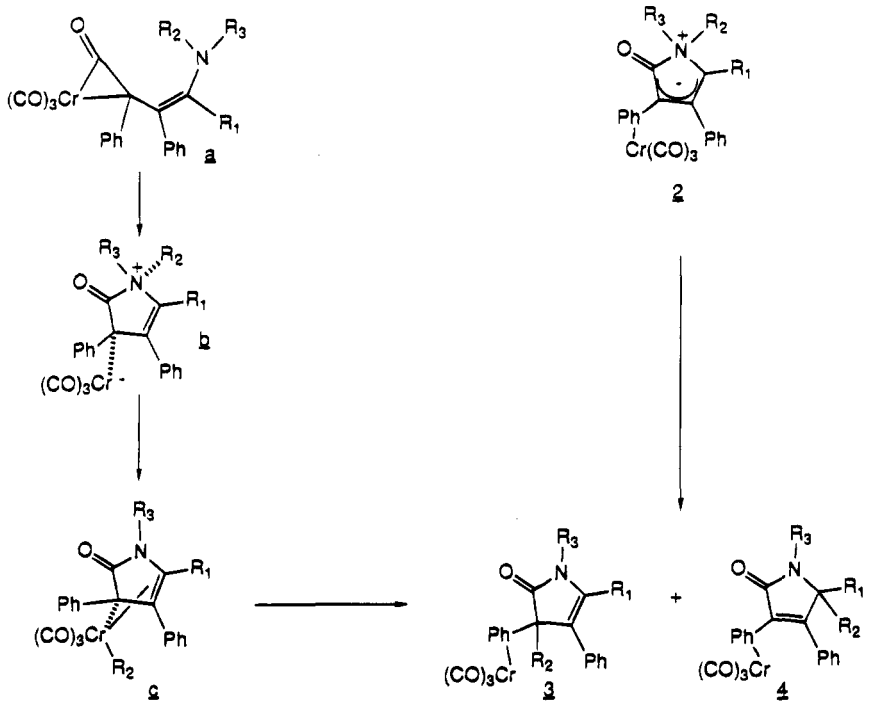
Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL GX 400 or on a Bruker WM 200 spectrometer. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Mass spectra were recorded on a

(21) Goering, H. L.; Eikenberry, J. N.; Koerner, G. S. *J. Am. Chem. Soc.* **1971**, *93*, 5913.

(22) Fraser, R. R.; Petit, M. A.; Saunders, J. K. *J. Chem. Soc., Chem. Commun.* **1971**, 1450.

Scheme 3



ZAB HSQ (Fisons) instrument. Column chromatography was performed with Merck silica gel (70–230 mesh) using various ratios of ethyl acetate/light petroleum or dichloromethane/light petroleum as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under an argon atmosphere in carefully dried glassware. Benzene, tetrahydrofuran (THF), and diethyl ether were distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride under a nitrogen atmosphere.

Complexes **5a**, **5b**, and **17** were prepared according to the literature.[1,2]

Preparation of Aminocarbene Complexes. Two methods were used, either aminolysis of an alkoxycarbene complex[6,23,24] or reaction of $Na_2Cr(CO)_5$ with an amide followed by dehydration with Me_3SiCl/Al_2O_3.[8]

Complex 7 was obtained from the corresponding amide according to the second method, as yellow crystals (20% yield): mp 80 °C; IR ($CHCl_3$) 2020, 1970, 1925 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 11.41 (s, 1H, Cr=CH), 7.54–7.31 (m, 5H, Ar), 3.81 (s, 3H, NCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 271.63 (Cr=C), 224.18, 217.03 (CO), 148.0, 130.22, 129.28, 125.68 (Ar), 57.95 (NMe). Anal. Calcd for $C_{13}H_9NO_5Cr$: C, 50.16; H, 2.89; N, 4.50. Found: C, 49.81; H, 2.92; N, 4.62. MS (*m/z*) for $C_{13}H_9NO_5Cr^+$: calcd, 311; found, 311.

$(CO)_5Cr$=C(Me)NHPh (10) was obtained from complex **5b** by aminolysis with aniline. Thus freshly distilled aniline (0.70 g, 7.5 mmol) was added to a dry-ice-cooled solution of complex **5b** (1.7 g, 6.5 mmol) in diethyl ether (50 mL). Heating to room temperature followed by evaporation of the volatiles under vacuum gave an oil which was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (9/1) gave, after evaporation of the solvent under vacuum, complex **10** (1.6 g, 80%, 65/35 **E,Z** mixture) as yellow crystals: mp 104 °C; IR ($CHCl_3$) 2020, 1975, 1925 cm^{-1}; (**E,Z** mixture) ^1H NMR (200 MHz, $CDCl_3$) δ 10.4 and 10.2 (s, 1H, NH), 7.45–7.11 (m, 5H, Ar), 2.66 and 2.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 290.4 and 287.21 (Cr=C), 223.72, 212.22 (CO), 139.35, 130.77, 130.51, 130.03, 128.09, 126.35 (Ar), 47.57 and 38.60 (CH_3). Anal. Calcd for $C_{13}H_9NO_5Cr$: C, 50.16; H, 2.89; N, 4.50. Found: C, 50.13; H, 2.86; N, 4.48. MS (*m/z*) for $C_{13}H_9NO_5Cr^+$: calcd, 311; found, 311.

$(CO)_5Cr$=C(Me)N(Me)Ph (11). Complex **10** (3.6 g, 11.6 mmol) in THF (150 mL) was treated with LDA (13 mmol) in THF, at −78 °C. Then methyl iodide (1.85 g, 13 mmol) was added. After being heated to room temperature, the mixture was kept at this temperature for 2 h. After evaporation of the volatiles under vacuum, followed by addition of H_2O, extraction with diethyl ether, and evaporation of the solvent, the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (9/1) gave, after evaporation of the solvent under vacuum, a yellow solid (3.5 g, 94%, 75/25 *E,Z* mixture): mp 88 °C; ^1H NMR (200 MHz, $CDCl_3$) δ **11***E* 7.52–7.00 (m, 5H, Ar), 4.10 (s, 3H, NMe), 2.45 (s, 3H, Me), **11***Z* &.46–7.24 (m, 5H, Ar), 3.58 (s, 3H, NMe), 2.95 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ **11***E* 279.96 (Cr=C), 224.41 and 218.9 (CO), 147.50–125.17 (Ar), 54.72 (Me), 43.52 (NMe), **11***Z* 279.96 (Cr=C), 224.45 and 216.46 (CO), 147.50–125.17 (Ar), 46.93 (Me), 41.96 (NMe). Anal. Calcd for $C_{14}H_{11}NO_5Cr$: C, 51.69; H, 3.38; N, 4.30. Found: C, 51.90; H, 3.47; N, 4.27.

$(CO)_5Cr$=C(Me)N(Me)(*sec*-Bu) (22) was obtained from complex **5b** (5.5 g, 20.8 mmol) in diethyl ether (100 mL) and a slight excess of (±)-*sec*-butylamine (1.8 g, 25 mmol). After 3 h at room temperature the volatiles were evaporated under vacuum to give complex **21**, $(CO)_5Cr$=C(Me)NH(*sec*-Bu) as a yellow solid (5.5 g, 91%): mp 36 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.5 (s, 1H, NH), 3.90 (m, 1H, NCH), 2.66 (s, 3H, Me), 1.70 (m, 2H, CH_2CH_3), 1.28 (d, 3H, $CHCH_3$), 1.00 (t, 3H, $CHCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 277.62 (Cr=C), 222.9 and 217.95 (CO), 55.4 (CH), 35.17 (Cr=C(Me)), 29.5 (CH_2), 20.21 (Me), 10.19 (Me). Anal. Calcd for $C_{11}H_{13}NO_5Cr$: C, 45.36; H, 4.47; N, 4.81. Found: C, 45.43; H, 4.39; N, 4.67. A solution of complex **21** (5 g, 17.2 mmol) in THF (200 mL) was treated with LDA (19 mmol) at −65 °C and then with methyl iodide (2.44 g, 19 mmol). After being heated to room temperature, the volatiles were evaporated under vacuum. After addition of water and extraction as above, the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (9/1) gave, after evaporation of the solvent under vacuum, complex **22** as a yellow oil (3 g, 58%): ^1H NMR (200 MHz, $CDCl_3$) δ 4.97 (m, 1H, NCH), 3.03 (s, 3H, NMe), 2.69 (s, 3H,

(23) Denise, B.; Goumont, R.; Parlier, A.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Organomet. Chem.* **1989**, *377*, 89.
(24) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599.

C—Me), 1.74 (m, 2H, CH_2), 1.35 (d, 3H, $CHCH_3$), 1.00 (t, 3H, CH_2CH_3). Anal. Calcd for $C_{12}H_{15}NO_5Cr$: C, 47.21; H, 4.92; N, 4.59. Found: C, 47.38; H, 4.93; N, 4.44.

$(CO)_5Cr$=C(Ph)N(Me)(*sec*-Bu) (24a,b) were obtained from complex **5a** via complexes **23a,b**. Thus complex **5a** (6.2 g, 19 mmol) in diethyl ether (100 mL) was treated with (±)-*sec*-butylamine (1.7 g, 22.8 mmol). After 3 h at room temperature, the volatiles were evaporated under vacuum and the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (9/1) followed by evaporation of the solvent gave a yellow solid of complex **23a** (3.7 g, 55%, 60/40 *E,Z* mixture: mp 50 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ *E* isomer 8.7 (s, 1H, NH), 7.38–6.80 (m, 5H, Ar), 3.46 (m, 1H, NCH), 1.59 (m, 2H, CH_2), 1.19 (d, 3H, $CHCH_3$), 0.92 (t, 3H, CH_2CH_3), *Z* isomer 8.4 (s, 1H, NH), 7.26–6.95 (m, 5H, Ar), 4.47 (m, 1H, NCH), 1.77 (m, 2H, CH_2), 1.45 (d, 3H, $CHCH_3$), 1.18 (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ *E* isomer 278.5 (Cr=C), 223.0 and 217.3 (CO), 149.65–118.71 (Ar), 58.6 (NCH), 29.52 (CH_2), 21.18 and 10.43 (2Me), *Z* isomer 278.5 (Cr=C), 223.0 and 217.3 (CO), 149.65–118.71 (Ar), 60.87 (NCH), 29.69 (CH_2), 20.6 and 10.12 (2Me). Anal. Calcd for $C_{16}H_{15}NO_5Cr$: C, 54.39; H, 4.25; N, 3.97. Found: C, 54.24; H, 4.32; N, 3.84. **23a** (2 g, 5.7 mmol) in THF (100 mL) was treated at −65 °C with LDA (6.3 mmol) in THF (20 mL) and then with methyl iodide (0.9 g, 6.3 mmol). After the sample was heated to room temperature for 2 h, extraction was carried out as above to give an oil which was filtered over silica gel. Elution with petroleum ether/CH_2Cl_2 (95/5) gave complex **24a** as an oil (1.65 g, 79%, 65/35 *E,Z* mixture): ^{1}H NMR (200 MHz, $CDCl_3$) δ *E* isomer 7.40–6.58 (m, 5H, Ar), 3.97 (m, 1H, NCH), 3.73 (s, 3H, NMe), 1.59 (m, 2H, CH_2), 1.12 (d, 3H, $CHCH_3$), 0.79 (t, 3H, CH_2CH_3), *Z* isomer 7.40–6.58 (m, 5H, Ar), 5.18 (m, 1H, NCH), 2.78 (s, 3H, NMe), 1.81 (m, 2H, CH_2), 1.45 (d, CH_3, $CHCH_3$), 1.08 (t, 3H, CH_2-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ *E* isomer 275.2 (Cr=C), 224.14 and 217.47 (CO), 152.31–118.02 (Ar), 63.48 (NCH), 41.63 (NMe), 27.2 (CH_2), 19.15 and 10.82 (2Me), *Z* isomer 275.2 (Cr=C), 223.96 and 217.16 (CO), 152.31–118.02 (Ar), 69.8 (NCH), 36.7 (NMe), 27.5 (CH_2), 18.4 and 10.21 (2Me). Anal. Calcd for $C_{17}H_{17}NO_5Cr$: C, 55.58; H, 4.63; N, 3.81. Found: C, 55.43; H, 4.58; N, 3.76.

Complexes **23b** and **24b** were obtained from **5a** according to the same procedure as above by using for the aminolysis reaction (**R**)-(−)-*sec*-butylamine (99%, $\alpha_D = -7.5°$). Complex **23b**: Yellow solid; yield 60%; α_D^{25} −52° (*c* = 2.16, $CHCl_3$). Complex **24b**: Yellow solid; yield 90%; α_D^{25} −77° (*c* = 1.01, $CHCl_3$).

Aminofuran 9 was obtained upon heating complex **7** (0.60 g, 2 mmol) in refluxing benzene (30 mL) in the presence of diphenylacetylene (0.50 g, 3 mmol) for 12 h. Evaporation of the solvent under vacuum followed by silica gel chromatography of the residue gave first with petroleum ether excess diphenylacetylene and then with petroleum ether/CH_2Cl_2 (9/1) complex **8** as a yellow solid (0.65 g, 70%): mp 180 °C; IR ($CHCl_3$) 1970, 1895 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.57 (s, 1H, =CH), 7.28–6.71 (m, 10H, Ar), 5.00 (d, 2H), 4.60 (t, 2H), 4.57 (t, 1H, Ar—Cr), 2.94 (s, 3H, NMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.85 (CO), 152.10, 148.05, 137.46, 129.25, 129.05–113.77 (C—O—C and Ar), 102.60, 93.22, 92.17, 91.30 (Ar—Cr), 38.41 (NMe). Anal. Calcd for $C_{26}H_{19}NO_4Cr$: C, 67.67; H, 4.12; N, 3.03. Found: C, 67.69; H, 4.23; N, 2.91.

Heating of complex **8** in refluxing pyridine (20 mL) for 6 h gave quantitatively, after evaporation of the solvent under vacuum, compound **9** as a white solid. Crystals of **9** were grown from hexane/dichloromethane solutions: mp 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H, =CH), 7.21–6.67 (m, 15H, Ar), 3.04 (s, 3H, NMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.48, 147.81, 135.61, 132.46, 131.62, 129.05–113.66 (C=C, Ar), 38.83 (NMe). MS (*m/z*): cald for $C_{23}H_{19}NO^+$, 325; found, 325.

Aminofuran complex 12, pyrrolinone 13, ketone 14, and imine 15 were obtained upon heating complex **11** (2.5 g, 7.7 mmol) in refluxing benzene (50 mL) in the presence of diphenylacetylene (1.6 g, 9 mmol) for 12 h. Evaporation of the solvent under vacuum, followed by silica gel chromatography of the residue with petroleum ether containing increasing amounts of ethyl acetate (99/1–80/20), first gave complex **12** (0.52 g, 14%) as a yellow solid: mp 111 °C; IR ($CHCl_3$) 1965 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44–6.90 (m, 10H, Ar), 5.31–5.05 (m, 5H, Ar—Cr), 3.31 (s, 3H, NMe), 2.17 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.14 (CO), 148.3, 147.7, 146.2, 132.7, 130.3, 129.4, 128.7, 127.6, 120.8, 119.65, 114.0, 112.26 (C=C, Ar), 102.0, 93.2, 91.9, 91.6 (Ar—Cr), 38.4 (NMe), 11.9 (Me). Anal. Calcd for $C_{27}H_{21}NO_4Cr$: C, 68.21; H, 4.42; N, 2.95. Found: C, 68.07; H, 4.57; N, 2.86.

Then pyrrolinone **13** (0.245 g, 10%) formed as a white solid: mp 151 °C; IR ($CHCl_3$) 1690, 1600 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.56–6.96 (m, 15H, Ar), 2.59 (s, 3H, NMe), 1.51 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7 (CO), 139.98, 136.75, 134.52, 130.02, 129.89, 129.34, 129.01, 128.46, 128.3, 128.1, 127.09, 126.67, 122.46 (Ar), 66.72 (CPh_2), 29.96 (NMe), 11.78 (Me). Anal. Calcd for $C_{24}H_{21}NO$: C, 84.95; H, 6.19; N, 4.13. Found: C, 84.47; H, 6.16; N, 4.06. Then ketone **14** (0.21 g, 9%) formed, the ^{1}H NMR of which was compared to the spectrum of an authentic sample, and finally imine **15** (0.254 g, 15%) formed as a white solid: mp 127 °C; IR ($CHCl_3$) 1640 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29–6.96 (m, 15H, Ar), 3.03 (s, 3H, NMe), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (C=N), 143.55–126.5 (C=C, Ar), 40.83 (NMe), 28.15 (Me). HRMS (*m/z*): calcd for $C_{23}H_{21}N$ (M^+), 311.1673; found, 311.1628. **Ketoamide 16** was obtained upon refluxing complex **12** (1g, 2.1 mmol) in pyridine (20 mL) for 12 h. Evaporation of the solvent under vacuum followed by silica gel chromatography gave with 90/10 petroleum ether/ethyl acetate as eluent compound **16** (0.37 g, 50%) as a white solid: mp 54 °C; IR ($CHCl_3$) 1685 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.05–6.44 (m, 15H, Ar), 3.31 (s, 3H, NMe), 2.17 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8 (CO), 170.73 (CON), 143.25–126.06 (C=C, Ar), 37.2 (NMe), 30.1 (COMe). HRMS (*m/z*): calcd for $C_{24}H_{21}NO_2$ (M^+), 355.1570; found, 355.1570.

N-ylide complex 18 was obtained by refluxing a solution of **6** (4.10 g, 11.7 mmol) and diphenylacetylene (2.6 g, 14.6 mmol) in hexane (160 mL) for 12 h. After the mixture was cooled to room temperature, the yellow precipitate (2.45 g, 42%) was isolated by filtration. Recrystallization from mixtures of dichloromethane/hexane gave orange crystals suitable for an X-ray analysis: mp 172 °C.

Thermolysis of Complex 18. Complex **18** (0.5 g, 1 mmol) was placed in refluxing benzene (40 mL) for 36 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel with petroleum ether/ethyl acetate (90/10) as eluent. Appropriate fractions were collected to give, after evaporation of the solvent, the pyrrolinone complex **19** as orange crystals (0.056 g, 11%) which were recrystallized from CH_2Cl_2/hexane: mp 115–116 °C; IR ($CHCl_3$) 1965, 1895, 1690, 1590 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.59–6.68 (m, 10H, Ar), 6.12–5.04 (m, 5H, Ar—Cr), 2.91 (s, 3H, NCH_3), 1.61 (m, 1H, CH), 1.25 (m, 1H, CH), 0.75–0.66 (m, 2H), 0.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.61 (CO), 175.75 (CO), 141.94 (C=C), 134.24–121.91 (Ar), 109.99 (C=C), 94.41, 94.30, 93.60, 90.04 (Ar—CH), 56.41 (C quat), 28.01 (NC), 18.72 (CH), 2.95 (CH_2), 2.24 (CH_2). HRMS (*m/z*): calcd for $C_{29}H_{23}NO_4Cr$ (M^+), 501.1032; found, 501.1031.

Thermolysis of complex 18 (1 g, 2 mmol) in refluxing toluene (30 mL) for 18 h gave, after evaporation of the solvent under vacuum, followed by silica gel chromatography with petroleum ether/ethyl acetate (90/10), pyrrolinone **20** (0.193 g, 26%) as white crystals: mp 127 °C; IR ($CHCl_3$) 1690, 1595 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69–6.71 (m, 15H, Ar), 2.96 (s, 3H, NCH_3), 1.50 (m, 1H), 1.26 (m, 1H), 0.75 (m, 1H), 0.47 (m, 1H), 0.14 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.86 (CO), 140.60–124.26 (C=C, Ar), 60.02 (C—Ph), 28.13 (NCH_3), 14.67 (CH), 2.17, 1.36 (2 CH_2). Anal. Calcd for $C_{26}H_{23}NO$: C, 85.48; H, 6.30; N, 3.84. Found: C, 84.95; H, 6.45; N, 3.82.

Table 6. Crystallographic Data

	compound				
	9	**13**	**15**	**18**	**19**
			Crystal Parameters		
formula	$C_{23}H_{19}ON$	$C_{24}H_{21}ON$	$C_{23}H_{21}N$	$C_{29}H_{23}O_4NCr$	$C_{29}H_{23}O_4NCr$
fw	325.4	339.4	311.4	501.5	501.5
cryst system	triclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$Pc2_1n$	$P2_1/a$
a, Å	8.861(1)	9.957(6)	9.290(2)	12.763(11)	4.044(5)
b, Å	9.814(2)	9.767(4)	22.324(3)	13.854(14)	9.664(2)
c, Å	10.817(1)	19.244(19)	9.630(1)	13.577(26)	18.035(3)
α, deg	102.08(1)				
β, deg	94.67(1)		116.14(1)		97.93(2)
γ, deg	105.93(1)				
V, Å^3	875(5)	1871(2)	1793(13)	2401(6)	2424(7)
Z	2	4	4	4	4
ϱ, g cm^{-3}	1.24	1.20	1.15	1.39	1.37
μ(Mo Kα), cm^{-1}	0.71	0.68	0.62	4.98	4.93
			Data Collection		
diffractometer	CAD4	CAD4	CAD4	CAD4	CAD4
monochromator	graphite	graphite	graphite	graphite	graphite
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan range q, deg	$0.8 + 0.34 \tan\theta$	$0.8 + 0.34 \tan\theta$	$0.8 + 0.34 \tan\theta$	$0.8 + 0.34 \tan\theta$	$0.8 + 0.34 \tan\theta$
2θ range, deg	2−46	2−46	3−50	3−46	2−50
reflcns collcd	2425	1511	3139	1749	4265
reflcns used ($I > 3\sigma(I)$)	1633	1101	977	1294	3132
			Refinement		
R	0.039	0.037	0.052	0.047	0.036
R_w	0.037	0.036	0.051	0.046	0.035
abs corr	DIFABS	DIFABS	DIFABS	DIFABS	DIFABS
min/max abs	0.81/1.21	0.85/1.05	0.93/1.07	0.85/1.17	0.82/1.22
second ext param	0.83×10^{-4}	5.51×10^{-4}	1.15×10^{-4}	none	1.52×10^{-4}
weighting scheme	unit weight	unit weight	unit weight	unit weight	unit weight
ls params	285	238	129	228	388

Imine 25 was obtained upon refluxing a solution of complex **23a** (0.5 g, 1.4 mmol) and diphenylacetylene (0.504 g, 2.8 mmol) in toluene for 18 h. Evaporation of the solvent under vacuum followed by treatment of the residue with pyridine (15 mL) under reflux gave, after evaporation of the solvent, a residue. Thick layer chromatography with petroleum ether/ethyl acetate as eluent gave compound **25** as an oil (0.153 g, 32%): IR ($CHCl_3$) 1600 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ (*E*/*Z* isomers) 8.02−7.18 (m, 15H, Ar), 3.53 (m, 1H, NCH), 1.46 (m, 2H, CH_2), 0.97 (d, J = 6 Hz, 3H, CHMe), 0.83 (d, J = 6 Hz, 3H, CHMe), 0.69 (t, 3H, CH_2CH_3), 0.66 (t, 3H, CH_2CH_3); ^{13}C NMR (200 MHz, $CDCl_3$) δ (*E*/*Z* isomers) 164.49 and 163.81 (C=N), 139.11−125.55 (C=C, Ar), 59.41 and 59.48 (NCH), 31.19 and 30.26 (CH_2), 20.09 and 19.90 (CH_3), 10.50 and 10.39. HRMS (*m*/*z*): calcd for $C_{25}H_{24}N$ (M^+), 339.1987; found, 339.1987.

Pyrrolinone 26 was obtained upon heating complex **22** (2.3 g, 7.5 mmol) in the presence of diphenylacetylene (2 g, 11.25 mmol) in boiling benzene (100 mL) for 12 h. After evaporation of the solvent under vacuum, the residue was treated with pyridine (50 mL) for 6 h. Evaporation of the solvent followed by silica gel chromatography gave with petroleum ether/ethyl acetate (90/10) first compound **26** (0.015 g, 0.5%) as an oil: IR ($CHCl_3$) 1690, 1595 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28−7.16 (m, 10H, Ar), 3.12 and 3.11 (NMe), 2.34 (m, 1H, $CHCH_3$), 2.05 and 2.04 (CH_3), 1.55−1.20 (m, 2H, CH_2CH_3), 0.85 (m, 6H, CH_3). HRMS (*m*/*z*): calcd for $C_{22}H_{25}ON$ (M^+), 319.1936; found, 319.1935. Then with petroleum ether/ethyl acetate (80/20) ketone **14** was produced (0.2 g, 12% yield), the physical properties of which agreed with those of an authentic sample.

Pyrrolinones 27a, indenone 28, and indanone 29 were obtained upon heating complex **24a** (2.44 g, 6.65 mmol) in the presence of diphenylacetylene (2.37 g, 13.3 mmol) in refluxing benzene for 12 h. After evaporation of the solvent, the residue was treated with pyridine for 6 h. Evaporation of pyridine gave a residue which was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (85/15) first gave indenone **28** (0.076 g, 4%) as orange crystals: mp 146 °C; IR ($CHCl_3$) 1700, 1595 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60−7.10 (Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8 (CO), 155.30, 145.21, 130.71−127.73, 122.97, 121.25 (C=C, Ar). HRMS (*m*/*z*): calcd for $C_{21}H_{14}O$ (M^+), 282.1044; found, 282.1046.

Table 7. Fractional and Thermal Parameters for Compound 9

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
O(1)	0.3539(2)	0.0896(2)	0.9358(2)	0.0581
N(1)	0.1645(3)	0.2141(3)	0.9715(2)	0.0535
C(1)	0.4779(4)	0.0939(4)	0.8667(3)	0.0574
C(2)	0.0285(4)	0.2192(5)	0.8894(4)	0.0684
C(3)	0.1502(3)	0.1983(3)	1.0965(3)	0.0484
C(4)	0.2838(4)	0.2289(3)	1.1862(3)	0.0563
C(5)	0.2692(4)	0.2135(4)	1.3085(3)	0.0625
C(6)	0.1210(5)	0.1687(4)	1.3452(3)	0.0657
C(7)	−0.0108(4)	0.1399(4)	1.2575(3)	0.0631
C(8)	0.0010(4)	0.1543(3)	1.1340(3)	0.0552
C(9)	0.2985(3)	0.2035(3)	0.9178(3)	0.0492
C10	0.3823(3)	0.2748(3)	0.8394(2)	0.0449
C(11)	0.4994(3)	0.2013(3)	0.8056(3)	0.0476
C(12)	0.3552(3)	0.3994(3)	0.7952(3)	0.0447
C(13)	0.3589(4)	0.4059(4)	0.6692(3)	0.0538
C(14)	0.3275(4)	0.5197(4)	0.6261(3)	0.0630
C(15)	0.2935(4)	0.6288(4)	0.7091(4)	0.0664
C(16)	0.2910(4)	0.6260(4)	0.8339(4)	0.0627
C(17)	0.3223(4)	0.5129(3)	0.8780(3)	0.0562
C(18)	0.6274(3)	0.2402(3)	0.7284(3)	0.0482
C(19)	0.6620(4)	0.1335(4)	0.6394(3)	0.0632
C(20)	0.7866(5)	0.1705(5)	0.5722(4)	0.0718
C(21)	0.8785(5)	0.3121(5)	0.5915(4)	0.0700
C(22)	0.8454(4)	0.4190(4)	0.6790(3)	0.0638
C(23)	0.7213(4)	0.3838(4)	0.7461(3)	0.0550

Elution with petroleum ether/CH_2Cl_2 (70/30) gave a mixture of diphenylindanones **29** (0.50 g, 27%, 90/10 cis/trans isomers) which were separated by preparative layer chromatography. **29**-*cis*: white solid, mp 86 °C; IR ($CHCl_3$) 1730 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.90−7.05 (m. 14H, Ar), 4.56 (d, J = 5 Hz, 1H), 3.80 (d, J = 5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.58 (CO), 156.42−124.33 (Ar), 64.91 (CH), 55.16 (CH). **29**-*trans*: oil; IR ($CHCl_3$) 1730 cm^{-1}; ^{1}H NMR (200 MHz,

Table 8. Fractional and Thermal Parameters for Compound 13

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²
O(1)	0.4514(3)	0.1074(3)	0.3341(2)	0.0585
N(1)	0.5792(3)	0.2118(4)	0.2506(2)	0.0488
C(1)	0.7103(4)	0.2671(4)	0.2457(2)	0.0437
C(2)	0.7769(4)	0.2515(4	0.3051(2)	0.0379
C(3)	0.6834(4)	0.1853(4)	0.3586(2)	0.0386
C(4)	0.5560(4)	0.1621(4)	0.3144(2)	0.0435
C(5)	0.7551(5)	0.3372(5)	0.1800(2)	0.0555
C(6)	0.4793(6)	0.2072(6)	0.1946(3)	0.0728
C(21)	0.9112(4)	0.3107(4)	0.3211(2)	0.0410
C(22)	1.0265(5)	0.2324(5)	0.3239(3)	0.0621
C(23)	1.1503(5)	0.2908(6)	0.3369(3)	0.0631
C(24)	1.1603(5)	0.4279(5)	0.3503(3)	0.0610
C(25)	1.0485(5)	0.5055(5)	0.3473(3)	0.0733
C(26)	0.9248(5)	0.4488(5)	0.3326(3)	0.0646
C(31)	0.7246(4)	0.0438(4)	0.3846(2)	0.0394
C(32)	0.6721(5)	−0.0083(5)	0.4460(2)	0.0516
C(33)	0.7015(6)	−0.1406(5)	0.4673(2)	0.0616
C(34)	0.7835(6)	−0.2220(5)	0.4280(3)	0.0626
C(35)	0.8357(5)	−0.1724(5)	0.3668(3)	0.0570
C(36)	0.8058(5)	−0.0399(4)	0.3451(2)	0.0473
C(37)	0.6582(4)	0.2872(4)	0.4174(2)	0.0403
C(38)	0.5410(5)	0.3647(5)	0.4207(2)	0.0516
C(39)	0.5245(5)	0.4612(5)	0.4723(3)	0.0617
C(40)	0.6233(6)	0.4838(5)	0.5207(3)	0.0643
C(41)	0.7393(6)	0.4092(5)	0.5181(2)	0.0641
C(42)	0.7569(5)	0.3093(5)	0.4668(2)	0.0519

Table 9. Fractional and Thermal Parameters for Compound 15

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²	*U*(iso), Å²
N(1)	0.0316(6)	0.3211(3)	0.1289(6)	0.0619	
C(1)	0.0908(7)	0.3045(3)	0.0399(7)	0.0475	
C(2)	0.0342(9)	0.3843(4)	0.1665(8)	0.0819	
C(3)	0.0924(8)	0.2383(3)	0.0099(8)	0.0667	
C(4)	−0.0960(7)	0.3860(3)	−0.2199(7)	0.0459	
C(5)	0.0834(7)	0.3826(3)	−0.1482(7)	0.0451	
C(6)	0.1677(7)	0.3445(3)	−0.0342(6)	0.0437	
C(42)	−0.1909(7)	0.3366(3)	−0.2825(7)		0.052(2)
C(43)	−0.3593(8)	0.3417(3)	−0.3514(8)		0.064(2)
C(44)	−0.4279(8)	0.3963(3)	−0.3546(8)		0.072(2)
C(45)	−0.3358(9)	0.4456(3)	−0.2939(9)		0.076(2)
C(46)	−0.1689(8)	0.4415(3)	−0.2279(8)		0.065(2)
C(51)	0.1588(7)	0.4276(3)	−0.2116(7)		0.047(2)
C(52)	0.1209(7)	0.4291(3)	−0.3675(7)		0.053(2)
C(53)	0.1873(8)	0.4734(3)	−0.4245(8)		0.066(2)
C(54)	0.2857(8)	0.5155(3)	−0.3280(8)		0.068(2)
C(55)	0.3221(8)	0.5160(3)	−0.1764(8)		0.068(2)
C(56)	0.2603(8)	0.4718(3)	−0.1137(7)		0.062(2)
C(61)	0.3443(7)	0.3360(3)	0.0327(7)		0.044(2)
C(62)	0.4343(7)	0.3305(3)	0.1920(7)		0.056(2)
C(63)	0.5993(8)	0.3221(3)	0.2560(7)		0.061(2)
C(64)	0.6756(8)	0.3192(3)	0.1624(8)		0.063(2)
C(65)	0.5882(8)	0.3229(3)	0.0067(7)		0.061(2)
C(66)	0.4245(7)	0.3319(3)	−0.0604(7)		0.055(2)

$CDCl_3$) δ 8.00−6.76 (Ar), 4.86 (s, 1H, CH), 3.24 (s, 1H, CH). HRMS (*m/z*): calcd for $C_{21}H_{16}O$ (M^+), 284.1044; found, 282.1048. Finally, elution with petroleum ether/ethyl acetate (95/5) gave pyrrolinone **27a** (0.435 g, 17%) as an oil: IR ($CHCl_3$) 1690, 1595 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.32−6.71 (m, 15H, Ar), 2.97 and 2.96 (s, NCH_3), 2.44 (m, 1H, CH), 1.40 (m, 2H, CH_2), 0.98 (d, 3H, $CHCH_3$), 0.91 (t, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.25 and 180.18 (CO), 141.23−122.90 (C=C, Ar), 65.69 and 65.61 (C quat), 38.43 and 38.12 (CH), 28.19 and 28.13 (NCH_3), 24.66 and 23.80 (CH_2), 14.33 and 13.16 (CH_3), 12.92 and 12.68 (CH_3). HRMS (*m/z*): calcd for $C_{27}H_{27}ON$ (M^+), 381.2092; found, 381.2091.

Pyrrolinones **27b** were obtained under the same conditions from complex **24b**: yield 22.5%; α_D^{25} −11 (*c*, 1.405, $CHCl_3$).

Crystal Data. All pertinent information concerning every compound is summarized in Table 6c. Corrections were made for Lorentz, polarization, and absorption effects.

For compounds **9** and **13** the structures were solved by standard Patterson−Fourier techniques; for compound **15**, **18**,

Table 10. Fractional and Thermal Parameters for Compound 18

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²	*U*(iso), Å²
Cr(1)	0.1072(1)	0.9692(2)	0.54535(9)	0.0469	
C(21)	0.2038(7)	0.9390(6)	0.6372(8)	0.0575	
O(21)	0.2648(6)	0.9162(6)	0.6975(6)	0.0869	
C(22)	0.1127(8)	1.0949(7)	0.5899(7)	0.0583	
O(22)	0.1175(6)	0.1747(5)	0.6165(6)	0.0801	
C(23)	0.2127(9)	1.0000(9)	0.4636(9)	0.0789	
O(23)	0.2815(8)	1.0207(8)	0.4117(7)	0.1243	
O(1)	0.0311(5)	0.6617(4)	0.6874(4)	0.0487	
N(1)	−0.0292(5)	0.7151(4)	0.8474(5)	0.0360	
C(1)	−0.0688(6)	0.8114(6)	0.8791(6)	0.0363	
C(2)	−0.1097(7)	0.6376(6)	0.8476(7)	0.0536	
C(3)	0.0618(7)	0.6863(6)	0.9094(6)	0.0428	
C(4)	0.1644(8)	0.7292(7)	0.8948(8)	0.0638	
C(5)	0.1500(9)	0.6258(7)	0.8745(7)	0.0659	
C(6)	−0.0602(6)	0.8733(5)	0.8061(6)	0.0311	
C(7)	−0.0211(6)	0.8299(5)	0.7154(5)	0.0328	
C(8)	0.0009(6)	0.7333(6)	0.7331(6)	0.0375	
C(11)	−0.0955(6)	0.8270(6)	0.9860(6)		0.043(2)
C(12)	−0.0256(7)	0.8751(7)	1.0442(7)		0.056(2)
C(13)	−0.0469(9)	0.8894(8)	1.1434(8)		0.071(3)
C(14)	−0.1374(8)	0.8546(7)	1.1814(7)		0.066(3)
C(15)	−0.2088(9)	0.8087(8)	1.1256(8)		0.074(3)
C(16)	−0.1877(8)	0.7934(7)	1.0250(7)		0.061(3)
C(61)	−0.0858(5)	0.9771(6)	0.8195(5)		0.032(2)
C(62)	−0.1868(7)	1.0061(6)	0.8432(6)		0.044(2)
C(63)	−0.2099(7)	1.1040(6)	0.8524(7)		0.055(3)
C(64)	−0.1324(8)	1.1713(7)	0.8365(7)		0.059(3)
C(65)	−0.0321(7)	1.1430(7)	0.8171(7)		0.054(2)
C(66)	−0.0071(7)	1.0458(6)	0.8058(7)		0.047(2)
C(71)	−0.0118(6)	0.8702(6)	0.6175(6)		0.041(2)
C(72)	−0.0616(6)	0.9581(7)	0.5903(6)		0.048(2)
C(73)	−0.0538(7)	0.9934(7)	0.4925(7)		0.060(3)
C(74)	−0.0001(8)	0.9443(7)	0.4227(7)		0.066(3)
C(75)	0.0508(8)	0.8586(8)	0.4452(8)		0.068(3)
C(76)	0.0441(7)	0.8231(6)	0.5428(7)		0.051(2)

Table 11. Fractional and Thermal Parameters for Compound 19

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²
Cr(1)	0.19822(3)	0.15930(5)	0.15174(2)	0.0431
O(1)	0.3367(1)	0.5439(2)	0.1206(1)	0.0548
O(21)	0.3853(2)	0.2417(2)	0.2387(1)	0.0686
O(22)	0.1678(2)	−0.0048(4)	0.2857(2)	0.0954
O(23)	0.3045(2)	−0.0895(3)	0.1096(2)	0.0867
N(1)	0.3356(2)	0.5416(2)	0.2467(1)	0.0468
C(1)	0.2659(2)	0.5275(3)	0.2964(2)	0.0441
C(2)	0.4389(2)	0.5580(4)	0.2681(2)	0.0601
C(3)	0.1357(2)	0.6421(3)	0.1367(2)	0.0553
C(4)	0.1176(3)	0.6595(5)	0.0534(2)	0.0662
C(5)	0.0357(3)	0.6414(5)	0.0962(2)	0.0736
C(6)	0.1779(2)	0.5111(3)	0.2589(2)	0.0426
C(7)	0.1839(2)	0.5130(3)	0.1752(1)	0.0427
C(8)	0.2943(2)	0.5341(3)	0.1752(2)	0.0433
C(11)	0.2975(2)	0.5342(4)	0.3776(2)	0.0534
C(12)	0.2684(3)	0.6429(5)	0.4187(2)	0.0772
C(13)	0.2961(4)	0.6453(7)	0.4946(3)	0.0980
C(14)	0.3509(3)	0.5433(8)	0.5296(2)	0.0972
C(15)	0.3821(3)	0.4366(6)	0.4897(2)	0.0915
C(16)	0.3548(3)	0.4329(5)	0.4133(2)	0.0727
C(21)	0.3125(2)	0.2122(3)	0.2044(2)	0.0491
C(22)	0.1780(2)	0.0610(4)	0.2342(2)	0.0653
C(23)	0.2626(2)	0.0069(3)	0.1246(2)	0.0594
C(61)	0.0909(2)	0.4984(3)	0.2972(2)	0.0471
C(62)	0.0104(3)	0.5798(4)	0.2784(2)	0.0646
C(63)	−0.0671(3)	0.5726(4)	0.3187(3)	0.0795
C(64)	−0.0630(3)	0.4855(5)	0.3788(2)	0.0804
C(65)	0.0144(3)	0.4012(5)	0.3975(2)	0.0782
C(66)	0.0911(2)	0.4061(4)	0.3556(2)	0.0652
C(71)	0.1510(2)	0.3795(3)	0.1344(1)	0.0429
C(72)	0.1925(2)	0.3336(4)	0.0710(2)	0.0503
C(73)	0.1602(2)	0.2157(4)	0.0324(2)	0.0570
C(74)	0.0850(3)	0.1384(4)	0.0542(2)	0.0609
C(75)	0.0421(2)	0.1814(4)	0.1153(2)	0.0581
C(76)	0.0748(2)	0.3017(3)	0.1551(2)	0.0492

and **19** the structures were solved by direct methods (SHELXS[25]). Computations were performed by using CRYSTAL[26] adapted on a Microvax-II computer. Form factors and corrections for anomalous dispersion were from ref 27. For each compound, the number and the choice of the refined parameters depended upon the number of available reflections.

Compounds **9** and **19**. Non-hydrogen atoms were refined anisotropically, except the aromatic carbon atoms which were left isotropic. Hydrogen atoms were located on successive difference Fourier maps and put in the last refinement as fixed contributors with an overall refinable isotropic thermal parameter.

Compounds **13** and **15**. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located on successive difference Fourier maps, and their coordinates were refined with an overall refinable isotropic thermal parameter.

Compound **18**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on successive Fourier maps and put in the last refinement as fixed contributors with an overall refinable isotropic thermal parameter.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **9**, **13**, **15**, **18**, and **19** (14 pages). Ordering information is given on any current masthead page.

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(25) Sheldrick, G. M. SHELXS 86, Program for Crystal Structure Solution. University of Gottingen, 1986.

(26) Watkins, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1985.

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.