Reaction of Aminocarbene Complexes of Chromium with Alkynes. 1. Formation and Rearrangement of Ketene and Nitrogen Ylide Complexes

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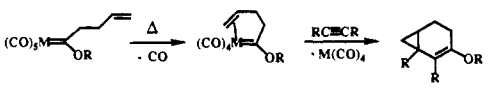
Abstract: The title reactions of chromium-containing carbene complexes $(CO)_5Cr{=}C(R_1)N(R_2R_3)$ (R_1 = H, Me, Ph; R_2 = Me; R_3 = Me, C_3H_5, $CH_2C_3H_5$; R_2R_3 = $(CH_2)_5$) **8** and $(CO)_5Cr{=}C[(CH_2)_3C{\equiv}CPh]N(R_1R_2)$ (R_1 = R_2 = Me; R_1R_2 = $(CH_2)_5$; R_1R_2 = $(CH_2)_4$) **9**, bearing alkyl groups of low migratory aptitude on nitrogen, have been examined. In contrast to complexes in which nitrogen bears either an alkyl and an allyl or a benzyl group or is part of a strained cycle, which give heterocycles upon alkyne/CO insertions followed by nitrogen-to-carbon migrations (e.g., **1** → **7**), complexes **8** and **9** lead to stable nitrogen ylides, which could be fully characterized by X-ray crystallography in the case of **8a** and **9a**. Moreover, in the case of complexes of the general structure **9**, ketene precursors of the ylides could either be detected (R_1 = Me; R_2 = CH_2Ph) or isolated and characterized (R_2R_3 = $(CH_2)_5$). The new ylide complexes undergo, upon moderate heating, Stevens-type rearrangements to the expected heterocyclic compounds as a result of nitrogen-to-carbon migrations of various alkyl groups, and upon treatment with dimethyldioxirane, they undergo oxidation to lactone complexes.

Introduction

Insertion of alkynes into alkoxycarbene complexes of chromium and tungsten has been established thoroughly since 1975 and during the last years by several groups.[1-4] In contrast, although aminocarbene complexes had been known since 1967[5,6] and their reactivity per se determined,[7,8] no attempts had been made to exploit them as nitrogen-containing synthons, a fact probably attributable to their lower reactivity. The first use of these complexes was for the classical synthesis, by way of the benzannulation reaction of indanones, starting from phenyl-substituted morpholinocarbene complexes of chromium with loss of the nitrogen functionality.[9] It is only recently that several groups also became active in the use of these complexes either as starting material for the photochemical preparation of β-lactams[10] or for the synthesis of nitrogen-containing heterocycles.[11-14]

Several years ago,[15,16] we began to explore the reactivity of alkene–carbene complexes of tungsten and chromium and discovered a new, room-temperature insertion of alkynes followed by an intramolecular cyclopropanation reaction according to eq 1. At the inception of this work, we had thought to extend this new reaction to alkene–aminocarbene complexes of chromium, and as expected, these complexes underwent the same reaction (eq 2) at yet a higher temperature, leading to nitrogen-containing polycyclic compounds.[17]



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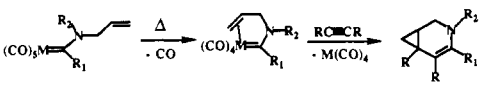

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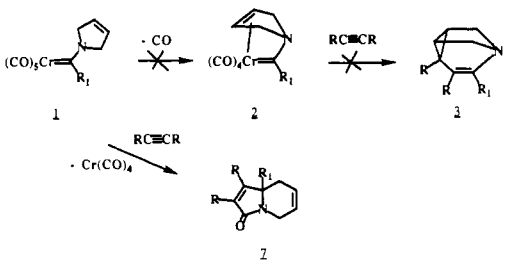
As an extension of these studies, we synthesized complex **1** and found fundamentally different behavior toward alkynes; instead of the insertion–cyclopropanation reaction leading to **3** (eq 3), we observed the insertion of both the alkyne and CO, together with a rearrangement giving the lactam **7**[18] probably via the mechanistic hypothesis of eq 4. We have examined this new



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reaction in a systematic fashion and provided evidence for its generality.[19] Recently[20] we reported, in a preliminary commu-

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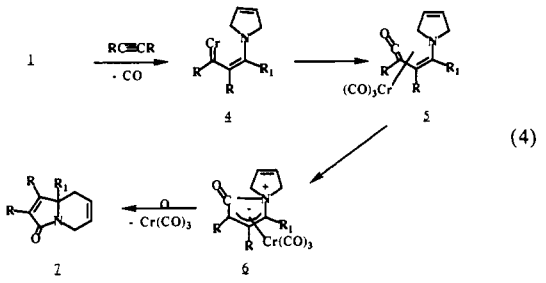
nication, the isolation and transformation of the suspected nitrogen ylide intermediates **6**, starting from carbene complexes of the type **8** bearing alkyl groups of low migratory aptitude on nitrogen. Here, and in a forthcoming paper, we report the full version of these and related studies, including attempts to elucidate the mechanism for the transformation **6** → **7** in relation to the Stevens rearrangement of classically generated nitrogen ylides.



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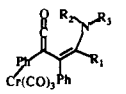
Results

Preparation of Nitrogen Ylide Complexes by Intermolecular Alkyne Insertions. (a) Synthesis of the Starting Carbene Complexes. The starting aminocarbene complexes **8** were prepared, in high yield, from pentacarbonyl(1-ethoxyethylidene)chromium and pentacarbonyl(1-ethoxybenzylidene)chromium complexes by aminolysis, followed (for **8c–g**) by an alkylation at nitrogen (LDA, ICH_3).[8,21] In the case of the bulky piperidino group, the direct substitution at room temperature did not lead to the expected aminocarbene complex; instead, elimination of the carbene ligand with formation of the chromium pentacarbonyl complex of piperidine was observed. Access to complex **8b** was nevertheless achieved by carrying out the substitution reaction at dry ice/acetone temperature, which led first to a zwitterionic adduct, $(CO)_5Cr^-–C(OR)MeN^+H(CH_2)_5$, and upon elimination of ethanol under vacuum, led to the expected complex **8b** in about 50% yield.[23] A second more general method used the reaction of the amides $R_1CONR_2R_3$ with $Na_2Cr(CO)_5$, which led to complexes **8** in good to excellent yields.[13]

(b) Reactions with Diphenylacetylene. Complex **8a** reacted in boiling cyclohexane with a slight excess (1.2 equiv) of diphenylacetylene to give an insoluble, polar, moisture- and oxygen-sensitive orange precipitate (60% yield), which could be purified by recrystallization from anhydrous methylene chloride/hexane solutions. The elemental analysis as well as the spectroscopic data of this new complex were in agreement with a structure resulting from the insertion of both the alkyne and CO, suggesting the formation of a ketene complex such as **10**. Indeed,



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the ^1H NMR spectrum displayed signals for both a chromium tricarbonyl coordinated and a free phenyl group, confirming the loss of only one CO ligand. The $^{13}C(^1H)$ NMR spectrum was, however, very revealing: besides resonances for the coordinated and free phenyl groups, a signal for a carbonyl group was observed at δ 169.11 ppm, a value which is incompatible with the presence of a simple ketene function such as in **10**. This latter result was confirmed by the infrared spectrum with an absorption around 1700 cm^{-1}. The peculiar spatial arrangement of the different functional groups could be established by carrying out an X-ray analysis on the complex obtained from **8a** (Figure 1), which shows it to have the structure **11a** (important bond distances and bond angles are found in Tables I and II). **11a** is best described as an arene–tricarbonylchromium complex resulting from a through-space interaction of the tertiary amine with the carbonyl group of the ketene function.

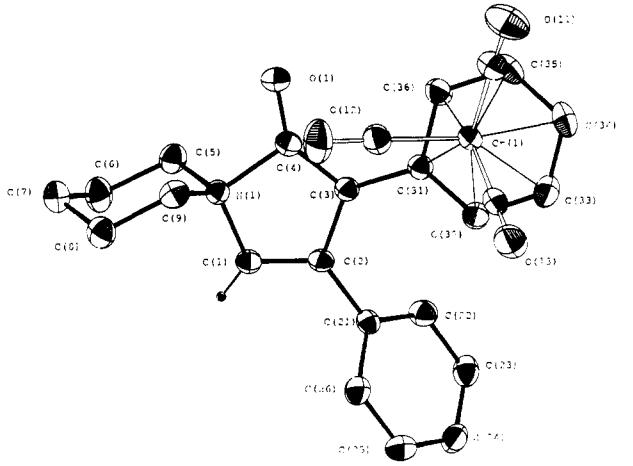

Figure 1. Perspective drawing of ylide chromium tricarbonyl complex **11a** with hydrogen atoms omitted for clarity.

Table I. Selected Bond Distances (Å) for Complexes **11a**, **18d**, **19**, **21b**, **23a**, and **25**

	$C_{24}H_{21}O_4NCr$ (**11a**)		
C(1)–C(2)	1.327 (5)	C(1)–N(1)	1.449 (5)
C(2)–C(3)	1.458 (5)	C(2)–C(21)	1.472 (5)
C(3)–C(4)	1.368 (5)	C(3)–C(31)	1.453 (5)
C(4)–O(1)	1.225 (5)	C(4)–N(1)	1.590 (5)
N(1)–C(5)	1.506 (5)	N(1)–C(9)	1.516 (5)
	$[C_{27}H_{22}O_4NCr]BF_4$ (**18d**)		
N(1)–C(1)	1.51 (2)	N(1)–C(4)	1.56 (2)
N(1)–C(5)	1.49 (2)	N(1)–C(6)	1.51 (2)
O(1)–C(4)	1.16 (2)	C(1)–C(2)	1.52 (2)
C(1)–C(11)	1.50 (2)	C(2)–C(3)	1.33 (2)
C(2)–C(21)	1.45 (2)	C(3)–C(4)	1.49 (2)
C(3)–C(31)	1.49 (2)		
	$C_{22}H_{19}O_5NCr$ (**19**)		
O(1)–C(1)	1.498 (6)	O(1)–C(4)	1.355 (5)
C(1)–C(2)	1.519 (6)	C(1)–N(1)	1.411 (6)
C(1)–C(5)	1.536 (8)	C(2)–C(3)	1.329 (5)
C(2)–C(21)	1.471 (6)	C(3)–C(4)	1.481 (6)
C(3)–C(31)	1.482 (5)	C(4)–O(2)	1.196 (5)
N(1)–C(6)	1.455 (9)	N(1)–C(7)	1.439 (8)
	$C_{21}H_{21}O_4NCr$ (**21b**)		
Cr(1)–N(1)	2.188 (4)	Cr(1)–C(1)	2.136 (4)
Cr(1)–C(5)	2.196 (4)	Cr(1)–C(6)	2.204 (4)
Cr(1)–C(7)	2.019 (5)	O(1)–C(7)	1.201 (5)
N(1)–C(1)	1.408 (5)	N(1)–C(8)	1.497 (6)
N(1)–C(12)	1.489 (6)	C(1)–C(5)	1.400 (6)
C(1)–C(2)	1.512 (6)	C(5)–C(6)	1.417 (6)
C(5)–C(4)	1.510 (6)	C(6)–C(7)	1.438 (6)
C(6)–C(13)	1.500 (6)	C(2)–C(3)	1.532 (8)
C(3)–C(4)	1.527 (7)	C(8)–C(9)	1.516 (7)
C(9)–C(10)	1.513 (8)	C(10)–C(11)	1.534 (9)
C(11)–C(12)	1.489 (8)		
	$C_{18}H_{17}O_4NCr$ (**23a**)		
O(1)–C(7)	1.21 (2)	N(1)–C(1)	1.38 (4)
N(1)–C(7)	1.62 (3)	N(1)–C(8)	1.40 (4)
N(1)–C(9)	1.45 (6)	C(1)–C(5)	1.50 (3)
C(1)–C(2)	1.45 (3)	C(5)–C(6)	1.40 (3)
C(5)–C(4)	1.35 (3)	C(6)–C(7)	1.43 (3)
C(6)–C(31)	1.46 (2)	C(2)–C(3)	1.54 (4)
C(3)–C(4)	1.51 (3)		
	$C_{24}H_{21}O_4NCr$ (**25**)		
O(1)–C(4)	1.223 (5)	N(1)–C(1)	1.398 (5)
N(1)–C(4)	1.354 (5)	N(1)–C(20)	1.441 (6)
C(1)–C(2)	1.318 (5)	C(1)–C(8)	1.497 (6)
C(2)–C(3)	1.510 (5)	C(2)–C(6)	1.477 (6)
C(3)–C(4)	1.562 (5)	C(3)–C(5)	1.548 (5)
C(3)–C(31)	1.528 (5)	C(5)–C(51)	1.503 (6)
C(6)–C(7)	1.558 (7)	C(7)–C(8)	1.527 (8)

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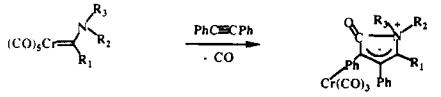


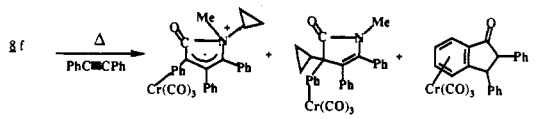
8 a	R_1=H R_2R_3=$(CH_2)_5$	11 60%
b	R_1=Me R_2R_3=$(CH_2)_5$	70%
c	R_1=Me R_2=R_3=Me	80%
d	R_1=Ph R_2=R_3=Me	55%
e	R_1=Me R_2=Me R_3=cyclopropyl	57%
f	R_1=Ph R_2=Me R_3=cyclopropyl	47%
g	R_1=Me R_2=Me R_3=cyclopropylcarbinyl	

The C(4)–N(1) bond (1.590 (5) Å) is rather long for a carbon–nitrogen σ bond. However, the fact that the nitrogen atom is in a tetrahedral environment clearly indicates the existence of this bond. Moreover, the bent geometry of the ketene function with a C(3)–C(4)–O(1) angle of 138.6° and the length of the C(4)–O(1) bond (1.225 as compared to 1.150 Å in ketenes) confirm this interaction. The result is the formation of a zwitterionic species with a delocalized negative charge on the five-membered-ring system. However, conversions to the amino acid **12a** and to the corresponding amino ester **13a** are observed during silica gel chromatography and treatment with methanol, respectively. Both results confirm that N(1)–C(4) is the weakest bond in the complex.

The behavior of carbene complexes **8b,c,e** paralleled that of **8a**; in all cases and under the same experimental conditions, fairly good yields of the different ylides were observed. The physical data as well as the chemical properties were in all respects similar to those of complex **11a**.

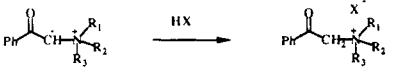
Preparation of Nitrogen Ylides from Phenyl-Substituted Aminocarbene Complexes. Phenyl-substituted alkoxycarbene complexes of chromium usually lead, upon alkyne insertions, to benzannulation products.[1] This type of reaction has also been observed in the case of phenyl-substituted aminocarbene complexes.[9] For example, as already indicated, morpholino– and alkene–aminocarbene complexes gave high yields of indanones.[9,11,24] However, in the case of complexes **8d** and **8f**, only minor amounts of benzannulation products were isolated; again, the nitrogen ylides were obtained in high yield.

Thus, complex **8f** (R_1 = Ph, R_2 = Me, R_3 = cyclopropyl) reacted with diphenylacetylene in boiling cyclohexane to give, after 12 h, the ylide **11f**, as an orange powder (47% yield), along with pyrrolinone **17** (14% yield) and diphenylindanone **16** (21% yield). The spectroscopic data of **11f** were also in agreement with those of the isolated ylides. Besides the IR (ν CO 1700 cm^{-1}) and the $^{13}C\{^1H\}$ NMR spectra (δCO 166.9 ppm), which confirm the presence of a ketene in interaction with the tertiary amine, the ^1H NMR spectrum displays signals for the NCH_3 group at δ 3.08 ppm, and for the NCH proton at δ 2.67 ppm, the signals of the protons associated with the cyclopropane appearing at δ 1.77 (m), 1.92 (m), and 0.66 (m) ppm, respectively.



Surprisingly, ylides derived from these phenyl-substituted carbene complexes were less moisture sensitive than those derived from alkyl-substituted complexes, a fact attributable both to steric hindrance for the protonation at carbon C(1) and to carbanion stabilization by the phenyl group.

Protonation of the Nitrogen Ylide Complexes 11 by Strong Acids: Formation and X-ray Structure of 18d, a Stable Ammonium Salt Complex. One of the characteristic reactions of isolated, chemically generated, carbonyl-stabilized nitrogen ylides such as those occurring in the Stevens rearrangement is their protonation to quaternary ammonium salts[27-30] (eq 5). Ylides **11** showed the



(5)

Table II. Selected Bond Angles (deg) for Complexes **11a**, **18d**, **19**, **21b**, **23a**, and **25**

	$C_{24}H_{21}O_4NCr$ (**11a**)		
N(1)–C(1)–C(2)	111.0 (3)		
C(3)–C(2)–C(1)	110.6 (3)	C(21)–C(2)–C(1)	123.3 (4)
C(21)–C(2)–C(3)	125.7 (3)	C(4)–C(3)–C(2)	109.4 (3)
C(31)–C(3)–C(2)	128.4 (3)	C(31)–C(3)–C(4)	121.9 (4)
O(1)–C(4)–C(3)	138.6 (4)	N(1)–C(4)–C(3)	105.7 (3)
N(1)–C(4)–O(1)	115.7 (3)	C(4)–N(1)–C(1)	103.0 (3)
C(5)–N(1)–C(1)	113.8 (3)	C(5)–N(1)–C(4)	109.1 (3)
C(9)–N(1)–C(1)	112.9 (3)	C(9)–N(1)–C(4)	106.9 (3)
C(9)–N(1)–C(5)	110.6 (3)	C(6)–C(5)–N(1)	112.3 (4)
	$[C_{27}H_{22}O_4NCr]BF_4$ (**18d**)		
C(4)–N(1)–C(1)	106.3 (13)	C(5)–N(1)–C(1)	119.2 (14)
C(5)–N(1)–C(4)	107.0 (14)	C(6)–N(1)–C(1)	111.8 (15)
C(6)–N(1)–C(4)	105.6 (14)	C(6)–N(1)–C(5)	106.1 (15)
C(2)–C(1)–N(1)	103.4 (13)	C(11)–C(1)–N(1)	114.
C(11)–C(1)–C(2)	115.	C(3)–C(2)–C(1)	112.9 (16)
C(21)–C(2)–C(1)	119.	C(21)–C(2)–C(3)	128.
C(4)–C(3)–C(2)	111.0 (16)	C(31)–C(3)–C(2)	131.
C(31)–C(3)–C(4)	118.	O(1)–C(4)–N(1)	121.2 (16)
C(3)–C(4)–N(1)	104.7 (14)	C(3)–C(4)–O(1)	134.1 (17)
	$C_{22}H_{19}O_5NCr$ (**19**)		
C(4)–O(1)–C(1)	110.3 (3)		
C(2)–C(1)–O(1)	101.8 (3)	N(1)–C(1)–O(1)	110.3 (4)
N(1)–C(1)–C(2)	112.7 (4)	C(5)–C(1)–O(1)	106.2 (4)
C(5)–C(1)–C(2)	111.3 (4)	C(5)–C(1)–N(1)	113.6 (5)
C(3)–C(2)–C(1)	110.5 (4)	C(21)–C(2)–C(1)	120.5 (4)
C(21)–C(2)–C(3)	128.7 (4)	C(4)–C(3)–C(2)	109.0 (4)
C(31)–C(3)–C(2)	129.0 (4)	C(31)–C(3)–C(4)	122.0 (4)
C(3)–C(4)–O(1)	108.4 (4)	O(2)–C(4)–O(1)	121.9 (4)
O(2)–C(4)–C(3)	129.7 (4)	C(6)–N(1)–C(1)	116.6 (6)
C(7)–N(1)–C(1)	114.0 (5)	C(7)–N(1)–C(6)	114.2 (7)
	$C_{21}H_{21}O_4NCr$ (**21b**)		
C(8)–N(1)–Cr(1)	125.1 (3)	C(8)–N(1)–C(1)	116.0 (4)
C(12)–N(1)–Cr(1)	118.9 (3)	C(12)–N(1)–C(1)	114.2 (4)
C(12)–N(1)–C(8)	108.2 (4)	C(5)–C(1)–N(1)	120.9 (4)
C(2)–C(1)–N(1)	126.7 (4)	C(2)–C(1)–C(5)	111.6 (4)
C(6)–C(5)–C(1)	126.2 (4)	C(4)–C(5)–C(1)	108.6 (4)
C(4)–C(5)–C(6)	124.7 (4)	C(7)–C(6)–C(5)	122.3 (4)
C(13)–C(6)–C(7)	115.8 (4)	C(6)–C(7)–O(1)	136.8 (4)
C(3)–C(2)–C(1)	101.3 (4)	C(4)–C(3)–C(2)	105.8 (4)
C(3)–C(4)–C(5)	104.0 (4)	C(9)–C(8)–N(1)	110.0 (4)
	$C_{18}H_{17}O_4NCr$ (**23a**)		
C(7)–N(1)–C(1)	103.8 (17)		
C(8)–N(1)–C(1)	108.6 (30)	C(8)–N(1)–C(7)	107.7 (21)
C(9)–N(1)–C(1)	114.8 (35)	C(9)–N(1)–C(7)	106.5 (27)
C(9)–N(1)–C(8)	114.7 (32)	C(5)–C(1)–N(1)	110.1 (20)
C(2)–C(1)–N(1)	134.6 (31)	C(2)–C(1)–C(5)	106.3 (26)
C(6)–C(5)–C(1)	106.4 (19)	C(4)–C(5)–C(1)	109.3 (20)
C(4)–C(5)–C(6)	143.4 (22)	C(7)–C(6)–C(5)	111.2 (17)
N(1)–C(7)–O(1)	114.8 (18)	C(6)–C(7)–O(1)	140.3 (19)
C(6)–C(7)–N(1)	104.8 (16)	C(3)–C(2)–C(1)	107.7 (23)
C(4)–C(3)–C(2)	103.0 (20)	C(3)–C(4)–C(5)	111.4 (22)
	$C_{24}H_{21}O_4NCr$ (**25**)		
C(4)–N(1)–C(1)	108.7 (3)	C(20)–N(1)–C(1)	127.9 (4)
C(20)–N(1)–C(4)	123.4 (4)	C(2)–C(1)–N(1)	113.8 (4)
C(8)–C(1)–N(1)	131.8 (4)	C(8)–C(1)–C(2)	114.4 (4)
C(3)–C(2)–C(1)	108.5 (3)	C(6)–C(2)–C(1)	112.8 (4)
C(6)–C(2)–C(3)	138.6 (4)	C(4)–C(3)–C(2)	100.7 (3)
C(5)–C(3)–C(2)	113.5 (3)	C(5)–C(3)–C(4)	107.4 (3)
C(31)–C(3)–C(2)	114.2 (3)	C(31)–C(3)–C(4)	106.7 (3)
C(31)–C(3)–C(5)	113.1 (3)	N(1)–C(4)–O(1)	125.7 (4)
C(3)–C(4)–O(1)	126.0 (4)	C(3)–C(4)–N(1)	108.3 (3)
C(51)–C(5)–C(3)	114.1 (3)	C(7)–C(6)–C(2)	101.6 (4)
C(8)–C(7)–C(6)	108.8 (4)	C(7)–C(8)–C(1)	100.9 (4)

(24) Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *Organometallics* **1989**, *8*, 2253.

(25) For other examples, see: Wulff, W. D.; Anderson, B. A.; Isaacs, L. D. *Tetrahedron Lett.* **1989**, *30*, 4061. Rudler, H.; Audouin, M.; Parlier, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1238.

(26) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615.

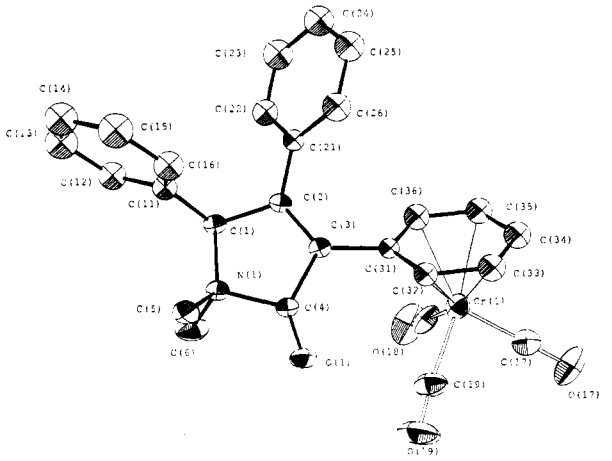


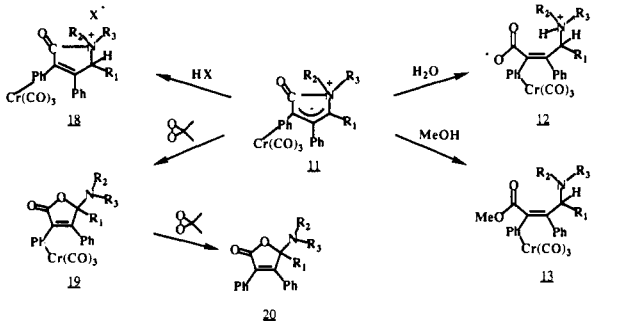
Figure 2. Perspective drawing of ammonium tetrafluoroborate tricarbonylchromium complex **18d** with hydrogen atoms omitted for clarity.

same behavior and gave, upon protonation by strong acids, ammonium salts **18**. Thus, a yellow solution of **11a** in dichloromethane instantaneously turned deep red upon addition of trifluoroacetic acid. The formation of a new complex could be monitored by ^1H NMR spectroscopy in CD_2Cl_2; the most important modifications were the disappearance of the signal due to the proton associated with the carbon–carbon double bond in **11a**, at δ 6.00 ppm, and the appearance of two broad signals at δ 3.9 (1 H) and 5.5 ppm (1 H).

The more stable complex **11d** showed the same behavior: when tetrafluoroboric acid was used, red crystals precipitated from the methylene chloride solution. Recrystallization from acetone/methylene chloride gave crystals suitable for an X-ray determination. An ORTEP view of this complex appears in Figure 2; it confirms that the site of protonation is the carbon γ with respect to the carbonyl group, a reaction leading to an *N*-acylium tetrafluoroborate. Of interest in this structure is the N(1)–C(4) bond distance (1.526 (2) Å), slightly shorter than in **11a** (1.590 (5) Å).

The ^1H NMR spectrum of this new complex displays signals for the NC(H) proton, at δ 6.91 ppm, and for the two methyl groups on nitrogen at δ 3.86 and 2.96 ppm, besides those for a free and a $Cr(CO)_3$-coordinated phenyl group.

Complex **18d** is air stable and does not react with water. However, deprotonation leading to the ylide **11d** then followed by hydrolysis to the amino acid **12d** is observed during silica gel chromatography. Attempts to alkylate **12d** at oxygen with trimethyloxonium tetrafluoroborate failed. Instead, high yields of **18d** were again obtained, a result which can only be explained by the presence of tetrafluoroboric acid in the alkylating agent.



Attempts to Generate the Metal-Free Ylides: Oxidation of the Ylide Complexes 11 to Lactone Complexes 19. Since carbonyl-stabilized nitrogen ylides such as those involved in the Stevens rearrangement could be isolated and fully characterized, we attempted to demetalate complexes **11** under anhydrous conditions both by ligand exchange and by oxidative means. However, treatment of **11c** with tributylphosphine[50] at room temperature did not lead to the metal-free ylide: no reaction could be observed.

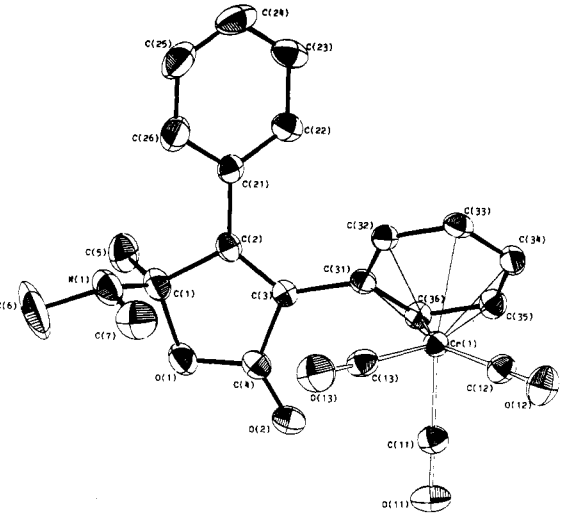


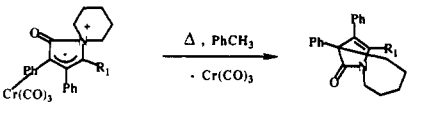
Figure 3. Perspective drawing of amino lactone complex **19c** with hydrogen atoms omitted for clarity.

The oxidative demetalations were no more decisive. They led nevertheless to an interesting observation. Whereas irradiation of **11c**, in diethyl ether, under oxygen[51] gave the metal-free lactone **20c**, the oxidation carried out in the presence of dimethyldioxirane led, when used in a *stoichiometric* amount, to complex **19c**. The structure of this complex could be definitively established by X-ray analysis, which appears in Figure 3 (important bond distances and bond angles are found in Tables I and II). It confirms that cleavage of the weak N(1)–C(4) bond again took place with insertion of an oxygen atom between the carbonyl carbon atom and C(3). When used in excess, this reagent again led to the metal-free lactone **20**. Similar results were observed with complexes **11e** and **11f**.

Although a recent publication[52] advocates the use of dimethyldioxirane as a mild demetalation reagent for chromium–tricarbonyl derivatives, in the case described herein the oxidation of the ligand precedes the oxidation of the metal, a result which precludes the observation and/or isolation of the metal-free ylide.

The transformations of **11** to **20** are reminiscent of those observed by Wulff and co-workers during cerium(IV)-induced oxidations of alkoxy vinyl ketene complexes into alkoxy lactones.[14,53]

Rearrangement of Nitrogen Ylides 11 to Lactams 14. Reflux of complex **11a** in anhydrous toluene for 12 h led to a mixture of lactam **14a** (70% yield) and toluene chromium tricarbonyl. The presence of a bridgehead lactam was confirmed both by the infrared (νCO 1710 cm^{-1}) and the ^{13}C NMR spectra (δCO 187.80 ppm). The ^1H NMR spectrum displayed signals for the olefinic proton, at δ 7.04 ppm as a singlet, and for the various methylene protons of the starting piperidine ring system [δ 4.20 (1 H, m), 3.38 (1 H, m), 2.68 (2 H, m), and 1.24–1.97 (6 H, m) ppm].

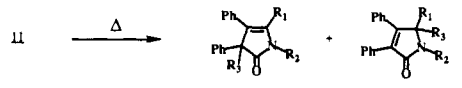


Ylides **11b,c,e** behaved similarly and gave, upon nitrogen-to-carbon migrations of various alkyl groups, either a bridgehead lactam (**11b** → **14b**) or pyrrolinones (**11c,e** → **14c,e**).

The assignment of isomers **14** was based on the following grounds: (1) on the one hand, the X-ray structures of both types of isomers had been established previously in the cases where R_3 = CH_2Ph and R_2R_3 = $CH_2CH{=}CHCH_2$.[22] (2) On the basis of

(27) Stevens, T. S.; Creighton, E. M.; Gordon, A. B.; MacNicol, M. *J. Chem. Soc.* **1928**, 3193.
(28) Jemison, W. R.; Mageswaran, S.; Ollis, W. D.; Sutherland, I. O.; Thebtaranonth, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1154.
(29) Kral, V.; Arnold, Z. *Collect. Czech. Chem. Commun.* **1977**, *42*, 3455.
(30) Newcomb, M.; Beata Manek, M. *J. Am. Chem. Soc.* **1990**, *112*, 9662 and references cited therein.

these X-ray structures, the ^{13}C NMR spectra of isomers **14** were found to display a signal around δ 180 ppm for the carbonyl group, whereas the isomers **15** showed a signal around 170 ppm. (3) On the other hand, in the cases where $R_1 = CH_3$, a signal for the methyl group associated with a double bond appears at $\delta \sim 2$ ppm, whereas for isomer **15** the signal of the methyl group is observed around δ 1 ppm.

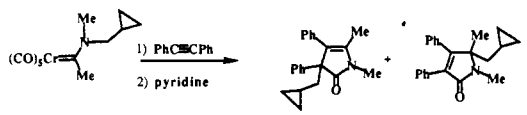


	14	15
a	70%	
b	81%	
c	50%	
d	52%	
e	79%	
f	66%	
g	29%	5%

Rearrangement of Nitrogen Ylides Derived from Phenyl-Substituted Aminocarbene Complexes. Considering the structure of the isolated ylides, R_1 is far away from the ketene function. It is thus obvious that, in the cases where R_1 = Ph, no benzannulation should be observed, provided that no rotation around the C(1)–C(2) single bond, after a C(4)–N(1) bond rupture, takes place. This hypothesis could be confirmed experimentally.

Thus, heating complex **11f** (R_1 = Ph, $R_2 = CH_3$, R_3 = cyclopropyl) in boiling toluene for 12 h gave a 66% yield of pyrrolinones **14f**; no product **16** resulting from a benzannulation reaction could be detected. The structure of the pyrrolinone **14f** could be ascertained by comparison of its spectroscopic data with those of compounds of similar structures.[19] Of interest in the case of **14f** is the ^1H NMR spectrum, where the signals for the five hydrogen atoms of the cyclopropane are cleanly separated.

Reaction of Complex 8g Derived from Cyclopropylmethylamine with Diphenylacetylene: Migration without Rearrangement of the Cyclopropylcarbinyl Group. The cyclopropylcarbinyl group is known as one of the best radical clocks and very readily rearranges to the homoallyl group.[30-32] Therefore, from a mechanistic point of view, we chose to synthesize the aminocarbene complex **8i** and submit it to the insertion of alkynes. Thus, upon reaction with diphenylacetylene in boiling benzene, complex **8g** gave, after 12 h, a mixture of organic products and a yellow precipitate. Attempts to purify the latter failed. Therefore, after evaporation of the benzene, both the residue and the precipitate were refluxed in toluene for 6 h to give, besides toluene chromium tricarbonyl, a mixture of pyrrolinones **14g** and **15g** (34%). No products arising from the rearrangement of the cyclopropylcarbinyl group during the migration could be detected.



Formation of Ketene and Nitrogen Ylide Complexes upon Intramolecular Alkyne Insertions. In order to provide evidence for the generality of the alkyne insertion into aminocarbene complexes with the involvement of nitrogen ylides, we synthesized complexes of the general structure **9**. Since in the previous examples the presence of an aromatic ring allowed the isolation of reaction intermediates, in the form of arene chromium tricarbonyl complexes, we chose to substitute the acetylenic function by a phenyl group. Complexes **9a–c** were prepared either by alkylating complexes **8** ($R_1 = CH_3$) at carbon by using the appropriate trifluoromethanesulfonate, in the presence of LDA,[25] or by using the appropriate ω-acetylenic amide in conjunction with $Na_2Cr(CO)_5$.

When complex **9b** was refluxed in benzene or cyclohexane for a few minutes, its solution turned deep red. After 1 h, red air-

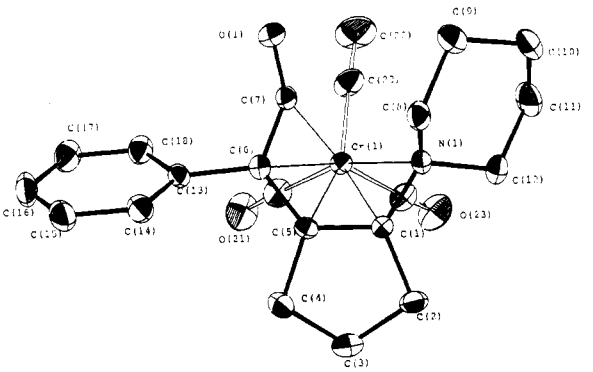
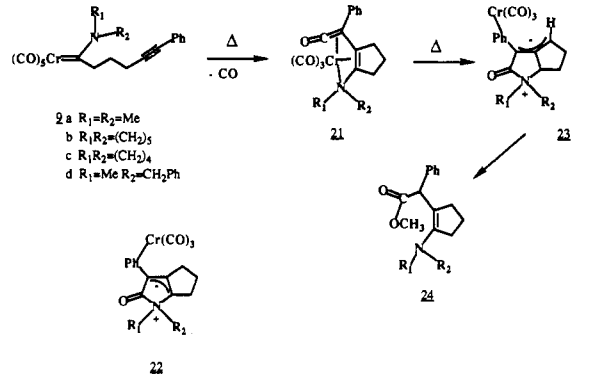


Figure 4. Perspective drawing of enamino ketene tricarbonylchromium complex **21b** with hydrogen atoms omitted for clarity.

stable crystals separated out upon cooling (81% yield). The infrared and NMR data for this new complex were in complete agreement with those already reported by Wulff and Anderson for an η^4-vinylketene complex obtained by a similar intramolecular reaction.[26] Confirmation of this structure was obtained by a single-crystal X-ray analysis, which revealed on the one hand that the intramolecular insertion took place with formation of a C(1)–C(5) double bond and, on the other hand, that CO insertion leading to a coordinated ketene occurred. An ORTEP projection of complex **21b** appears in Figure 4 (important bond distances and bond angles are given in Tables I and II).

However, heating complex **9b** for a longer period of time (4 h), in benzene, led to a new yellow, polar, moisture-sensitive complex. The infrared spectrum of this complex showed an absorption at 1710 cm^{-1} besides those for a $Cr(CO)_3$ group at 1875 and 1955 cm^{-1}. The ^{13}C NMR spectrum confirmed the presence of an arene chromium tricarbonyl group, but also displayed a signal at 168 ppm. All of these data were therefore again in agreement with those of a nitrogen ylide complex such as **22b**. However, confirmation for such a structure could not be obtained since crystals suitable for X-ray analysis could not be grown.



When the related complex **9a** ($R_2 = R_3 = CH_3$) was treated under identical conditions, the same type of behavior was observed; first, a deep red η^4-vinylketene complex **21a** formed, which upon further heating transformed into a yellow complex **22a**, the chemical properties and spectroscopic data of which were in all respects similar to those of complex **22b**. Fortunately, in spite of its hygroscopic character, complex **22a** could be recrystallized from solutions of anhydrous hexane/methylene chloride to give crystals suitable for X-ray analysis. An ORTEP projection of this complex is shown in Figure 5 and reveals, as for complex **11a**, that an intramolecular interaction between the nitrogen atom and the central carbon of the ketene function is taking place. A concomitant shift of the $Cr(CO)_3$ group from the enamino ketene function in **21a** to the phenyl group is also observed. However, as a result of the poor diffracting ability of the crystals of **22a**, the bond distances could not be established with precision (important bond distances and bond angles are given in Tables I and II). Nevertheless, within the limits of error for the bond distances,

(31) Bullock, R. M.; Rapoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261.

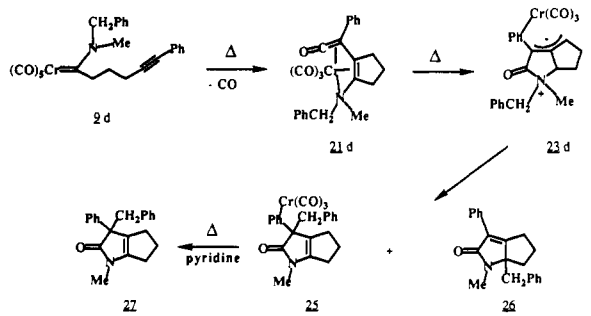
(32) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687.

several points are worth noting: (1) the N(1)–C(7) distance (1.62 (3) Å) is of the same order of magnitude as for complex **11a**. (2) In spite of the high esd's, it seems likely that in contrast to complexes of the type **11**, the negative charge is delocalized over carbons C(4), C(5), and C(6) (**23**) rather than over C(1), C(5), and C(6) (**22**), the shortest bonds in the molecule being C(4)–C(5), 1.35 (3) Å, and C(5)–C(6), 1.40 (3) Å. This finding could also be corroborated by the ^{1}H NMR spectra of the different ylides **23a–c**: in all cases a low-field doublet for one proton (δ 5.25 ppm), attributable to C(4)–H, and a multiplet, around δ 4.10 ppm, attributable to C(1)–H, are observed. Irradiation experiments confirmed that C(4)–H is indeed coupled with one of the protons C(3)–H_2.

Complex **9c**, bearing the pyrrolidino group, revealed exactly the same behavior: the insertion could again clearly be separated into two steps leading successively to the ketene and the ylide complexes **21c** and **23c**, which were characterized by spectroscopic data. The formation of this type of ylide might be the result of either a keto–enol prototropy or a chromium-mediated hydrogen shift during the transformation of complexes **21** into **23**.

As far as the hydrolysis and methanolysis reactions of these ylides are concerned, they appear to be more complicated than in the case of complex **11**, since in both the amino esters and the amino acids formed, intramolecular reactions between the two functions spontaneously take place. Another striking difference between the two types of ylides comes from their thermal transformation: no clean rearrangement of ylides **23** was observed upon heating.

As a last example, and in order to obtain more insight into the mechanism of the alkyl migration reaction, we synthesized complex **9d** bearing a benzyl group on nitrogen. In the case of intermolecular alkyne insertions with aminocarbene complexes bearing this substituent on nitrogen, no intermediate could be detected: direct transfer of the benzyl group was observed.[18] Complex **9d**, however, behaved differently. Upon heating in boiling hexane, complete transformation into a deep red transient complex, presumably the enamino ketene complex **21d**, easily detectable by TLC was observed. However, after 2 h this new complex reacted further to give finally a mixture of organic compounds **26** (9%) and **27** (45%) and small amounts of complex **25** (2%). Heating of **25** in pyridine gave, upon removal of $Cr(CO)_3$, compound **27**. The ^{1}H and ^{13}C NMR spectra of **27**, the main product of the reaction, compared to those of the starting carbene complex displayed the following features: (1) an important upfield shift of the signals associated with the methylene protons of the benzyl group, from δ 5.45 (s) to δ 3.27 (d, J = 12 Hz) and δ 3.19 ppm (d, J = 12 Hz), which means that migration of the benzyl group from nitrogen to carbon indeed occurred, the two hydrogens being now diastereotopic; (2) the presence of a signal at δ 182.2 (CO), which confirmed that CO insertion took place with formation of a lactam.



Crystals of **25** were obtained that allowed the determination of its structure confirming a clear-cut insertion of the alkyne with formation of a first five-membered ring and, then insertion of CO, leading to the second five-membered ring. Finally, transfer of the benzyl group from nitrogen to the carbon γ with respect to nitrogen gave **25**. A perspective view of this complex is given in Figure 6 (important bond distances and bond angles appear in Tables I and II).

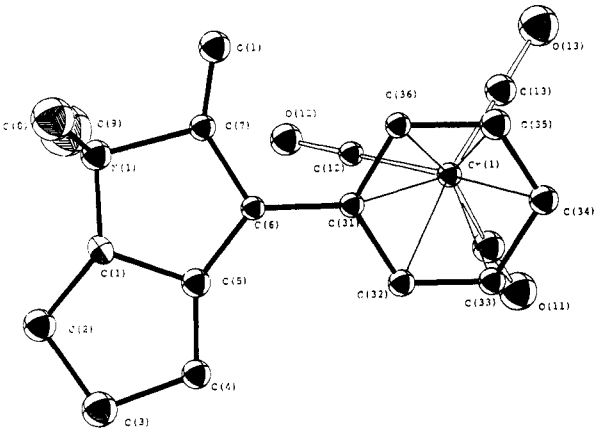


Figure 5. Perspective drawing of ylide tricarbonylchromium complex **23a** with hydrogen atoms omitted for clarity.

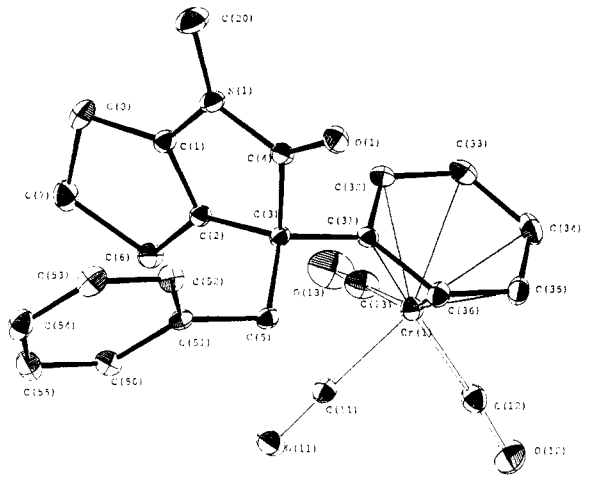


Figure 6. Perspective drawing of cyclopentanopyrrolinone tricarbonylchromium complex **25** with hydrogen atoms omitted for clarity.

Discussion

The mechanism which is generally accepted for the alkyne insertion into alkoxycarbene complexes has been thoroughly discussed.[1,2,14] An accepted common intermediate for all of these reactions is a substituted vinylketene complex, the result of both the alkyne and CO insertions. In a few instances, such intermediates could be isolated or detected indirectly by trapping experiments with alcohols, oxidants, alkynes, and alkenes.[14,33,36,53] However, to the best of our knowledge, no direct evidence has been offered for their transformation into rearranged reaction products in the absence of external reagents. The peculiar behavior observed for aminocarbene complexes in their reactions with alkynes comes from the close proximity of the nucleophilic nitrogen atom and the electrophilic central carbon atom of the ketene function; depending on whether the ketenyl group is *Z* or *E* with respect to the amino group, a through-space interaction of the two groups might occur (eq 6). It is obvious that, if R_2 = H in the *Z*

(6)

configuration, this interaction can lead to an amide by a classical 1,4 addition of the NH group to the vinylketene group. Such a reaction has indeed been observed in the reaction of molybdenum

(33) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449.
(34) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132.
(35) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.
(36) Hegedus, L. S.; Miller, D. B., Jr. *J. Org. Chem.* **1989**, *54*, 1241.

aminocarbene complexes derived from primary amines with alkynes (eq 7).[37] However, if R_2 and R_3 are different from H, it is clear that the ratios $10Z/10E$ will be highly dependent on the steric demand of R_2, R_3, and R_1. It is probable that such reasons govern the discrepancy observed for phenyl-substituted aminocarbene complexes between the results described herein and those reported by Yamashita.[9] Less crowded amines than morpholine probably allow the formation of isomers $10Z$ and, as a consequence, promote a nucleophile-assisted CO insertion followed by an interaction between nitrogen and the ketene function. Such a situation also precludes the benzannulation reaction resulting from the interaction of the phenyl group with the newly formed carbene (or ketene) complexes.

(7)

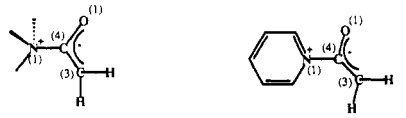
The key point in all of the reactions described herein is therefore the existence, as stable complexes, of intermediate nitrogen ylides. Whereas the interaction of a secondary amine with a ketene giving an amide is obvious (eq 7), the interaction of a tertiary amine with a ketene (**10** → **11**) is less obvious, although such elusive intermediates have been put forward in several instances. For example,[38-41] it is known that tertiary amines catalyze the addition of alcohols to ketene. Moreover, silylated tertiary amines have been found to add to ketenes to give products arising from the migration of a silyl group from nitrogen to the terminal carbon of the ketene function. In both cases, ylide intermediates have been suspected. Finally, γ-amino acid chlorides have been shown to react intramolecularly to give lactams presumably via *N*-acylammonium halides.[48,49]

The formation and isolation of complexes of the types **11** and **23** thus constitute the first direct evidence for the existence of adducts between tertiary amines and ketenes. Moreover, since the treatment of complexes **11** and **23** with methanol gives amino esters upon cleavage of the labile nitrogen–carbon bond, the chemistry described herein represents a good model for the tertiary amine catalyzed methanolysis of ketenes. It is clear however that in the cases described herein the intramolecular location of the two reactive centers γ from each other probably favors such an interaction. For that purpose and since the interaction of nucleophiles with ketenes has been the topic of many studies,[42,43] we have undertaken, in relation to our findings and in order to determine the general reasons for such interactions, theoretical calculations which are discussed in the subsequent section.

Table III. Calculated Optimized Geometries of the Most Stable Conformers for the Experimentally Observed Ylides and Those Derived from Ketene and Trimethylamine or Pyridine

	compound			
	11a	**11a** optimized	Me_3N → ketene	pyridine → ketene
	Bond Distances and Bond Orders[a] (Å)			
C(1)–C(2)	1.328	1.381		
	1.689	*1.629*		
C(2)–C(3)	1.457	1.439		
	1.119	*1.159*		
C(3)–C(4)	1.368	1.417	1.350	1.352
	1.304	*1.256*	*1.620*	*1.590*
C(4)–O(1)	1.225	1.231	1.247	1.253
	1.754	*1.770*	*1.640*	*1.607*
N(1)–C(4)	1.589	1.613	1.659	1.564
	0.645	*0.640*	*0.515*	*0.579*
	Bond Angle (deg)			
O(1)–C(4)–C(3)	138.90	139.20	136.55	133.47
	Net Charges[b]			
C(3)	−0.346	−0.334	−0.522	−0.505
C(4)	0.314	0.319	0.262	0.274
O(1)	−0.339	−0.336	−0.423	−0.442
N(1)	−0.035	0.001	−0.064	−0.046

[a] Bond orders are in italic type. [b] Fraction of an electron.



28 **29**

Figure 7. Drawings of the ketene–trimethylamine and ketene–pyridine adducts **28** and **29**.

Theoretical Calculations

Calculations for **11a**, the molecule for which we have carried out an X-ray determination, were performed with the semiempirical AM1 (Austin model 1) method.[44] In addition, for the sake of completion and comparison, the interactions of trimethylamine and pyridine with ketene were also studied. Calculations used standard molecular orbital theory, and they were carried out with the AMPAC program[45] using gradient optimization techniques for geometry optimizations.

In general, several conformations were considered for each ylide to ensure that the global minimum had been located. The optimized geometries of the most stable conformers for the nitrogen ylides derived from trimethylamine and pyridine are given in Table III, and the corresponding atom numberings are presented in Figure 7. There appears to be an overall agreement between the AM1 calculated structures and the X-ray experimental geometry. In particular, we note that the N(1)–C(4) bond length, which is calculated to be 1.613 Å (bond order 0.640), is in excellent agreement with the experimental bond length (1.589 Å) in **11a**. In the case of the hypothetical ylides **28** and **29**, these nitrogen-to-carbon bond lengths are also close to the experimental values (1.659 and 1.564 Å, respectively) with a slightly lower bond order, a result which can probably again be assigned to the intermolecular nature of the interaction.

As far as the bond angles are concerned, large deviations from linearity for the ketene function are observed in all cases, the C(3)–C(4)–O(5) angles being equal to 139.2° for the optimized geometry of **11a** (138.6° experimentally) and 136.5° and 133.4° for the ylides from trimethylamine and pyridine. Moreover, both in the experimental and in the theoretical structures, the lone pair of the amine is pointing toward the central carbon atom of the ketene, in the plane of the carbon–carbon double bond of the ketene function.

It appears therefore that the calculations not only reproduce the experimentally observed geometries and interactions but can

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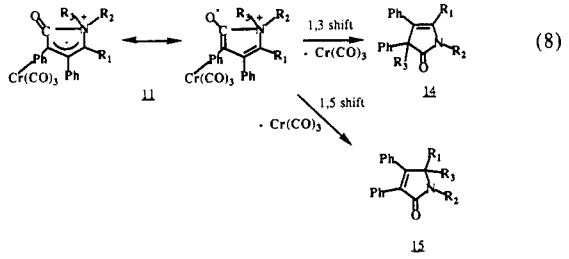
also explain the general enhanced reactivity of ketenes toward nucleophiles in the presence of tertiary amines.

Mechanism of the Nitrogen Ylide Rearrangement Reactions. Stable, chemically generated nitrogen ylides, the X-ray structure of which has been determined,[46] have been shown to undergo, upon heating, the Stevens rearrangement.[28] Elegant mechanistic studies on this reaction resulted in the conclusion that the (1,2) rearrangements of acyl-stabilized ammonium ylides normally involve a radical pair mechanism.[47] The fact that for the migration of a chiral group little or no racemization could be observed has been attributed to the presence of a tight radical pair, the second step of the reaction being too fast to permit stereorandomization. The rearrangement of ylides of the type **11** described herein parallels that of the Stevens-type ylides: carbene complexes bearing allyl groups on nitrogen react with alkynes to give products directly, the formation of which could be explained by means of both sigmatropic and (1,2) anionic rearrangements.[19] However, apart from the observation of trace amounts of 1,2-diphenylethane when benzyl-substituted aminocarbene complexes were used,[20] no direct evidence for the formation of radicals during these migrations could be provided. The case of complex **8g** is remarkable in this connection: no rearrangement of the cyclopropylcarbinyl to the homoallyl group was observed during the migration, although such a rearrangement is fast and typical for radical rearrangement reactions. Thus, to avoid the hypothesis of intermediate radical pairs, thermally allowed $\sigma_2 s + \pi_4 s$ and $\sigma_2 a + \pi_6 s$ 1,3 and 1,5 alkyl shifts would constitute a sound mechanism to explain the formation of both **14** and **15** from ylides **11** (eq 8). A point which has also



(8)

to be mentioned is the role of the aryl groups; in all of the examples described herein, a phenyl group is present either in the carbene complex or in the acetylenic derivatives or in both. However, their presence is not crucial: examples which will be described in a forthcoming paper demonstrate that such insertion/rearrangement reactions can take place in the absence of these groups. Finally, participation of the metal during the rearrangement step must also be considered since, in most cases, chromium tricarbonyl stays in close proximity to the reactive centers until the last step of the reaction. Thus, pending further studies, the role of the metal may for the moment be to bring all of the ligands involved in these cycloaddition reactions in close proximity, whereas the presence of the phenyl groups allowed us to follow with precision the different steps of these new organometallic reactions involving aminocarbene complexes of chromium.

Conclusion

Aminocarbene complexes of chromium react with alkynes inter- and intramolecularly to give enamino ketene complexes. An intramolecular reaction between the nucleophilic nitrogen atom and the ketene function leads to isolable, stable, yet moisture-sensitive nitrogen ylide complexes which have been fully characterized. The general behavior of these new ylides parallels that of classical nitrogen ylides: they can be protonated to stable ammonium salts and more interestingly, on a synthetic point of view, they rearrange thermally according to the rules of the Stevens rearrangement to a large variety of heterocyclic compounds.

Experimental Section

General. Tetrahydrofuran (THF), diethyl ether, and benzene were distilled from blue solutions of sodium benzophenone ketyl under argon prior to use. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride. NMR spectra were obtained on a Bruker WM 200, a Bruker AM 500, or a JEOL GX400Q NMR spectrometer; chemical shifts are reported in δ units (ppm) relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Beckman 4240 spectrophotometer, and mass spectra were recorded with a Kratos MS 3P. Melting points were determined on a Reichert Köfler block and are uncorrected.

Preparation of Aminocarbene Complexes. Two general methods were used: either aminolysis of an alkoxycarbene complex.[19,21,22,24] or reaction of $Na_2Cr(CO)_5$ with an amide followed by dehydration with Me_3SiCl/Al_2O_3.[13]

$(CO)_5Cr{=}C(H)NC_5H_{10}$ (8a). This complex was obtained from 1-formylpiperidine: yield, 93%, yellow crystals; mp 43 °C; IR ($CHCl_3$) 2025, 1970, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 10.65 (s, Cr=C(H)), 4.11 (m, 2 H, NCH_2), 3.72 (m, 2 H, NCH_2), 1.86 (m, 6 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 257.76 (Cr=C), 225.0, 217.7 (CO), 67.3 (NC), 57.3 (NC), 27.8, 27.12, 23.6 (CH_2); MS $C_{11}H_{11}NO_5Cr^+$ 289, found 289. Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.67; H, 3.80; N, 4.84. Found: C, 45.52; H, 3.80; N, 4.58.

$(CO)_5Cr{=}C(CH_3)NC_5H_{10}$ (8b) was obtained from 1-acetylpiperidine: yield, 50%; mp 57–58 °C; IR 2040, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.31 (t, J = 4 Hz, NCH_2), 3.78 (t, J = 5 Hz, NCH_2), 2.69 (s, Me), 1.76 (m, 3 CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 267.84 (Cr=C), 223.8, 217.9 (CO), 63.07 and 51.67 (NC), 39.04 (Me), 27.9, 27.24, 24.21 ($3CH_2$). Anal. Calcd for $C_{12}H_{13}NO_5Cr$: C, 47.52; H, 4.29; N, 4.62. Found: C, 47.63; H, 4.21; N, 4.48.

$(CO)_5Cr{=}C(CH_3)N(CH_3)_2$ (8c). A solution of $(CO)_5Cr{=}C(Me)NHMe$ (4 g, 0.016 mol) in THF (100 mL) at −60 °C was treated with a solution of LDA (0.02 mol) in THF (50 mL) at −60 °C. Then methyl iodide (1.4 mL, 0.021 mol) was added. After the mixture was heated to room temperature and stirred for 2 h, water was added and the solvent evaporated. Extraction with diethyl ether followed by evaporation under vacuum gave an oil, which was chromatographed over a short column of silica gel. Elution with CH_2Cl_2/petroleum ether gave a yellow solid (3.7 g, 88%): mp 47 °C; IR ($CHCl_3$) 2020, 1970, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.87 (s, 3 H, NMe), 3.30 (s, 3 H, NMe), 2.68 (s, 3 H, Cr=C(Me)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 273.5 (Cr=C), 223.45, 217.8 (CO), 53.1, 42.45 (NC), 40.27 (=CMe). Anal. Calcd for $C_9H_9NO_5Cr$: C, 41.06; H, 3.42; N, 5.32. Found: C, 41.15; H, 3.45; N, 5.18.

$(CO)_5Cr{=}C(Ph)N(CH_3)_2$ (8d) was prepared from $(CO)_5Cr{=}C(Ph)OEt$ in 95% yield: mp 87–88 °C, lit. mp 88 °C; ^{13}C NMR (50 MHz, $CDCl_3$) δ 275.20 (Cr=C), 223.8, 217.2 (CO), 152.82, 128.59, 125.85, 118.87 (Ar), 51.33, 45.91 (NMe_2).

$(CO)_5Cr{=}C(CH_3)NHC_3H_5$ was obtained by aminolysis of $(CO)_5Cr{=}C(OEt)Me$: yield, 94%, yellow crystals; mp 35 °C (4/1 E/Z mixture); ^1H NMR (200 MHz, $CDCl_3$) δ 8.81 (major) and 8.50 (minor) (s, 1 H, NH), 3.55 (m, 1 H, NCH), 2.83 (major) and 2.72 (minor) (s, 3 H, Me), 1.16, 0.99, 0.86, 0.83 (cyclopropane); ^{13}C NMR (50 MHz, $CDCl_3$) δ 285.81 and 278.71 (Cr=C), 223.86 and 217.78 (CO). Anal. Calcd for $C_{10}H_9NO_5Cr$: C, 43.64; H, 3.27; N, 5.09. Found: C, 43.83; H, 3.24; N, 5.10.

$(CO)_5Cr{=}C(CH_3)N(CH_3)C_3H_5$ (8e) was obtained by alkylation of $(CO)_5Cr{=}C(Me)NHC_3H_5$ (LDA, ICH_3): yield, 76%, yellow solid; mp 45 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.82 (s, 3 H, NMe), 2.93 (s, 3 H, Me), 0.98 (m, 5 H, cyclopropane); ^{13}C NMR (50 MHz, $CDCl_3$) δ 281.51 (Cr=C), 223.7, 217.9 (CO), 50.8, 40.96, 37.93 (2 Me, NC), 9.24, 8.12 (cyclopropane). Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.67; H, 3.80; N, 4.84. Found: C, 45.28; H, 3.94; N, 4.58.

$(CO)_5Cr{=}C(Ph)NHC_3H_5$ was prepared from $(CO)_5Cr{=}C(Ph)OEt$ and cyclopropylamine: yield, 79%, yellow crystals; mp 57 °C; IR ($CDCl_3$) 2025, 1975, 1940 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ (1/1 E/Z mixture) 8.77 and 8.47 (s, 1 H, NH), 7.28 (m, 5 H, Ar), 3.66 (s, 1 H, C(H)N), 2.77 (s, 1 H, C(H)N), 1.27, 1.00, 0.85, 0.75 (m, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 284.19 and 282.87 (Cr=C), 224.16, 223.35, 217.35, 217.18 (CO), 155.10, 150.47, 128.51, 127.9, 126.8, 121.0, 119.5 (Ar), 35.35, 35.61 (CH), 9.52 2.19 (CH_2). Anal. Calcd for $C_{15}H_{11}NO_5Cr$: C, 53.41; H, 3.26; N, 4.15. Found: C, 53.35; H, 3.23; N, 4.11.

$(CO)_5Cr{=}C(Ph)N(CH_3)C_3H_5$ (8f) was prepared from $(CO)_5Cr{=}C(Ph)NHC_3H_5$ by alkylation (LDA, ICH_3): yield, 96.6%, yellow crystals; mp 78 °C; IR ($CHCl_3$) 2025, 1970, 1940 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ (1/1 E/Z mixture) 7.25 (m, 5 H, Ar), 4.06 and 2.94 (m, 1 H, NCH), 3.89 and 2.84 (s, 3 H, NMe), 1.25, 0.83, 0.56 (m, 4 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 281.34 (Cr=C), 224.54, 224.13, 217.51, 217.34 (CO), 154.18, 153.28, 128.83–118.56 (Ar), 48.51, 45.14 (CH), 42.46, 41.39 (NMe), 19.68, 9.04, 8.26 (CH_2). Anal. Calcd for $C_{16}H_{13}NO_5Cr$: C, 54.70; H, 3.70; N, 3.98. Found: C, 54.59; H, 3.72; N, 3.85.

$(CO)_5Cr{=}C(CH_3)NHCH_2C_3H_5$ was prepared from $(CO)_5Cr{=}C(OEt)Me$ and cyclopropylcarbinylamine: yield, 75% (10/1, E/Z mixture), yellow crystals; mp 45 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.75

(s, 1 H, NH), 3.75 (m, 2 H, NCH_2, minor), 3.25 (m, 2 H, NCH_2, major), 2.74 (s, 3 H, Me, minor), 2.61 (s, 3 H, Me, major), 1.15 (m, 1 H), 0.74 (m, 2 H), 0.39 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 274.9 (Cr=C), 223.10, 218.0 (CO), 58.3, 52.9, 45.3, 35.7, 10.1, 9.8. Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.67; H, 3.80; N, 4.84. Found: C, 45.60; H, 3.94; N, 4.94.

$(CO)_5Cr=C(CH_3)N(CH_3)CH_2(C_3H_5)$ (8g) was prepared from the previous complex by alkylation (LDA, ICH_3): yield, 98%, yellow crystals; mp 51 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 4.09 (s, 1 H, NCH), 4.06 (s, 1 H, NCH), 3.32 (s, 3 H, NCH_3), 2.69 (s, 3 H, CH_3), 1.10 (m, 1 H), 0.72 (m, 2 H), 0.41 (m, 2 H), cyclopropane; ^{13}C NMR (50 MHz, $CDCl_3$) δ 271.7 (Cr=C), 223.5, 212.9 (CO), 69.5, 40.4, 39.7, 10.3, 4.2. Anal. Calcd for $C_{12}H_{13}NO_5Cr$: C, 47.52; H, 4.29; N, 4.62. Found: C, 47.56; H, 4.29; N, 4.61.

Complex 11a ($C_{24}H_{21}NO_4Cr$). A solution of complex **8a** (3 g, 0.010 mol) in benzene (200 mL) was refluxed in the presence of diphenylacetylene (2.2 g, 0.012 mol) for 12 h. Upon cooling to room temperature, a yellow solid (2.6 g, 60%) separated and was isolated by filtration: mp 195 °C dec; IR (KBr) 1975, 1940, 1920, 1700 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 7.2 (m, 5 H, Ar), 5.76, 4.74, 4.12 (m, 5 H, ArCr), 5.25 (s, 1 H), 3.05 (m, 2 H), 2.30 (m, 2 H), 0.91 (m, 6 H); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 235.57 (CO), 169.86 (CO), 147.68, 134.32, 129.0, 128.81, 128.32 (Ar, C=C), 111.66 (C=CH), 96.44, 89.10, 87.47 (ArCr) 54.46 (NC), 22.16, 21.70 (CH_2); MS (CI) $C_{24}H_{21}NO_4Cr^+$ 439, found 439. Anal. Calcd for $C_{24}H_{21}NO_4Cr$: C, 65.60; H, 4.78; N, 3.18. Found: C, 65.53; H, 4.72; N, 3.08.

Complex 11b ($C_{25}H_{23}NO_4Cr$). The same procedure as for **11a** was used: yield 70%, yellow solid; mp 150 °C dec; IR (KBr) 1950, 1840, 1870, 1710 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 7.54 (m, 5 H), 5.68, 4.75, 4.09 (m, 5 H, ArCr), 3.07 (m, 2 H, NCH_2), 2.29 (m, 2 H, NCH_2), 1.69 (m, 2 H, CH_2), 1.29 (s, 3 H, Me), 1.0 (m, 4 H, $2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 235.32 (CO), 170.6 (CO), 140–114 (Ph, C=C), 95.81, 88.16, 86.82 (ArCr), 55.21 (NC), 21.15, 20.75 (CH_2), 12.08 (Me); MS $C_{25}H_{23}NO_4Cr^+$ 453, found 453. Anal. Calcd for $C_{25}H_{23}NO_4Cr$: C, 66.22; H, 5.07; N, 3.09. Found: C, 65.30; H, 5.02; N, 2.83.

Complex 11c ($C_{19}H_{19}NO_4Cr$). The same procedure as for **11a** was used: yield, 80%, yellow solid; mp 159 °C dec; IR (KBr) 1920, 1825, 1695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.4–7.2 (m, 5 H, Ar), 5.34, 4.81 (m, 5 H, ArCr), 2.93 (s, 6 H, NMe_2), 1.89 (s, 3 H, NC(Me)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 237.17 (CO), 168.66 (CO), 139.7–113.6 (Ar, C=C), 95.72–79.03 (ArCr), 45.50 (NMe_2), 8.42 (NCMe); MS $C_{19}H_{19}NO_4Cr^+$ 413, found 413. Anal. Calcd for $C_{19}H_{19}NO_4Cr$: C, 63.92; H, 4.60; N, 3.39. Found: C, 63.43; H, 5.21; N, 3.19.

Complex 11d ($C_{27}H_{21}NO_4Cr$). The same procedure as for **11a** was used: yield, 55%, yellow solid; mp 176–177 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 7.23 (m, 10 H, Ar), 5.37, 4.87 (m, 5 H, ArCr), 2.96 (s, 6 H, NMe_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 235.04 (CO), 168.09 (CO), 163.0–113.2 (Ar, C=C), 95.47, 88.75, 87.11 (ArCr), 46.47 (NMe_2). Anal. Calcd for $C_{27}H_{21}NO_4Cr$: C, 68.21; H, 4.42; N, 2.94. Found: C, 68.05; H, 4.48; N, 2.77.

Complex 11e ($C_{24}H_{21}NO_4Cr$) was obtained from **8e** in cyclohexane as solvent: yield, 57%, yellow solid; mp 177 °C; IR (KBr) 1950, 1860, 1840, 1700 cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2) δ 7.45, 7.27 (m, 5 H, Ar), 5.49–5.21 (m, 5 H, ArCr), 2.84 (s, 3 H, NMe), 2.80 (m, 1 H, NCH), 1.85 (s, 3 H, NCMe), 1.53 (m, 1 H), 1.15 (m, 1 H), 0.76 (m, 2 H); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 235.86 (CO), 168.92 (CO), 142.0, 129.10, 123.0, 116.0 (C=C, Ar), 96.29, 88.68, 87.54 (ArCr), 42.73 (NCH), 41.0 (NMe), 10.0 (Me), 1.98 (CH_2); MS $C_{24}H_{21}NO_4Cr^+$ 439, found 439. Anal. Calcd for $C_{24}H_{21}NO_4Cr$: C, 65.60; H, 4.78; N, 3.19. Found: C, 65.42; H, 4.81; N, 2.99.

Complex 11f ($C_{29}H_{23}NO_4Cr$). The same procedure as for **8a** was used: yield, 47.6%, yellow solid; mp 172 °C; IR (KBr) 1950, 1870, 1850 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.22 (m, 10 H, Ar), 5.51, 5.29, 4.86 (m, 5 H, ArCr), 3.08 (s, 3 H, NMe), 2.67 (m, 1 H, NCH), 1.78 (m, 1 H, CH), 1.22 (m, 1 H, CH), 0.68 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.90 (CO), 143.07 (C=C), 133.18–126.78 (Ar), 113.41 (C=C), 95.36, 95.27, 88.96, 87.22 (ArCr), 44.13 (NCH), 42.65 (NMe), 2.25, 1.90 (CH_2). Anal. Calcd for $C_{29}H_{23}NO_4Cr$: C, 69.46; H, 4.59; N, 2.79. Found: C, 68.85; H, 4.49; N, 2.89.

Amino Acid Complex 12a ($C_{24}H_{23}NO_5Cr$). Recrystallization of complex **11a** in moist mixtures of hexane/CH_2Cl_2 gave complex **12a** as yellow crystals: mp 180 °C; IR ($CHCl_3$) 1990, 1910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.27 (m, 5 H, Ar), 5.83, 5.27, 4.95 (m, 5 H, ArCr), 3.77 (m, 2 H, NCH_2), 3.5, 3.0 (broad m, 4 H, NCH_2), 1.93 (m, 6 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 232.60 (CO), 169.83 (CO), 140.15–127.70 (Ar), 103.37, 97.56, 93.65, 89.24 (ArCr), 61.0, 59.1, 52.77 (NCH_2), 24.24, 21.76 (CH_2); MS $C_{24}H_{23}NO_5Cr^+$ 355, found 355. Anal. Calcd for $C_{24}H_{23}NO_5Cr$: C, 63.02; H, 5.03; N, 3.06. Found: C, 62.74; H, 5.05; N, 2.97.

Amino Ester Complex 13a ($C_{25}H_{25}NO_5Cr$). A solution of complex **11a** in CH_2Cl_2 was treated with MeOH. A reaction took place immediately, giving ester **13a** as a yellow complex: mp 153 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2 (m, 5 H, Ar), 5.39, 5.29, 4.91 (m, 5 H, ArCr), 3.88 (s, 1 H, OMe), 3.29 (s, 2 H, NCH_2), 2.35 (m, 4 H, NCH_2), 1.45 (m, 6 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 237.39 (CO), 168.42 (CO), 144.15, 139.56 (C=C), 129.6–127.8 (Ar), 101.9–88.53 (ArCr), 63.6 (OMe), 54.30 (NC), 52.0 (NC), 25.81, 24.25 (CH_2). Anal. Calcd for $C_{25}H_{25}NO_5Cr$: C, 63.69; H, 5.30; N, 2.97. Found: C, 63.22; H, 5.67; N, 2.83.

Amino Acid Complex 12b ($C_{25}H_{25}NO_5Cr$). A solution of complex **8b** (3 g, 0.01 mol) in benzene (100 mL) was refluxed for 12 h in the presence of diphenylacetylene (2 g, 0.011 mol). After evaporation of the solvent, the residue was chromatographed on silica gel with CH_2Cl_2/petroleum ether and finally acetone as eluents. The appropriate fractions were collected and evaporated to give complex **12b** (1 g, 21%) as yellow crystals: mp 170 °C dec; IR ($CHCl_3$) 1890, 1970 cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2) δ 7.25 (m, 5 H, Ar), 6.59, 5.31, 5.15, 4.72 (m, 5 H, ArCr), 3.62 (q, 1 H, CHMe), 3.90, 3.62, 2.8, 2.4 (m, 4 H, NCH_2), 1.95 (m, 6 H, CH_2), 1.44 (d, 3 H, CHMe); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 232.6 (CO), 169.7 (CO), 139.2–104.4 (Ar, C=C), 99.1–88.6 (ArCr), 66.48 (CHMe), 24.08, 21.69, 14.41 (CH_2, CH_3). Anal. Calcd for $C_{25}H_{25}NO_5Cr$: C, 63.69; H, 5.30; N, 2.97. Found: C, 63.20; H, 5.27; N, 2.77. The same complex was obtained in 42% yield when moist benzene was used for the insertion.

Metal-Free Amino Ester from Complex 13e. Complex **11e** reacts with ethanol in the presence of air to give the amino ester: IR (CH_2Cl_2) 1970 cm^{-1}; ^1H NMR (200 MHz, $CHCl_3$) δ 7.05 (m, 10 H, Ar), 4.13 (m, 2 H, OCH_2), 3.53 (q, 1 H, CHMe), 2.49 (s, 3 H, NMe), 1.67 (m, 1 H, NCH), 1.33 (d, 3 H, CH(Me)), 1.28 (t, 3 H, CH_2CH_3), 0.51 (m, 4 H, cyclopropane); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.80 (CO), 146.24, 139.24, 137.31, 130.23–126.73 (C=C, Ar), 66.72, 60.37, 42.35, 36.74; 17.70, 14.11, 9.20, 5.50; MS $C_{23}H_{27}O_2N^+$ 349, found 349.

Ammonium Tetrafluoroborate Complex 18d. To a solution of **11d** (0.56 g, 0.0011 mol), in methylene chloride (100 mL) at 0 °C, was added trimethyloxonium tetrafluoroborate (0.18 g, 0.0012 mol). The solution rapidly turned deep red. Upon cooling at −20 °C, red crystals deposited (0.47 g, 70%): mp 204.5 °C dec; IR (KBr) 1930, 1880, 1800, 1620 cm^{-1}; ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 7.69 (m, 10 H, Ar), 6.91 (s, 1 H, PhCH), 6.21, 5.84, 5.52 (m, 5 H, ArCr), 3.86 (s, 3 H, NMe), 2.97 (s, 3 H, NMe); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 235.5 (CO), 173.61 (CO), 169.77, 133.55, 129.4 (7 peaks, Ar, C=C), 97.74, 96.44, 95.95, 95.74, 92.76, 92.36 (ArCr), 78.75 (NC(Ph)H), 54.03, 46.53 (NMe). Anal. Calcd for $(C_{27}H_{22}NO_4Cr)^+BF_4^-$: C, 57.54; H, 3.90; N, 2.48. Found: C, 57.33; H, 4.11; N, 2.58.

Lactone Complex 19c. Ylide complex **11c** (0.295 g, 0.7 mmol) was dissolved in acetone (20 mL) at room temperature. A 0.1 M solution of dioxirane (20 mL) was then added. An immediate change in color and the formation of a precipitate were observed. After filtration through Celite and evaporation of the solvent, the residue was chromatographed on silica gel with 10–25% ethyl acetate/petroleum ether. Appropriate fractions were collected and evaporated in vacuo to give lactone **20c** (0.150 g, 75%) as white crystals: mp 129 °C; IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.31 (m, 5 H, Ar), 2.55 (s, 6 H, NMe_2), 1.66 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$, 80 MHz) δ 171.27 (CO), 159.40 (C=C), 132.68–128.04 (11 peaks, C=C, Ar), 102.84 (OCN), 38.48 (NMe_2), 23.91 (Me). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.71; H, 6.48; N, 4.77. Found: C, 77.66; H, 6.48; N, 4.73.

Lactone **19c** (0.060 g, 20%): orange crystals, mp 152 °C; IR ($CHCl_3$) 1975, 1910, 1900, 1740 cm^{-1}; ^1H NMR (CD_2Cl_2, 200 MHz) δ 7.60–7.26 (m, 5 H, Ar), 6.09, 5.40, 5.18, 5.06 (m, 5 H, ArCr), 2.50 (s, 6 H, NMe_2), 1.55 (s, 3 H, Me); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 232.0 (CO), 168.67, 161.43 (C=C), 130.54–123.45 (9 peaks, Ar), 102.31 (OCN), 95.06, 93.35, 92.84, 90.42, 89.73 (ArCr), 38.30 (NMe_2), 23.51 (Me). Anal. Calcd for $C_{22}H_{19}NO_5Cr$: C, 61.54; H, 4.43; N, 3.26. Found: C, 61.19; H, 4.50; N, 3.20.

Lactone Complex 19e was obtained according to the same procedure as above: orange crystals (47% yield); mp 164 °C; IR ($CHCl_3$) 1975, 1905, 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.51–7.25 (m, 5 H, Ar), 6.17, 5.35, 5.16, 5.01 (m, 5 H, ArCr), 2.53 (s, 3 H, NMe), 2.31 (m, 1 H, NCH), 1.60 (s, 3 H, Me), 0.58 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 231.97 (CO), 168.64, 161.39 (C=C), 130.69, 130.47, 128.99, 128.88, 128.71, 123.28 (Ar), 102.73 (OCN), 95.65, 93.14, 92.70, 90.35, 89.61 (ArCr), 36.42 (NMe), 32.52 (NCH), 23.70 (Me), 10.68 (CH_2), 8.97 (CH_2). Anal. Calcd for $C_{24}H_{21}NO_5Cr$: C, 63.30; H, 4.61; N, 3.08. Found: C, 63.45; H, 4.70; N, 2.97.

Reaction of Ylide Complex 11c with Oxygen: Obtention of Lactone 20c. Complex **11c** (0.5 g, 1.2 mmol) in methylene chloride (50 mL) was irradiated under a flow of oxygen with a Philipps 400-W lamp for 3 h at room temperature. The solution turned green-brown with formation

of a precipitate. After filtration through Celite and evaporation of the solvent in vacuo, the residue was purified by flash chromatography through silica gel with 20% ethyl acetate/petroleum ether. The lactone **20c** was obtained as white crystals (0.2 g, 56%), mp 129 °C, and was characterized by its spectroscopic data (vide supra).

Lactone 20d from Ylide Complex 11d. Lactone **20d** was obtained as above from ylide complex **11d** (0.35 g, 0.74 mmol) as white crystals (0.180 g, 72%): mp 145 °C; IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.27 (m, 15 H, Ar), 2.57 (s, 6 H, NMe_2); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.69 (CO), 160.52, 137.15, 130.98–125.22 (8 peaks, C=C, Ar), 105.63 (OCN), 40.57 (NMe), 37.88 (NMe). Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.12; H, 5.91; N, 3.58. Found: C, 80.58; H, 6.01; N, 3.94.

Lactam 14a. A solution of complex **11a** (0.32 g) in dry toluene (30 mL) was refluxed for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel with petroleum ether/ethyl acetate as eluent. Appropriate fractions were collected to give **14a** as white crystals (0.15 g, 70%): mp 160 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.26–7.07 (m, 10 H, Ar), 7.04 (s, 1 H, C=C(H)), 4.20 (m, 1 H, NCH), 3.38 (m, 1 H, NCH), 2.68 (m, 2 H, CH_2), 1.97 (m, 6 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 187.8 (CO), 138.5–124.9 (Ar, C=C), 60.88 (PhCC(O)), 46.6 (NC), 41.75, 36.36, 25.61, 24.05 (CH_2); HRMS calcd for $C_{21}H_{21}NO$ (M^+) 303.1621, found *m/e* 303.1624. Anal. Calcd for $C_{21}H_{21}NO$: C, 83.17; H, 6.93; N, 4.62. Found: C, 82.42; H, 6.93; N, 4.74.

Lactam 14b was obtained from complex **11b** by the same procedure as for **14a**: yield, 81%, white solid; mp 135 °C; IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 6.75 (m, 10 H, Ar), 3.78 (m, 1 H, NCH), 2.34 (m, 1 H, NCH), 1.92 (m, 2 H, CH_2), 1.17 (m, 1 H, CH), 1.04 (m, 1 H, CH), 1.15 (s, 3 H, Me), 0.90 (m, 2 H, CH_2), 0.75 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9 (CO), 138.7–122.2 (Ar, C=C), 61.68 (PhCC(O)), 44.10, 41.14 (NCH_2), 36.10, 25.11, 23.65 (CH_2), 11.44 (Me). Anal. Calcd for $C_{22}H_{23}NO$: C, 83.28; H, 7.25; N, 4.41. Found: C, 82.89; H, 7.31; N, 4.55.

Pyrrolinone 14c was obtained from complex **11c** by the same procedure as for **14a**: yield, 50%, white solid; mp 100 °C; IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.28–7.16 (m, 10 H, Ar), 3.16 (s, 3 H, NMe), 2.19 (s, 3 H, NC(Me)), 1.57 (s, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.38 (CO), 139.06–124.08 (Ar, C=C), 55.80 (C-(Me)Ph), 26.72 (NMe), 21.31 (NC(Me)), 11.65 (Me); HRMS calcd for $C_{19}H_{19}NO$ (M^+) 277.1466, found *m/e* 277.1460.

Pyrrolinone 14d was obtained from complex **11d** by the same procedure as for **14a**: yield, 52%, an oil; IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.45 (m, 15 H, Ar), 2.96 (s, 3 H, NMe), 1.74 (s, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3 (CO), 140–124.71 (Ar, C=C), 55.73 (PhC(Me)), 28.20 (NMe), 20.12 (Me); MS $C_{24}H_{21}N^+$ 339, found 339.

Pyrrolinone 14e was obtained from complex **11e** by the same procedure as for **11a**: yield, 79%, white solid; mp 132 °C; IR ($CHCl_3$) 1685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49, 7.37, 7.34, 7.29, 6.80 (m, 10 H, Ar), 3.14 (s, 3 H, NMe), 2.17 (s, 3 H, C=C(Me)), 1.40 (m, 1 H), 0.96 (m, 1 H), 0.60 (m, 1 H), 0.44 (m, 1 H), 0.00 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 179.19 (CO), 140.7, 135.9, 134.7, 130.4–122.6 (Ar, C=C), 59.85 (PhCC), 26.59 (NMe), 14.80, 11.52, 2.44 (cyclopropane). Anal. Calcd for $C_{21}H_{21}NO$: C, 83.17; H, 6.93; N, 4.62. Found: C, 82.45; H, 6.97; N, 4.51.

Pyrrolinone 14f was obtained from the mother liquors of the insertion reaction after treatment with pyridine (21% yield) or from the ylide by the usual procedure (66% yield): white crystals; mp 123 °C; IR (KBr) 1690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.64–6.64 (m, 15 H, Ar), 2.93 (s, 3 H, NMe), 1.21 (m, 1 H), 1.70 (m, 1 H), 0.70 (m, 1 H), 0.45 (m, 1 H), 0.10 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.9 (CO), 140.7–124.2 (Ar), 59.97 (PhC), 28.19 (NMe), 14.63 (NC), 2.19, 1.35 (CH_2); HRMS calcd for $C_{26}H_{23}NO$ (M^+) 365.1779, found *m/e* 365.1778. Anal. Calcd for $C_{26}H_{23}NO$: C, 85.48; H, 6.30; N, 3.83. Found: C, 84.74; H, 6.28; N, 3.77.

Diphenylindanone was obtained from the mother liquors of the alkyne insertion reaction after treatment with pyridine: 21% yield as an oil; IR ($CDCl_3$) 1705 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.80–7.10 (m, 14 H, Ar), 4.60 (d, 1 H, PhCH), 3.85 (d, 1 H, PhCH); MS $C_{21}H_{16}O^+$ 284, found 284.

Pyrrolinones 14g and 15g. Complex **8g** (2 g, 0.0066 mol) was refluxed for 6 h in cyclohexane (50 mL); after evaporation of the solvent, the residue was taken up in toluene, and refluxed in this solvent for 12 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel with petroleum ether/ethyl acetate as solvents. Appropriate fractions were collected and evaporated to give first **14g** (0.6 g, 29%) as white crystals and then **15g** as an oil (0.110 g, 5%). **14**: mp 123 °C; IR ($CHCl_3$) 1705 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.26–6.90 (m, 10 H, Ar), 3.16 (s, 3 H, NMe), 2.30 (s, 3 H, CCH_3), 2.24 (dd, 1 H), 1.94 (dd, 1 H), 0.55 (m, 1 H), 0.26 (m, 3 H), –0.05 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.83 (CO), 140.38, 136.71 (C=C), 134.31–121.38 (Ar), 60.39 (CPh), 37.40 (CH_2-cycl), 26.69 (NMe), 11.91, 6.20, 3.88, 3.75 (CH_3, CH_2). Anal. Calcd for $C_{22}H_{23}NO$: C, 83.28; H, 7.25; N, 4.42. Found: C, 82.87; H, 7.13; N, 4.46. **15**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.80–7.20 (m, 10 H, Ar), 3.0 (s, 3 H, NMe), 1.85 (dd, 1 H), 1.45 (dd, 1 H), 1.70 (s, 3 H, Me), 0.45 (m, 3 H), 0.0 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.35 (CO), 156.90, 134.15 (C=C), 133.18–127.56 (Ar), 67.43 (CMe), 39.56 (CH_2-cycl), 24.91 (NMe), 22.44, 5.31, 4.70, 3.72 (Me, CH_2 cyclopropane); MS $C_{22}H_{23}NO^+$ 317, found 317.

$(CO)_5Cr{=}C(NMe_2)(CH_2)_3C{\equiv}CPh$ (9a). 4-Phenyl-3-butyn-1-yl trifluoromethanesulfonate was prepared from the corresponding alcohol and trifluoromethanesulfonic acid anhydride. A solution of complex **8d** (4.4 g, 0.016 mol) in THF (10 mL) was added. After heating to room temperature, the solution was stirred for 2 h. After addition of water, evaporation of the solvent under vacuum, extraction with ether, and again evaporation of the solvent under vacuum, the residue was chromatographed on silica gel with petroleum ether/methylene chloride as eluents. Appropriate fractions were evaporated to give first the starting carbene complex (3.2 g) and then complex **9a** (0.8 g, 12%) as a yellow oil: IR ($CHCl_3$) 2040, 1965, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.30 (m, 5 H, Ar), 3.83 (s, 3 H, NMe), 3.36 (s, 3 H, NMe), 3.26 (m, 2 H, $Cr{=}CCH_2$), 2.56 (m, 2 H, $CH_2C{\equiv}C$), 1.70 (m, 2 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 277.4 ($Cr{=}C$), 223.1, 217.9 (CO), 131.5, 128.3, 127.9, 123.5 (Ar), 88.40, 81.9 ($C{\equiv}C$), 53.3 (NMe), 51.7 ($Cr{=}CC$), 42.2 (NMe), 24.0 ($CH_2C{\equiv}C$), 19.4 (CH_2). Anal. Calcd for $C_{19}H_{17}NO_5Cr$: C, 58.31; H, 4.35; N, 3.58. Found: C, 58.40; H, 4.74; N, 3.32.

$(CO)_5Cr{=}C[N(CH_2)_5](CH_2)_3C{\equiv}CPh$ (9b). Complex **9b** was prepared by reacting the corresponding amide (obtained from acetylpiperidine and $PhC{\equiv}C(CH_2)_2OTf$) with $Na_2Cr(CO)_5$: yield, 31%, yellow oil; IR ($CHCl_3$) 2040, 1965, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.29 (m, 5 H, Ar), 4.29 (m, 2 H, NCH_2), 3.80 (m, 2 H, NCH_2), 3.26 (m, 2 H, $Cr{=}CCH_2$), 2.54 (m, 2 H, $CH_2C{\equiv}C$), 1.80 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 271.3 ($Cr{=}C$), 223.3, 217.7 (CO), 131.4–123.4 (Ar), 88.4, 81.8 ($C{\equiv}C$), 63.3, 52.1 (NCH_2), 50.8 ($Cr{=}CCH_2$), 28.0, 27.8, 24.6, 24.1, 19.3 (CH_2). Anal. Calcd for $C_{22}H_{21}NO_5Cr$: C, 61.25; H, 4.87; N, 3.25. Found: C, 61.41; H, 4.95; N, 3.10.

$(CO)_5Cr{=}C(NC_4H_8)(CH_2)_3C{\equiv}CPh$ (9c). Complex **9c** was prepared by reacting the corresponding amide (obtained from acetylpyrrolidine and $PhC{\equiv}C(CH_2)_2OTf$) with $Na_2Cr(CO)_5$: yield, 72%, yellow oil; IR ($CHCl_3$) 2040, 1960, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2 (5 H, m, Ph), 4.06 (2 H, m, NCH_2), 3.69 (2 H, m, NCH_2), 3.11 (2 H, m, $Cr{=}CCH_2$), 2.51 (2 H, t, $CH_2C{\equiv}C$), 2.03 (4 H, m, CH_2CH_2), 1.73 (2 H, m, $CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 273.3 ($Cr{=}C$), 223.2, 218.5 (CO), 131.6, 128.4, 128.0, 123.6 (C=C, Ar), 88.7, 81.9 ($C{\equiv}C$), 61.3, 52.8, 52.0 ($2NCH_2$, $Cr{=}CCH_2$), 25.7, 25.0, 24.4, 19.7 ($4CH_2$). Anal. Calcd for $C_{21}H_{19}NO_5Cr$: C, 60.43; H, 4.56; N, 3.36. Found: C, 60.56; H, 4.64; N, 3.35.

$(CO)_5Cr{=}C[N(Me)(CH_2Ph)](CH_2)_3C{\equiv}CPh$ (9d). Complex **9d** was prepared by reacting the corresponding amide (obtained from acetylmethylbenzylamine and $PhC{\equiv}C(CH_2)_2OTf$) with $Na_2Cr(CO_5)$: yield, 33%, yellow oil; IR ($CHCl_3$) 2050, 1965, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2 (m, 10 H, Ar), 5.43 (s, 1 H), 4.94 (s, 1 H, CH_2Ph), 3.76 (s, 3 H, NMe), 3.19 (s, 3 H, NMe), 3.30 (m, 2 H, $Cr{=}CCH_2$), 2.5 (m, 2 H, $CH_2C{\equiv}C$), 1.8 (m, 2 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.14 ($Cr{=}C$), 223.02, 217.67 (CO), 134.50–122.93 (Ar), 88.39, 82.12 ($C{\equiv}C$), 69.57 (NCH_2Ph), 52.10 ($Cr{=}CCH_2$), 39.72 (NMe), 24.32 ($CH_2C{\equiv}C$), 19.59 (CH_2). Anal. Calcd for $C_{25}H_{21}NO_5Cr$: C, 64.2; H, 4.50; N, 3.00. Found: C, 64.4; H, 4.65; N, 2.95.

Ylide Complex 23a ($C_{18}H_{17}NO_4Cr$). A solution of complex **9a** (0.54 g) was refluxed in cyclohexane (30 mL) for 4 h to give a yellow precipitate of the ylide (0.21 g, 42%). Recrystallization from CH_2Cl_2/hexane gave yellow crystals suitable for X-ray analysis: mp 150 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 6.18, 5.64, 5.54, 4.99 (m, 5 H, ArCr), 5.36 (m, 1 H, C=CH), 4.15 (t, 1 H, NCH), 2.89 (s, 3 H, NCH_3), 2.75 (m, 2 H, CH_2), 2.69 (s, 3 H, NCH_2), 2.14 (m, 1 H, CH), 1.87 (m, 1 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.27 (CO), 138.92, 112.83, 108.92 (C=C), 96.04, 95.64, 91.80, 89.06, 87.42, 86.98 (ArCr), 46.28 (NMe_2), 42.22, 34.01, 23.41 (NCH, CH_2CH_2); HRMS calcd for $C_{18}H_{17}NO_4Cr$ (M^+) 363.0562, found *m/e* 363.0561.

Enamino Ketene Complex 21b ($C_{21}H_{21}NO_4Cr$). A solution of complex **9b** (1 g) was refluxed in cyclohexane (50 mL) for 4 h. After cooling to room temperature, a dark red complex was obtained and isolated by filtration (0.75 g, 81%): mp 140 °C dec; IR ($CHCl_3$) 1990, 1935, 1895, 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.34 (m, 5 H, Ar), 3.43 (m, 1 H, NCH), 3.25 (m, 1 H, NCH), 3.15 (m, 1 H, NCH), 3.0 (m, 2 H, NCH_2), 2.39 (m, 2 H, NCH, CH), 2.02 (m, 2 H), 1.66 (m, 2 H), 1.32 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 251.0 (CO ketene), 230.1

(CO), 136.5, 131.1, 128.1, 126.7, 109.5, 107.8 (C=C, Ar), 62.5, 50.9 (NC), 33.4, 32.2, 30.6, 26.1, 23.3, 22.9 ($6CH_2$). Anal. Calcd for $C_{21}H_{21}NO_4Cr$: C, 62.53; H, 5.21; N, 3.47. Found: C, 62.47; H, 5.20; N, 3.45.

Ylide Complex 23b ($C_{21}H_{21}NO_4Cr$) was obtained from **9b** in refluxing benzene: yield, 40%, yellow powder: mp 175 °C dec; IR ($CHCl_3$) 1960, 1880, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.15, 5.75, 5.58, 5.05 (m, 5 H, Ar), 5.35 (d, 1 H), 4.05 (m, 1 H), 3.70 (m, 1 H), 3.15 (m, 1 H), 3.0 (m, 1 H), 2.85 (m, 1 H), 2.35 (m, 1 H), 1.95 (m, 2 H), 1.75 (m, 2 H), 1.65 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (CO), 112.8, 107.2, 96.0, 95.5, 89.4, 89.1, 87.6 (C=C, ArCr), 57.1, 49.3, 33.9, 30.3, 22.4, 21.3, 21.1; HRMS calcd for $C_{21}H_{21}NO_4Cr$ (M^+) 403.0875, found *m/e* 403.0885.

Ylide Complex 23c ($C_{20}H_{19}NO_4Cr$). Carbene complex **9c** (1 g) was refluxed in anhydrous benzene (50 mL). After 10 min, the solution turned deep red. Refluxing for an additional 10 h gave, after cooling to room temperature, complex **20c** (0.34 g, 40%) as a yellow powder: mp 175 °C dec; IR (CH_2Cl_2) 1960, 1880, 1700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.18 (d, 1 H), 5.66 (d, 1 H), 5.54 (m, 2 H), 5.29 (d, 1 H), 4.99 (m, 1 H), 3.98 (m, 2 H), 3.25 (m, 2 H), 2.92 (m, 1 H), 2.75 (m, 2 H), 2.11 (m, 4 H), 1.79 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 233.2 (CO), 170.9 (CO), 143.8, 107.9, 96.9, 95.4, 92.3, 92.1, 91.6, 56.7, 52.5, 33.6, 25.2, 24.8, 24.6; HRMS calcd for $C_{20}H_{19}NO_4Cr^+$ (M^+) 389.0720, found *m/e* 389.0721.

Pyrrolinones 25-27. Complex **9d** (2 g, 0.004 mol) was refluxed in anhydrous benzene (50 mL) for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel with petroleum ether/methylene chloride as eluents. Appropriate fractions were collected and evaporated to give first compound **27** (0.58 g, 45%) as an oil, then complex **25** (0.03 g, 2%) as yellow crystals, and finally compound **26** as an oil (0.11 g, 9%). **27**: IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (200 MHz, C_6H_6) δ 7.65, 7.10 (m, 10 H), 3.63 (d, 1 H, PhCH), 3.08 (d, 1 H, PhCH), 2.42 (s, 3 H, NCH_3), 2.32 (m, 2 H), 1.73 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5 (CO), 145.8, 139.8, 136.8, 129.5-126.3, 122.2 (C=C, Ar), 59.9, 42.9, 27.7, 27.3, 25.4, 24.3; HRMS calcd for $C_{21}H_{21}NO$ (M^+) 303.1623, found *m/e* 303.1624. **25**: mp 160 °C; IR ($CHCl_3$) 1965, 1895, 1690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 5 H), 5.91, 5.49, 5.28 (m, 5 H, ArCr), 3.30 (d, 1 H, CHPh), 3.10 (d, 1 H, CHPh), 2.60 (s, 3 H, NCH_3), 2.63 (m, 2 H), 2.40 (m, 1 H), 2.20 (m, 1 H), 2.06 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.72 (CO), 180.05 (CO), 147.8, 135.7, 129.6-126.8, 119.6, 110.6 (C=C, Ar), 93.4, 92.9, 92.7, 91.7, 91.5 (ArCr), 57.8, 45.2, 29.6, 28.9, 27.3, 25.2, 24.6; MS $C_{24}H_{21}NO_4Cr^+$ 439, found 439. **26**: IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53, 7.33, 7.26, 7.18, 7.11, 7.00 (m, 10 H), 3.08 (s, 3 H, NMe), 3.07 (2 doublets, 2 H, CH_2Ph), 2.84 (m, 1 H), 2.59 (m, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.41 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.6 (CO), 163.6, 135.5, 132.0, 129.0-126.9 (C=C, Ar), 72.8, 39.5, 32.7, 26.4, 25.6, 23.7; HRMS calcd for $C_{21}H_{21}NO$ (M^+) 303.1623, found *m/e* 303.1624.

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Supplementary Material Available: Crystal structure data (Tables S1-S39) for **11a**, **18d**, **19c**, **21b**, **23a**, and **25** including complete lists of interatomic distances (Tables S7-S12) and bond angles (Tables S13-S22), fractional parameters (Tables S23-S28), and anisotropic thermal parameters (Tables S29-S33) (33 pages); tables of observed and calculated structure factors (Tables S34-S39) (36 pages). Ordering information is given on any current masthead page.

Diamagnetic (Pentamethylcyclopentadienyl)tungsten Complexes Containing Unsubstituted, Monomethyl, or 1,1-Dimethyl Hydrazine or Hydrazido Ligands

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Abstract: Hydrazine adducts are formed upon adding hydrazine, methylhydrazine, or 1,1-dimethylhydrazine to $[Cp^*WMe_4]PF_6$. They are readily deprotonated to yield hydrazido(1-) complexes of the type $Cp^*WMe_4[\eta^2$-hydrazido(1-)], or they decompose by loss of methane to yield complexes of the type $\{Cp^*WMe_3[\eta^2$-hydrazido(1-)]$\}^+$. $\{Cp^*WMe_3[\eta^2$-hydrazido(1-)]$\}^+$ complexes are deprotonated at low temperature to give complexes of the type $Cp^*WMe_3[\eta^2$-hydrazido(2-)], which rearrange readily to complexes of the type $Cp^*WMe_3[\eta^1$-hydrazido(2-)] above approximately -20 °C. Addition of acid to complexes of the type $Cp^*WMe_3(\eta^1$-NNRR') yields $[Cp^*WMe_3(NNRR'H)]^+$ complexes first. Loss of a proton from N_β followed by addition of a proton to N_α yields the thermodynamically preferred $[Cp^*WMe_3(\eta^2$-NHNRR')$]^+$ complexes. $[Cp^*WMe_3(\eta^2$-$NHNH_2)]Cl$ decomposes much more readily than the triflate salt by losing methane to give *trans*-$Cp^*WMe_2Cl(\eta^1$-$NNH_2)$. Methylation of $Cp^*WMe_3(\eta^1$-$NNMe_2)$ yields $[Cp^*WMe_3(NNMe_3)]^+$; $[Cp^*WMe_3(NNMe_3)]^+$ also is obtained upon methylating $Cp^*WMe_3(\eta^1$-$NNH_2)$ in the presence of a base. $Cp^*WMe_3(\eta^1$-$NNH_2)$ reacts with $[Cp^*WMe_3(\eta^2$-$NHNH_2)]^+$ to yield $[Cp^*WMe_3]_2(\mu$-$N_2)$ and $[N_2H_5]^+$, while $Cp^*WMe_3(\eta^1$-$NNH_2)$ decomposes to $Cp^*WMe_3(\mu$-NNH)$Cp^*WMe_2(\mu$-NN)Cp^*WMe_3. These findings are discussed in relation to the proposal that both nitrogen atoms of an N_2H_x intermediate must bind to the metal in preparation for formation of a d^2 η^2-N_2H_4 complex in which the N-N bond is cleaved to yield 1 equiv of ammonia.

Introduction

Dinitrogen is reduced to ammonia by various nitrogenases, those containing molybdenum or vanadium having the highest activity.[1-11] Over the last 25 years, inorganic chemists have elucidated modes of bonding of both dinitrogen and partially reduced dinitrogen (N_2H_x) ligands to transition metals and have been gathering evidence in support of mechanisms by which dinitrogen can be reduced to ammonia.[1,8,12,13] However, important pieces

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