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Reaction of aminocarbene complexes of chromium with alkynes IV. New transformations of the nitrogen ylide complexes derived therefrom

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Abstract

Attempts to remove the $Cr(CO)_3$ group from a series of *N*-ylide complexes obtained from aminocarbene complexes of chromium and diphenylacetylene failed. With dioxygen under UV irradiation, insertion of an oxygen atom into the N–C(O) bond gave aminolactones **8** instead. With sulfur a series of aminofuran complexes **9** were obtained. Olefins such as cyclopentadiene and cyclooctene did not cycloadd to these ylide complexes. Whereas no reaction was observed with cyclooctene, with cyclopentadiene an overall protonation–demethylation–demetallation reaction of *N*-dimethyl ylide complexes **4a** and **4b** to the pyrrolinones **10a** and **10b** took place. The same protonation–dealkylation reaction was observed with $(ArPS_2)_2$. Thus **4a**, **4b** and **4d** led to **10a**, **10b** and **10d**. The fate of the leaving alkyl group was established by carrying out a similar reaction on the *N*-ylides **4f** and **4g** derived from piperidine which gave the lactone thiols **11f** and **11g**. The structure of the aminofuran complex **9b** was unambiguously established by X-ray crystallography. The relationship between the structures of the *N*-ylide complexes and the reaction products is discussed.

Keywords: Aminocarbene complexes; Chromium; Alkynes, Nitrogen ylide complexes; X-ray structure

1. Introduction

The formation of *N*-ylide complexes of $Cr(CO)_3$ by intramolecular reaction between a trisubstituted nitrogen atom and a ketene complex opened a new field in the chemistry of Fischer-type carbene complexes [1–3]. The thermolysis of these ylide complexes under mild conditions has already been described in several previous papers. The present publication deals with the use of these *N*-ylide complexes as starting material for new transformations and especially their behavior towards dioxygen, sulfur, sulfur-containing reagents and olefins.

2. Results

2.1. Attempts to isolate the metal-free N-ylides

Classical organic nitrogen ylides have been fully characterized by X-ray crystallography. Most are stable at room temperature but rearrange upon moderate heating [4–6]. It seemed therefore of interest to try to prepare the metal-free *N*-ylides of structure **5**, which might be obtained from the corresponding $Cr(CO)_3$ complexes **4** upon demetallation, in order to examine their thermal stability. There are several plausible methods to approach this goal, among which one might quote the ligand exchange and oxidative demetallation. In the first case, pyridine might be a good choice, since the lactam complexes so far obtained upon rearrangement of **4** react with pyridine to give the metal-free

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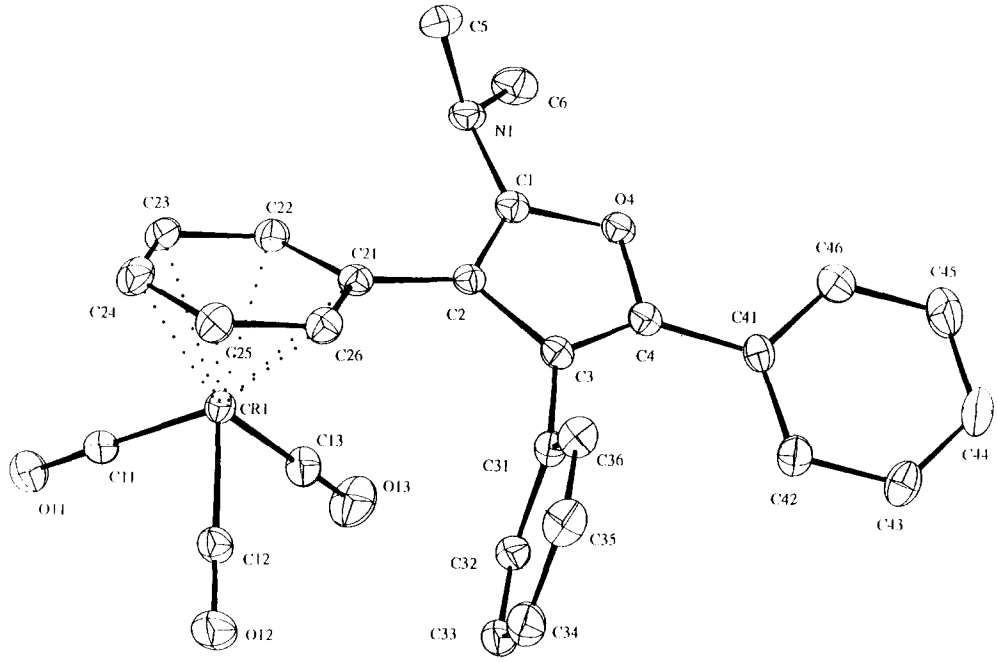
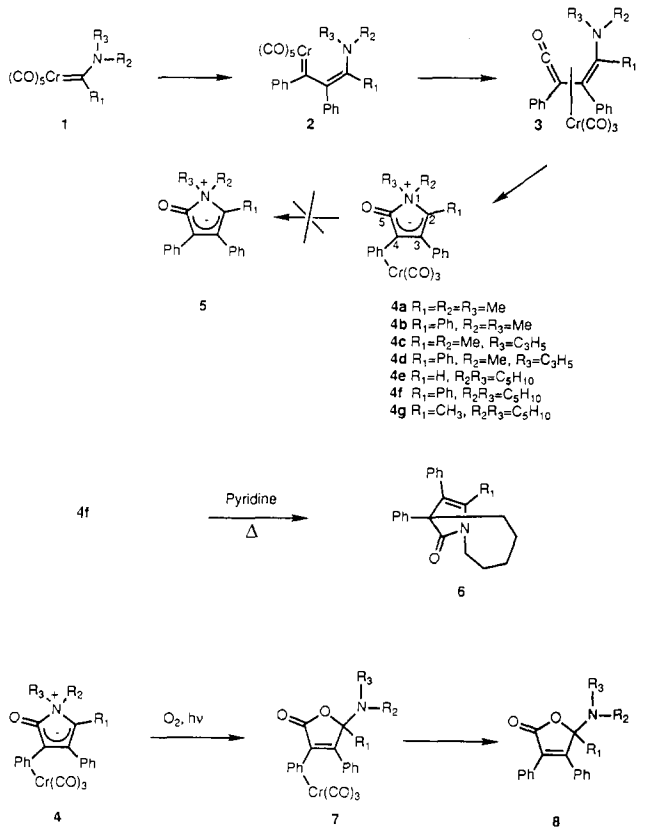


Fig. 1. ORTEP drawing of **9** showing the atom numbering.

organic products after a few hours under reflux [2,3]. However, heating **4f** at the reflux temperature of pyridine lead instead to the bridgehead lactam **6f**, the product of rearrangement of the *N*-ylide complex (Scheme 1).



Scheme 1

Attempts to insert the alkyne directly into the aminocarbene complex **1f** using pyridine as solvent led neither to the *N*-ylide nor to its rearrangement product and only the benzannulation product, diphenylindanone, could be isolated.

2.2. Reaction with oxygen

In a previous publication [2] we have already described the reaction of *N*-ylide complexes **4a–4c** with dimethyldioxirane, which led to lactone complexes **7a–7c** or to lactones **8a–8c**. It has now been established that this reaction is best carried out with dioxygen under UV irradiation and is general for *N*-ylides of the type **4** since it can also be applied to ylides **4d** and **4e** which led to the metal-free lactones **8d** and **8e**. The same oxidation reaction was also carried out on **4f** simply by dissolving the ylide in methylene chloride and exposing the solution to air and sunlight for 4 h. Under these conditions, aminolactone **8f** could be isolated with a 23% yield. The spectroscopic data of these new aminolactones (ν(CO) = 1740 cm^{-1}; δ(CO) = 171.77 ppm) were in all respects comparable with those previously described for **8a–8c**. These lactones can be detected in most alkyne-insertion reactions when trace amounts of dioxygen are present.

2.3. Reaction with sulfur and with Lawesson's reagent, a sulfur–phosphorus ylide

The observation of an unexpected oxygen insertion into the ylide complexes **4** prompted us to attempt to insert sulfur in the same way. However, the expected reaction did not take place. Thus, when **4a** and **4b** were

Table 1
Selected bond lengths (Å) and bond angles (°) for **9**

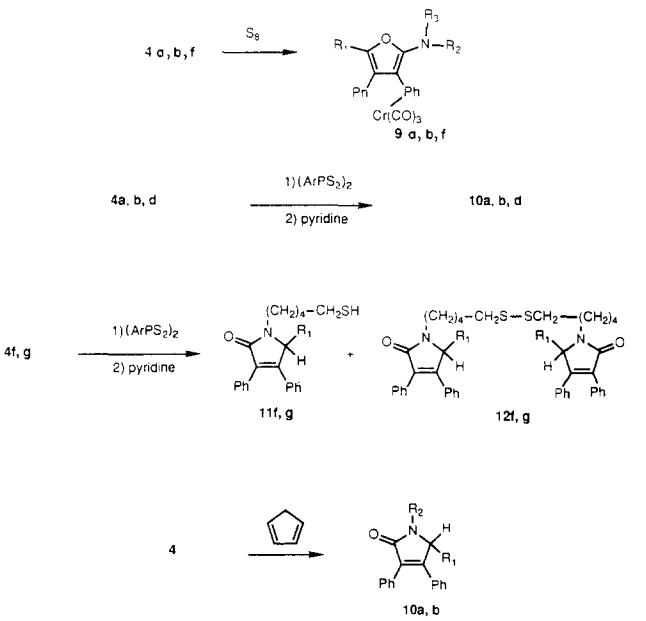
Bond lengths			
Cr(1)–C(11)	1.829(5)	O(11)–C(11)	1.152(5)
Cr(1)–C(12)	1.845(5)	O(12)–C(12)	1.141(5)
Cr(1)–C(13)	1.835(5)	O(13)–C(13)	1.132(5)
Cr(1)–C(21)	2.269(4)	Cr(1)–C(22)	2.218(4)
Cr(1)–C(23)	2.200(4)	Cr(1)–C(24)	2.223(4)
Cr(1)–C(25)	2.207(4)	Cr(1)–C(26)	2.230(4)
N(1)–C(1)	1.389(5)	N(1)–C(5)	1.461(6)
N(1)–C(6)	1.455(6)	O(1)–C(1)	1.350(5)
O(1)–C(4)	1.383(5)	C(1)–C(2)	1.357(6)
C(2)–C(3)	1.446(6)	C(2)–C(21)	1.467(6)
C(3)–C(4)	1.352(6)	C(3)–C(31)	1.480(6)
C(4)–C(41)	1.465(6)		
Bond angles			
C(12)–Cr(1)–C(11)	89.5(2)	O(11)–C(11)–Cr(1)	176.6(4)
C(13)–Cr(1)–C(11)	87.2(2)	O(12)–C(12)–Cr(1)	178.4(5)
C(13)–Cr(1)–C(12)	89.7(2)	O(13)–C(13)–Cr(1)	178.5(5)
C(5)–N(1)–C(1)	115.8(4)	C(6)–N(1)–C(1)	117.3(4)
C(6)–N(1)–C(5)	113.5(4)	C(4)–O(1)–C(1)	107.0(3)
O(1)–C(1)–N(1)	117.1(4)	C(2)–C(1)–N(1)	131.7(4)
C(2)–C(1)–O(1)	111.2(4)	C(3)–C(2)–C(1)	105.3(4)
C(21)–C(2)–C(1)	125.2(4)	C(21)–C(2)–C(3)	129.4(4)
C(4)–C(3)–C(2)	106.9(4)	C(31)–C(3)–C(2)	125.8(4)
C(31)–C(3)–C(4)	127.3(4)	C(3)–C(4)–O(1)	109.5(4)
C(41)–C(4)–O(1)	114.6(4)	C(41)–C(4)–C(3)	135.8(4)

heated in refluxing benzene for 6 h in the presence of sulfur, complete disappearance of the starting *N*-ylides was observed, with formation of new yellow non-polar complexes with about 30% yield. In the case of **4a**, the ^{1}H-NMR spectrum of the purified reaction product confirmed the presence of a $Cr(CO)_3$ (arene) moiety, of a vinylic methyl group ($\delta = 2.11$ ppm) and of a NMe_2 group ($\delta = 2.80$ ppm). The ^{13}C NMR spectrum showed a signal at $\delta = 155.71$ ppm, attributable to the OCN carbon, besides signals for metallic carbonyls, consistent with a structure such as **9a**, a $Cr(CO)_3$ complex of an aminofuran. A similar reaction was observed starting from **4b** which led to **9b**, the structure of which was finally confirmed by an X-ray diffraction study. The ORTEP view is shown in Fig. 1, the most important bond distances and bond angles being found in Table 1.

A further way to introduce sulfur into an oxygenated substrate would be to use Lawesson's reagent $(ArPS_2)_2$ (Ar = paramethoxyphenyl), a sulfur–phosphorus ylide which is able for example to convert lactones to thiolactones [7,8]. Thus, when **4a** was heated in refluxing benzene in the presence of this reagent, fast transformation of the starting complex was observed. After 6 h a new yellow complex was isolated with a 93% yield. Its spectroscopic data imply the $Cr(CO)_3$ complex of pyrrolinone **10a**. Treatment of this complex in refluxing pyridine led to an organic compound with a 76% yield, the physical properties of which are in all respects identical with those of **10a**. Under the same conditions, **4b** and **4d** led to **10b** and **10d**. In order to establish the fate of the leaving alkyl group in these two transformations, a similar reaction was carried out on the ylide complexes **4f** and **4g** derived from piperidine. Treatment of the residue of the reaction in refluxing pyridine gave an organic compound with a 35% yield, the spectroscopic data of which are consistent with structure **11f**. The mass spectrum ($m/z = 413$) consistent with the structural formula $C_{27}H_{27}NOS$ also exhibited an ion due to the loss of a SH group ($m/z = 380$). The IR spectrum ($\nu(CO) = 1670$ cm^{-1}) confirmed the presence of a conjugated carbonyl group. The ^{13}C NMR spectrum exhibited all the signals observed for pyrrolinone **10b** except that for the *N*-methyl group (signals for **10b** are given in parentheses): $\delta = 170.27$ (170.26), 152.47 (152.27), 135.55–129.97 (135.47–127.83) and 66.92 (68.80) ppm. Five extra signals for the carbon atoms originating from the piperidine ring system were also present. Moreover, the ^{1}H NMR spectrum confirmed the incorporation of sulfur as a sulfide with a triplet for the SH proton at $\delta = 1.31$ ppm and a quartet at $\delta = 2.45$ ppm for the two hydrogen atoms of the adjacent methylene group. A second, more polar compound, the spectroscopic data of which are very similar to those of **11f**, was also isolated. This had lost the triplet due to the SH proton in the ^{1}H NMR spectrum. Moreover, the mass spectrum exhibited an ion for a $C_{27}H_{26}NOS$ fragment. It is thus likely that this second product corresponds to the disulfide **12f**, the product of oxidation of **11f**. Similar results were obtained starting from the ylide complex **4g**.

2.4. Reaction of 4a and 4b with olefins

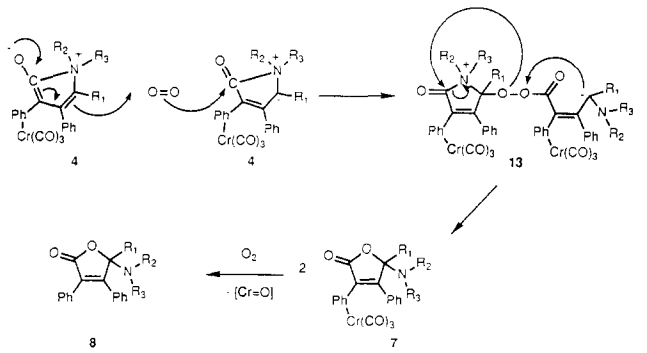
The *N*-ylide complexes **4** react with water and alcohols to give aminoacids and aminoesters [1] respectively



upon N–C(O) bond cleavage. Their behavior is thus similar to what would be expected from their precursors, the aminovinylketene complexes **3**. Since in general ketenes [9], and in particular aminoketenes [10], react with olefins to give (2 + 2) cycloaddition products, and moreover since ketene complexes generated from alkoxycarbene complexes upon alkyne–CO insertions react along the same lines with olefins [11,12], we examined the reaction of **4** with olefins and specifically with cyclopentadiene, pentamethylcyclopentadiene and cyclooctene.

When **4a** was heated in refluxing benzene for 12 h in the presence of a tenfold excess of cyclopentadiene, a new organic compound was detected by thin layer chromatography. It was isolated by silica gel chromatography with a 71% yield as white crystals. Both the elemental analysis and the spectroscopic data are consistent with a structure resulting from the protonation of **4a** with loss of a methyl group and of $Cr(CO)_3$. The ^{13}C NMR spectrum confirmed the presence of a conjugated amide ($\delta(CO) = 167.5$ ppm) and of an NCH_3 group ($\delta = 27.31$ ppm). The ^1H NMR spectrum showed a quartet for a proton geminal to a methyl group, at $\delta = 4.40$ ppm, together with a doublet for a methyl group at $\delta = 1.18$ ppm. All these data are consistent with a structure **10a**, a pyrrolinone resulting from **4a** by α-protonation with respect to nitrogen together, with an *N*-demethylation reaction. A similar reaction was observed starting from **4b**; **10b** was obtained with a 46% yield. Pentamethylcyclopentadiene reacts in the same way with **4a** to give a 33% yield of **10a**. However, neither **4d** nor **4e** reacted with cyclopentadiene. Decomposition of the starting complexes together with small amounts of rearrangement product **6f** was observed. In the case of cyclooctene, no reaction took place.

Since the ketene complexes **3** are formed on the way to the *N*-ylide complexes **4**, attempts were made to trap them by carrying out the alkyne insertion reactions into **1** in the presence of excess cyclopentadiene. However, almost the same results as with the ylide complexes **4** were observed; complexes **1a** and **1b** gave the corresponding pyrrolinones **10a** and **10b** with 62 and 59% yields respectively.



Scheme 2

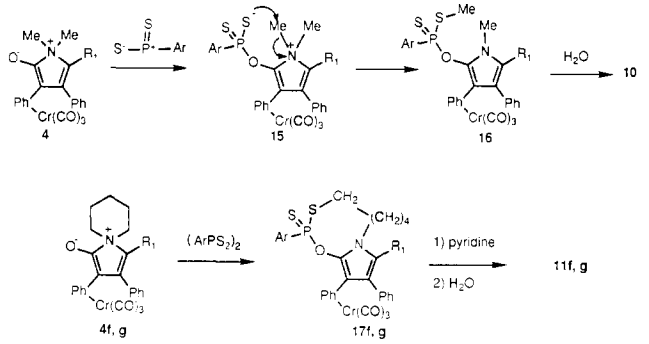
3. Discussion

3.1. Attempts to demetallate the N-ylide complexes 4

Release of the metal from the *N*-ylide complexes **4** would allow a direct comparison between ylides **5** and those prepared by Stevens et al. However, neither the ligand exchange nor the oxidative demetallation could be carried out successfully, since in the first case rearrangement took place either before or just after the demetallation reaction. Even though it was known that ketenes react easily with dioxygen to give lactones [13,14], the use of oxidizing agents such as oxygen or dimethyldioxirane seemed promising. Indeed, dimethyldioxirane had already been used to demetallate simple [(arene) $Cr(CO)_3$] complexes [15]. However, in the case of dioxygen, both the demetallation and the oxidation of the ylides **4** by insertion of an oxygen atom into the N–C(O) bound were observed. The overall result is thus what one would expect from the oxidation of the conjugated aminoketene complexes **3**, the formation of lactones **8**. As has been suggested for simple ketenes [13], dioxygen may react with two molecules of ylide complex **4** to give peroxide **13** which, upon cleavage of the peroxide link, leads to two molecules of lactone complex **7** and finally to lactone **8** (Scheme 2).

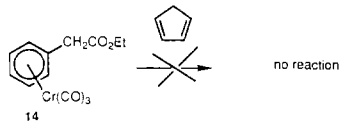
3.2. Olefins and Lawesson's reagent

The results observed with cyclopentadiene and cyclooctene confirm that the N–C(O) bond in these nitrogen ylide complexes is rather strong. No reverse reaction, to the aminoketene complexes, which might give (2 + 2) cycloaddition products with the external olefins, took place. At least two mechanisms could account for the protonation–demethylation–demetallation reactions. The cyclopentadiene may be a sufficiently strong acid to protonate the ylide complexes to ammonium complexes, which are then demethylated by the cyclopentadienide anion. Such a mechanism is consistent with the fact that these ylide complexes are very easily protonated, and also that *N*-methylammonium derivatives are known to undergo base-induced demethylation reactions [16,17]. Moreover, groups on nitrogen other than methyl do not, in general, undergo such reactions. This was observed in the present study since the piperidine-derived complex **4f** did not undergo the dealkylation reaction. Upon heating in refluxing benzene for 48 h, a slow transformation of 4f into the complexed and the metal-free lactam **6f** was observed.



Scheme 3

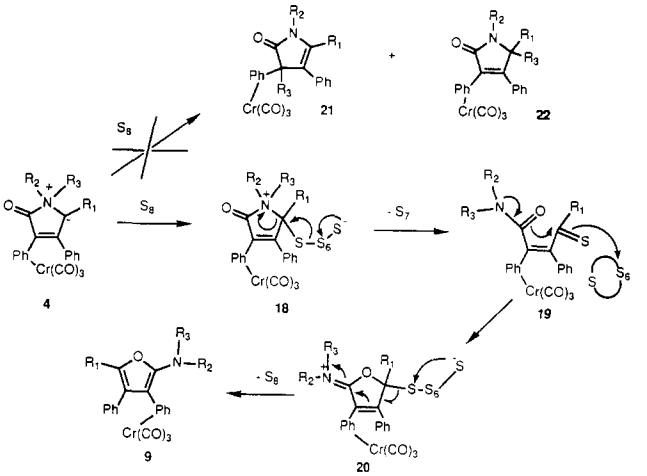
A second possibility is that the negative charge of the ylide is delocalized onto the metal so that direct interaction of chromium and cyclopentadiene might take place. Protonation would thus occur via the metal. In contrast with simple (arene) tricarbonyl chromium compounds such as **14**, which do not react with cyclopentadiene even upon heating for long periods of time in boiling benzene, loss of the $Cr(CO)_3$ group during the interaction of the ylide complexes **4** with cyclopentadiene is observed.



The reaction between complexes **4** and Lawesson's reagent can be considered along the same lines. Interaction between the positively charged phosphorus atom and the negative centre of the ylide complex (probably the oxygen atom) might again lead to an ammonium derivative **15**, which in turn suffers an intramolecular sulfur-induced demethylation reaction to give **16** and, after hydrolysis, the same lactams **10** as with cyclopentadiene (Scheme 3). The formation of a carbon–sulfur bond during this reaction was demonstrated by applying the same reaction to ylide complexes **4f** and **4g**. The ring-opened intermediate **17f**, which is supposed to be formed in this case by the interaction of the negatively charged sulfur with the carbon α to the nitrogen atom, as in **15a**, gave the lactam-thiol **11f** upon hydrolysis. Air oxidation of **11** then leads to the disulfide **12f**. Similar results were observed in the case of **4g**.

3.3. Reaction with sulfur: mechanism of formation of aminofurans

The same type of reaction as with dioxygen was expected to occur with sulfur: insertion of sulfur into the N–C(O) bond, leading to aminothiolactones. However, the reaction was again different. S_8 reacts with the *N*-ylide complexes **4** in the way that it does with

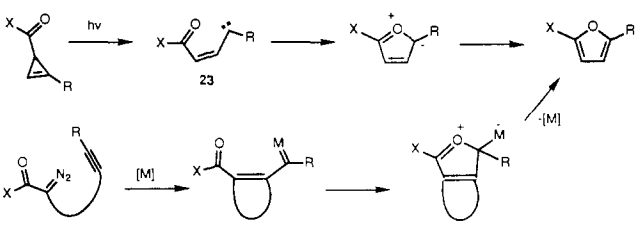


Scheme 4

P-ylide [18]. As in the case of phosphorus, cleavage of a carbon–heteroatom bond took place, in the present case C(2)–N(1), but this reaction was followed by the formation of a carbon–oxygen bond, O(1)–C(2), to give an aminofuran complex **9** [19]. The reaction probably occurred by sequential sulfur-assisted ring opening and ring closure of the *N*-ylide complex **4**. The first step is probably the same as in the case of *P*-ylides: the formation of a carbon–sulfur double bond (**4** → **18** → **19**) followed by nucleophilic addition of the oxygen atom of the amide function to the thione and finally elimination of S_8 (**19** → **20** → **9** (Scheme 4)). Thus sulfur inhibits the rearrangement reaction of ylide complexes **4** to the lactam complexes **21** and **22** and leads to the same products as the *N*-ylides with nitrogen-alkyl groups of low tendency to migrate. The intermediate **19**, if it forms, thus behaves like alkenone carbenes **23** or metal carbenoids **24** which are known to give furans (Scheme 5) [20,21].

4. Conclusion

Although the nitrogen ylides formed during the interaction of alkynes with aminocarbene complexes did not lead to the expected products, new transformations have been discovered. Moreover, some of the reagents used



Scheme 5

for these structural modifications do not interact directly with (arene)tricarbonylchromium. Whereas the formation of aminolactones from these ylides and oxygen may be characteristic of the reaction of a conjugated ketene, the reaction of olefins such as cyclopentadiene, of sulfur and of Lawesson's reagent are typical for these new zwitterionic species. Until now, most of the transformations observed in the case of the *N*-ylides studied by Stevens et al. can be observed starting from the aminocarbene complexes of chromium. The missing pathway, the migration of the alkyl groups from nitrogen to the carbon atom of the carbonyl group (**1** → **3** in Scheme 2) will be described in a forthcoming publication.

5. Experimental section

5.1. General methods

^{1}H 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 Fisons ZAB HSQ 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 dinitrogen. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride under dinitrogen.

5.2. Pyrrolinone 6

Pyrrolinone **6** was obtained upon heating **4f** (0.5 g, 0.0097 mol) in pyridine (40 ml) under reflux for 24 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel. Elution with petroleum ether: ethyl acetate (90 : 10) gave pyrrolinone **6** as a white solid (yield, 0.140 g (40%); melting point (m.p.), 195°C). IR ($CHCl_3$): ν 1700, 1590 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.42–6.86 (m, 15H, Ar), 4.18 (m, 1H, NCH), 3.23 (m, 1H, NCH), 2.98 (m, 1H), 2.70 (m, 1H), 2.17 (m, 1H), 1.78 (m, 2H), 1.45 (m, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 188.68 (CO), 141.98, 138.25, 134.34, 130.96, 129.56–127.83, 123.44 (C=C, Ar), 62.52 (C(O)C(Ph)), 45.98, 43.17, 35.43, 25.80, 24.57 ($5CH_2$) ppm. Anal. Found: C, 85.06; H, 6.57; N, 3.59. $C_{27}H_{25}NO$ Calc.: C, 85.49; H, 6.60; N, 3.69%.

5.3. Pyrrolinone 10a

Pyrrolinone **10a** was obtained upon heating **4a** (0.4 g, 0.0097 mol), in benzene (30 ml) under reflux for 2 h in the presence of cyclopentadiene (0.65 ml, 0.097 mol). After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with petroleum ether: ethyl acetate (60 : 40) gave **10a** (white crystals; yield, 71%; m.p. 93–94°C). IR ($CHCl_3$): 1670, 1600 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.10 (m, 10H, Ar), 4.40 (q, J = 6.8 Hz, 1H, CH), 3.08 (s, 3H, NCH_3), 1.18 (d, J = 6.8 Hz, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.68 (CO), 153.61, 132.89–127.80 (C=C, Ar), 59.24 (CH), 27.31 (NCH_3), 16.85 (CH_3). HRMS. Found: m/e 263.1311. $C_{18}H_{17}NO$ (M^+) Calc.: 263.1310.

5.4. Pyrrolinone 10b

Pyrrolinone **10b** was obtained from **4b** under the conditions as above (white crystals; yield, 46%; m.p., 195°C). IR ($CHCl_3$): ν 1680, 1600 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.30–7.03 (m, 15H, Ar), 5.28 (s, 1H, CH), 2.90 (s, 3H, NCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.26 (CO), 152.37, 135.47–127.83 (C=C, Ar), 68.80 (CH), 27.54 (NCH_3). HRMS. Found: m/e 325.1466. $C_{23}H_{19}NO$ (M^+) Calc.: 325.1466.

5.5. Direct formation of pyrrolinones 10a and 10b from carbene complexes 1a and 1b

A solution of carbene complex **1a** (0.5 g, 1.9 mmol) in benzene (30 ml) was heated under reflux in the presence of diphenylacetylene (0.422 g, 2.37 mmol) and cyclopentadiene (1.27 ml, 19 mmol) for 24 h. After evaporation of the solvent from the black solution, the residue was chromatographed on silica gel as above. Elution with the same mixtures of eluents gave **10a** (0.310 g (62%)). Starting from **1b**, pyrrolinone **10b** was obtained with a 59% yield. Under the same conditions, an excess of pentamethylcyclopentadiene gave, with **1a**, a 23% yield of **10a**.

5.6. Reaction of ylide complexes 4d and 4e with dioxygen; production of lactones 8d and 8e

5.6.1. Aminolactone 8d

This was obtained upon irradiation of a solution of **4d** (0.35 g, 0.70 mmol) in methylene chloride under a flow of dioxygen, with a Philips 400 W lamp for 3 h at room temperature. The solution turned green–brown with the formation of a precipitate. After filtration through Celite, and evaporation of the solvent under vacuum, the residue was purified by flash chromatography through silica gel with petroleum ether: ethyl acetate (80 : 20) as eluent. The aminolactone **8d** was ob-

tained as white crystals (yield, 0.19 g (70%); m.p., 162°C). IR ($CHCl_3$). ν 1740 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.58–7.10 (m, 15H, Ar), 2.67 (s, 3H, NMe), 2.30 (m, 1H, NCH), 0.70 (m, 1H, CH), 0.47 (m, 1H, CH), 0.34 (m, 2H, CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.28 (CO), 160.19, 137.33, 131.68–127.27 (C=C, Ar), 105.21 (O–C–N), 38.09, 33.75 (NCH, NMe), 8.07, 6.86 (CH_2) ppm. Mass spectroscopy (MS). Found: 381. $C_{22}H_{23}NO_2^+$ Calc.: 381.

5.6.2. Aminolactone 8e

This was obtained by a similar procedure as for **8d**, with a 75% yield, as white crystals (m.p., 150°C). IR ($CHCl_3$): ν 1750 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.44–7.25 (m, 10H, Ar), 6.55 (s, 1H, CH), 3.80 (m, 2H, NCH_2), 2.52 (m, 2H, NCH_2), 1.64 (m, 6H, CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.70 (CO), 152.17, 130.62, 130.18–124.75 (C=C, Ar), 103.86 (O–C–N), 58.40, 58.0 (NCH_2), 25.53, 25.41, 23.21 (CH_2) ppm. MS. Found: 319. $C_{21}H_{21}NO_2^+$ Calc.: 319.

5.7. Aminolactone 8f

Aminolactone **8f** was obtained by dissolving **4f** in methylene chloride and exposing it to sunlight and air, with a 23% yield, as white crystals (m.p., 153–154°C). IR ($CHCl_3$): ν 1740 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.35–7.17 (m, 15H, Ar), 2.88 (m, 2H, NCH_2), 1.69–1.57 (m, 6H, $3CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.77 (CO), 160.42, 137.34 (C=C), 131.21–126.77 (Ar), 105.97 (OCPh), 47.97 (NCH_2), 26.23, 24.58 (CH_2) ppm. HRMS. Found: m/e 395.1888. $C_{27}H_{27}NO_2$ (M^+) Calc.: 395.1885.

5.8. Aminofuran complex 9a

Aminofuran complex **9a** was obtained upon heating under reflux a solution of **4a** (0.6 g, 1.45 mmol) in benzene (40 ml) in the presence of sulfur (0.056 g, 1.74 mmol) for 12 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel. Elution with petroleum ether : ethyl acetate (99 : 1) gave **9a** (0.190 g (31%)) as yellow crystals (m.p., 118°C). IR ($CHCl_3$): ν 1970, 1890, 1610, 1595 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.40–7.25 (m, 5H, Ar), 5.53–5.17 (m, 5H, ArCr), 2.80 (s, 6H, NMe_2), 2.11 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.93 (CO), 155.71, 144.19, 133.69, 130.60, 128.85, 127.60, 106.04, 104.69 (C=C, Ar), 93.88, 92.14, 91.70 (ArCr), 43.53 (NMe_2), 12.06 (CH_3); ppm. MS. Found: 413. $C_{21}H_{19}NO_4Cr^+$ Calc.: 413. Anal. Found: C, 64.04; H, 4.70; N, 3.36. $C_{21}H_{19}CrNO_4$ calc.: C, 63.92; H, 4.60; N, 3.39%.

5.9. Aminofuran complex 9b

Aminofuran complex **9b** was obtained as for **9a** with a 30% yield from **4b** (m.p., 162°C). IR ($CHCl_3$): ν 1960, 1880, 1595 cm^{-1}. ^1H NMR (40 MHz, $CDCl_3$): δ 7.40–7.01 (m, 10H, Ar), 5.40–5.05 (m, 5H, ArCr), 3.80 (s, 6H, NMe_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 234.01 (CO), 156.30, 143.07, 133.51–121.95, 105.31, 104.41 (Ar, C=C), 93.06, 91.92, 90.99 (ArCr), 42.69 (NMe_2) ppm. HRMS. Found: m/e 475.0878. $C_{27}H_{21}NO_4Cr$ (M^+) Calc.: 475.0875. Anal. Found: C, 67.91; H, 4.31; N, 2.91. $C_{27}H_{21}CrNO_4$ Calc.: C, 68.21; H, 4.42; N, 2.95%.

5.10. Aminofuran complex 9f

Aminofuran complex **9f** was obtained as above from **4f**, as yellow crystals with a 61% yield (m.p., 170–171°C). IR ($CHCl_3$): ν 1960, 1880, 1600 cm^{-1}. ^1NH NMR (200 MHz, $CDCl_3$): δ 7.46–7.13 (m, 10H, Ar), 5.52–5.19 (m, 5H, ArCr), 3.23–3.18 (m, 4H, NCH_2), 1.76–1.65 (m, 6H, $3CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 233.52 (CO), 156.41, 143.0, 133.75–121.87, 105.75, 105.19 (C=C, Ar), 92.49, 92.36, 90.46 (ArCr), 51.96 (NCH_2), 25.87, 24.05 (CH_2) ppm HRMS. Found: m/e 515.1185. $C_{30}H_{25}NO_4Cr$ (M^+) Calc.: 515.1188.

5.11. Reaction of 4a with Lawesson's reagent; formation of lactam 10a

Complex **4a** (0.5 g, 1.2 mmol) was heated under reflux in benzene (30 ml) in the presence of Lawesson's reagent (0.27 g, 0.66 mmol) for 6 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with petroleum ether : ethyl acetate (70 : 30) gave the $Cr(CO)_3$ complex **10a** of lactam as a 65 : 35 mixture of isomers which were not separated (orange crystals; yield, 0.37 g, (93%)); m.p., 136–137°C). IR ($CHCl_3$): ν 1970, 1890, 1675, 1600 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.45–7.18 (m, 5H, Ar), 6.13–5.0 (m, 5H, ArCr), 4.45 (q, 1H, CH), 4.31 (q, 1H, CH), 3.08 (s, 3H, NCH_3), 1.24 (d, 3H, CH_3), 1.15 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.60 (CO), 167.54 (CO), 156.64, 153.37, 132.67, 129.19, 129.07, 127.97, 126.07 (Ar, C=C), 98.80, 93.18, 92.56, 90.77, 90.20 (ArCr), 59.66 (CH), 27.0 (NCH_3), 16.74, 16.34 (CH_3) ppm. MS. Found: 263 ($M^+ - Cr(CO)_3$). $C_{21}H_{17}NO_4Cr^+$ Calc.: 399. The mixture of complexes (0.35 g, 0.88 mmol) was heated under reflux in pyridine (20 ml) for 12 h to give, after silica gel filtration, pyrrolinone **12a** (0.175 g (76%)) as white crystals, the physical data of which were in all respects identical with those of an authentic sample prepared as above.

The $Cr(CO)_3$ complex of **10b** was obtained under similar conditions as above from **4b** as a yellow solid with a 74% yield (m.p., 58–60°C). IR ($CHCl_3$): ν 1970, 1900, 1680 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.43–6.94 (m, 10H, Ar), 5.85–5.09 (m, 6H, ArCr, CH), 2.90, 2.88 (NMe_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$):

δ 232.65 (CO), 168.58 (CO), 155.33, 133.98–126.76 (Ar, C=C), 94.48, 94.45, 93.93, 92.45, 90.75, 90.66 (ArCr), 65.62, 68.64 (CH), 27.57, 27.49 (NMe). HRMS. Found: *m/e* 325.1466. $C_{26}H_{19}NO$ (M^+-$Cr(CO)_3$) Calc.: 325.1466.

5.12. Pyrrolinone 10d

Pyrrolinone **10d** was obtained under similar conditions as above from **4d** after treatment of the residue of the reaction in boiling pyridine with an 80% yield (white solid; m.p., 152°C). IR ($CHCl_3$): ν 1680 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.47–7.01 (m, 15H, ArH), 5.29 (s, 1H, CHPh), 2.36 (m, 1H, NCH), 0.97–0.82 (m, 2H, CH_2), 0.72–0.56 (m, 2H, CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.35 (CO), 152.41, 136.08 (C=C), 132.93–127.90 (Ar), 68.21 (CHPh), 23.98 (NCH), 6.42 and 5.04 ($2CH_2$). Anal. Found: C, 84.67; H, 5.99; N, 4.03. $C_{25}H_{21}ON$ Calc.: C, 85.47; H, 5.98; N, 3.98%. HRMS. Found: 351.1623. $C_{25}H_{21}ON^+$ Calc.: 351.1623.

5.13. Pyrrolinone 11f and disulfide 12f

Pyrrolinone **11f** and disulfide **12f** were obtained under similar conditions as above from **4f** after treatment of the residue of the reaction in boiling pyridine, followed by silica gel chromatography. Elution with petroleum ether:ethyl acetate (90:10) gave **11f** with a 50% yield as a viscous oil. IR ($CHCl_3$): ν 1670 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.46–7.06 (m, 15H, Ar), 5.41 (s, 1H, CH), 3.80 (m, 1H, NCH), 2.85 (m, 1H, NCH), 2.45 (q, 2H, CH_2S), 1.68–1.40 (m, 6H, $3CH_2$), 1.31 (t, 1H, SH) ppm. ^{13}C NMR: δ 170.27 (CO), 152.47–127.97 (C=C, Ar), 66.92 (CH), 40.38 (NCH_2), 33.54 (CH_2SH), 27.97, 25.57, 24.48 ($3CH_2$). HRMS. Found: *m/e* 413.1812. $C_{27}H_{27}NOS$ (M^+) Calc.: 413.1813. Elution with petroleum ether:ethyl acetate (80:20) gave **12f** as an oil with a 12% yield. IR ($CHCl_3$): ν 1670, 1600 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.48–7.02 (m, 15H, ArH), 5.38 (s, 1H, CHPh), 3.79 (m, 1H, NCH), 2.81 (m, 1H, NCH), 2.61 (t, 2H, CH_2S), 1.71–1.35 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.41 (CO), 152.64, 135.71 (C=C), 133.14–128.11 (Ar), 67.08 (CHPh), 40.56, 38.94, 28.97, 28.28, 25.92 ($5CH_2$) ppm. MS. Found: *m/2e* 412. $C_{54}H_{52}N_2O_2S_2^+$ Calc.: 824.

5.14. Pyrroline 11g and disulfide 12g

Pyrroline **11g** and disulfide **12g** were obtained as above from **4g**. Silica gel chromatography of the residue of the reaction first gave with petroleum ether:ethyl acetate as eluent (80:20) compound **11g** with a 7.5% yield as an oil. IR ($CHCl_3$): ν 1670 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.40–7.25 (m, 10H, ArH), 4.54 (q, 1H, $CHCH_3$), 1.73–1.59 (m, 4H), 1.53–1.42 (m, 2H), 1.29 (t, 1H, SH), 1.13 (d, 3H, $CHCH_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.17 (CO), 153.76, 135.05 (C=C), 131.60–127.90 (Ar), 57.32 ($CHCH_3$), 40.08, 33.65, 28.20, 25.70, 24.54 ($5CH_2$), 17.15 (CH_3). HRMS. Found, 351.1658 $C_{22}H_{25}NOS^+$ Calc.: 351.1656. Elution with petroleum ether:ethyl acetate (70:30) gave **12g** as an oil with an 18.5% yield. IR ($CHCl_3$): ν 1670 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.36–7.17 (m, 10H, ArH), 4.55 (q, 1H, $CHCH_3$), 3.81 (m, 1H, NCH), 3.22 (m, 1H, NCH), 2.68 (m, 2H, CH_2S), 1.81–1.67 (m, 4H), 1.56–1.41 (m, 2H), 1.20 (d, 3H, $CHCH_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.63 (CO), 153.83, 133.06 (C=C), 131.63–127.88 (Ar), 57.33 (CHPh), 40.12, 38.81, 28.90, 28.36, 25.90 ($5CH_2$). HRMS. Found: *m/2e* 350.1650. $C_{44}H_{48}N_2O_2S_2^+$ Calc.: 700.3312.

Table 2
Crystallographic data for **9**

Compound	$C_{27}H_{21}O_4NCr$
Crystal parameters	
Formula weight	475.5
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	15.316(4)
b (Å)	13.347(3)
c (Å)	11.103(11)
β (°)	96.51(6)
V (Å^3)	2255(17)
Z	4
ρ (g cm^{-3})	1.40
μ(Mo Kα) (cm^{-1})	5.26
Data collection	
Diffractometer	CAD4
Monochromator	Graphite
Radiation	Mo Kα
Scan type	ω–2θ
Scan range *q* (°)	0.8 + 0.34 tan θ
2θ range (°)	2–56
Number of reflections collected	2724
Number of reflections used ($I > 3\sigma(I)$)	2298
Refinement	
R	0.035
R_w	0.035
Absorption correction	DIFABS [22]
Minimum absorption; maximum absorption	0.73; 1.26
Secondary extinction parameter	No
Weighting scheme	Unit weight
Is parameters	363

[a] $R_w = [\Sigma_i W_i(F_o - F_c)^2 / \Sigma_i W_i F_o^2]^{1/2}$.

5.15. Crystal data

All pertinent information concerning every compound is summarized in Table 2. Corrections were made for Lorentz, polarization and absorption effects.

Table 3
Fractional coordinates for **9**

Atom	x	y	z	U_{eq}
Cr(1)	0.90204(7)	0.15862(4)	0.30543(9)	0.0380
N(1)	0.0175(2)	0.4661(3)	0.1347(3)	0.0468
O(1)	0.9099(2)	0.5624(2)	0.2136(3)	0.0430
O(11)	1.0284(3)	0.0215(3)	0.4471(3)	0.0656
O(12)	0.7573(3)	0.0799(3)	0.4378(4)	0.0761
O(13)	0.9483(3)	0.3040(3)	0.5045(3)	0.0716
C(1)	0.9375(3)	0.4710(3)	0.1823(3)	0.0381
C(2)	0.8781(3)	0.3991(3)	0.2021(4)	0.0390
C(3)	0.8066(3)	0.4517(3)	0.2488(3)	0.0381
C(4)	0.8293(3)	0.5495(3)	0.2563(4)	0.0408
C(5)	0.0127(4)	0.4427(5)	0.0057(5)	0.0646
C(6)	1.0826(3)	0.5421(5)	0.1739(5)	0.0620
C(11)	0.9782(3)	0.0720(3)	0.3907(4)	0.0465
C(12)	0.8121(3)	0.1093(4)	0.3857(4)	0.0510
C(13)	0.9295(3)	0.2489(4)	0.4285(4)	0.0483
C(21)	0.8877(3)	0.2919(3)	0.1779(3)	0.0393
C(22)	0.9729(3)	0.2487(4)	0.1796(4)	0.0454
C(23)	0.9828(3)	0.1462(4)	0.1544(4)	0.0506
C(24)	0.9089(3)	0.0847(4)	0.1274(4)	0.0531
C(25)	0.8265(3)	0.1260(4)	0.1286(4)	0.0526
C(26)	0.8146(3)	0.2274(4)	0.1534(4)	0.0465
C(31)	0.7262(3)	0.4051(3)	0.2864(4)	0.0412
C(32)	0.7250(3)	0.3635(4)	0.4013(4)	0.0526
C(33)	0.6515(4)	0.3139(4)	0.4313(5)	0.0622
C(34)	0.5767(4)	0.3080(4)	0.3507(6)	0.0666
C(35)	0.5759(3)	0.3508(4)	0.2365(6)	0.0642
C(36)	0.6493(3)	0.3999(4)	0.2068(4)	0.0537
C(41)	0.7879(3)	0.6423(3)	0.2916(4)	0.0429
C(42)	0.7159(3)	0.6411(4)	0.3589(5)	0.0521
C(43)	0.6759(3)	0.7295(4)	0.3857(5)	0.0560
C(44)	0.7076(4)	0.8198(4)	0.3520(5)	0.0616
C(45)	0.7797(5)	0.8228(4)	0.2891(6)	0.0739
C(46)	0.8192(4)	0.7346(4)	0.2599(5)	0.0654

The structure of **9b** was solved by standard Patterson–Fourier techniques. Computations were performed using CRYSTALS [23] adapted on a Microwax-II computer. Form factors and corrections for anomalous dispersion were from [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference Fourier map and their coordinates were refined with an overall refinable isotropic thermal parameter.

Fractional coordinates for 9 are given in Table 3.

Complete tables of anisotropic thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. Calculated and observed structure factors for **9a** are available from the authors.

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References

[1] E. Chelain, R. Goumont, L. Hamon, A. Parlier, M. Rudler, H. Rudler, J.C. Daran and J. Vaissermann, *J. Am. Chem. Soc., 114* (1992) 8088.
[2] E. Chelain, A. Parlier, M. Audouin, H. Rudler, J.C. Daran and J. Vaissermann, *J. Am. Chem. Soc., 115* (1993) 10568.
[3] H. Rudler, A. Parlier, R. Yefsah, B. Denise, J.C. Daran, J. Vaissermann and C. Knobler, *J. Organomet. Chem., 358* (1988) 245.
[4] T.S. Stevens, E.M. Creighton, A.B. Gordon and M. MacNicol, *J. Chem. Soc.,* (1928) 3193.
[5] R.W. Jemison, S. Mageswaran, W.D. Ollis, S.E. Potter, A.J. Pretty, I.O. Sutherland and Y. Thebtaranonth, *J. Chem. Soc., Chem. Commun.,* (1970) 1201.
[6] N.A. Bailey, S.E. Hull, G.F. Kersting and J. Morrison, *J. Chem. Soc., Chem. Commun.* (1971) 1429.
[7] S. Scheibye, J. Kristensen and S.O. Lawesson, *Tetrahedron,* (1985) 5061.
[8] W. Adam and L. Haseman, *Chem. Ber., 123* (1990) 1449.
[9] B.B. Snider, *Chem. Rev. 88* (1988) 793.
[10] W.T. Brady and Y.-Q. Gu, *J. Org. Chem. Soc., 54* (1989) 2838.
[11] O.K. Kim, W.D. Wulff and W.-Q. Jian, *J. Org. Chem., 58* (1993) 5572.
[12] L.S. Hegedus, R.W. Bates and B.C. Soderberg, *J. Am. Chem. Soc., 113* (1991) 923.
[13] P.D. Bartlett and R.E. McCluney, *J. Org. Chem., 48* (1983) 4165.
[14] D.-C. Zhao, A.D. Allen and T.T. Tidwell, *J. Am. Chem. Soc., 115* (1993) 10097.
[15] A.M. Lluch, F. Sanchez-Baeza, F. Camps and A. Messeguer, *Tetrahedron Lett.,* (1991) 5629.
[16] B. Cross, R.L. Arotin and C.F. Ruopp, *J. Heterocycl. Chem., 17* (1980) 905.
[17] H.V. Patel., K.A. Vyas, S.P. Pandey and P.S. Fernandes, *Synth. Commun., 22* (1992) 3081.
[18] A. Schonberg, K.H. Brosowski and E. Singer, *Chem. Ber., 95* (1962) 2144.
[19] H. Rudler et al., *Organometallics,* in press.
[20] A. Padwa, M. Akiba, C.S. Cou and L. Cohen, *J. Org. Chem., 47* (1982) 183.
[21] A. Padwa and F.R. Kinder, *J. Org. Chem., 58* (1993) 21, and references cited therein.
[22] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 159.
[23] D.J. Watkins, J.R. Carruthers and P.W. Betteridge, *CRYSTALS User Guide,* Chemical Crystallography Laboratory, University of Oxford, Oxford, 1985.
[24] *International Tables for X-ray Crystallography,* Kynoch, Birmingham, 1974.