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# (Acylamino)carbene Complexes: Synthesis, Structure, and Reactivity[1]

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Fischer type aminocarbene complexes of chromium, molybdenum and tungsten undergo N-acylation under DMAP catalysis followed by decarbonylation affording tetracarbonyl ((acylamino)carbene) chelates. These complexes are characterized by a short metal–carbene and a long metal–oxygen bond in the chelate ring. A remarkable chemoselectivity is observed upon reaction with alkynes which is governed by the metal and the N-substitution pattern and which may be rationalized in terms of a stereoselective alkyne insertion into the metal–carbene bond. $(CO)_4Cr{=}C(p\text{-}Tol)NRCOC(CH_3)_3$ prefers *E* insertion leading either to carbene annelation (indene, naphthalene derivatives) or to double alkyne insertion products (phenol ester). The molybdenum analogues add the alkyne to give presumed *Z*-alkenylcarbene intermediates, reasonable precursors for the isolated pyrrol and pyrrolone cycloaddition products.

Fischer carbene complexes **1** as applied to organic synthesis represent valuable synthons for carbene ligands substituted by donor substituents Do.[3] With the ligand and metal kept constant, the properties and reactivity of complexes **1** depend strongly on the carbene substituent Do. For example, the reaction of **1a**, in which the carbene carbon is substituted by an aryl and an alkoxy group (Do = OR), with alkynes leads in many cases to a benzannelation of the aryl group. In contrast, amino analogues **1b** (Do = $NR_2$) generally prefer to give products containing the indane nucleus.

A mechanistic rationale for this discrepancy starts with the rate-determining loss of CO from **1a** followed by insertion (either concerted or stepwise)[4] of the alkyne to give a new *E*-alkenylcarbene complex **2a**. Subsequent CO insertion would give vinylketene derivative **3**, which could suffer electrocyclic ring closure and tautomerization to give isolated phenolic products **4** (Scheme I). These transformations have been applied to the syntheses of medicinally interesting natural products including vitamins K and E, anthracycline derivatives, and psoralen analogues.[5]

These reactions proceed at synthetically useful rates in the temperature range 45–75 °C; in contrast, similar reactions[6] of amino-substituted analogues **1b** with alkynes usually require higher temperatures,[7] consistent with the stronger donor character of amino groups[8] leading to an increased back-bonding of the metal to the carbonyl ligands expressed in canonical form **2′**. Furthermore, at the stage of **2** the superior donating ability of the amino substituent apparently strengthens the metal–CO bonds,[9] reducing the propensity for CO insertion in general[10] and leading to coupling of carbons a and b and finally to the isolation of products containing the indane nucleus.[11]

It occurred to us that the donor capability of the nitrogen in aminocarbene complex **5** could be reduced by introduction of a strongly electron-withdrawing group, such as a carbonyl function.[8] Moreover, the oxygen of the amido group in **6** would be ideally situated to replace a CO ligand, leading to chelate **7** (Scheme II); chelate complexes had been shown to be excellent substrates for the benzannelation with alkynes.[7] We have already communicated our preliminary realization of these expectations in the chromium series[12] and the surprising result that the four CO ligands of **7** exchange on the NMR time scale. Herein we report our studies in full, including Mo and W analogues of **7**. Subsequent to the inception of our work, two isolated reports of the synthesis of (acylamino)carbene complexes have appeared.[13] Other efforts have led to the isolation of iminocarbene ("azallenyl") complexes resulting from double acylation.[14] Iminocarbene ligands bearing a different substitution pattern have been shown to undergo heteroannelation or formal [3 + 2] cycloaddition upon reaction with alkynes to give pyrrole or pyridine derivatives.[10d-f]

**Preparation of (Acylamino)carbene Complexes.** Our search for reagents suitable for the acylation of aminocarbene complexes began with use of the isolobal analogy[15] between the $M(CO)_5$ fragment and an oxygen

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[2] NSF NATO Postdoctoral Fellow, 1988–9.

[3] Leading references: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1987; Vol. 1. (c) Hegedus, L.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Yoshitaka, S. *J. Am. Chem. Soc.* **1990**, *112*, 1109. (d) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433.

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[5] (a) Dötz, K. H.; Pruskil, I.; Mühlemeier, J. *Chem. Ber.* **1982**, *115*, 1278. (b) Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732. (c) Dötz, K. H.; Popall, M. *Chem. Ber.* **1988**, *121*, 665. Wulff, W. D.; Xu, Y.-C. *J. Am. Chem. Soc.* **1988**, *110*, 2312. (d) Wulff, W. D.; McCallum, J. S.; Kunng, F.-A. *J. Am. Chem. Soc.* **1988**, *110*, 7419.

[6] Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915.

[7] Variants involving chelate complexes or intramolecular cyclizations: (a) Dötz, K. H.; Popall, M.; Müller, G. *J. Organomet. Chem.* **1987**, *334*, 57. (b) Dötz, K. H.; Erben, H.-G.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 692. (c) Dötz, K. H.; Schäfer, T.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 176.

[8] Exner, O. In *Correlation Analysis in Chemistry: Recent Advances*; Chapman, N. B.; Shorter, J., Eds.; Plenum: New York, 1978; p 439.

[9] For similar considerations, see: Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070.

[10] In some cases, alkyne/aminocarbene coupling may also either be accompanied by CO insertion or proceed without benzannelation: (a) Rudler, H.; Parlier, A.; Yefsah, R.; Denise, B.; Daran, J. C.; Vaissermann, J.; Knobler, C. *J. Organomet. Chem.* **1988**, *358*, 245. (b) Denise, B.; Goumont, R.; Parlier, A.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Organomet. Chem.* **1989**, *377*, 89. (c) Audouin, M.; Blandinieres, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23. (d) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251. (e) Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *389*, C1; *391*, C7. (f) Aumann, R.; Heinen, H.; Krüger, C.; Betz, P. *Chem. Ber.* **1990**, *123*, 599. (f) Dötz, K. H.; Weber, R. *Chem. Ber.* **1991**, *124*, 1635.

[11] For earlier observations, see: Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *101*, 2059.

[12] Dötz, K. H.; Grotjahn, D. B.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1384.

[13] (a) Wulff, W. D.; Dragisich, V. G.; Huffman, J. C.; Kaesler, R. W.; Yang, D. C. *Organometallics* **1989**, *8*, 2196. (b) Hegedus, L. S.; Schultze, L. M.; Montgomery, J. *Ibid.* **1989**, *8*, 2189.

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[15] (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (b) Stone, F. G. A. *Ibid.* **1984**, *23*, 89.

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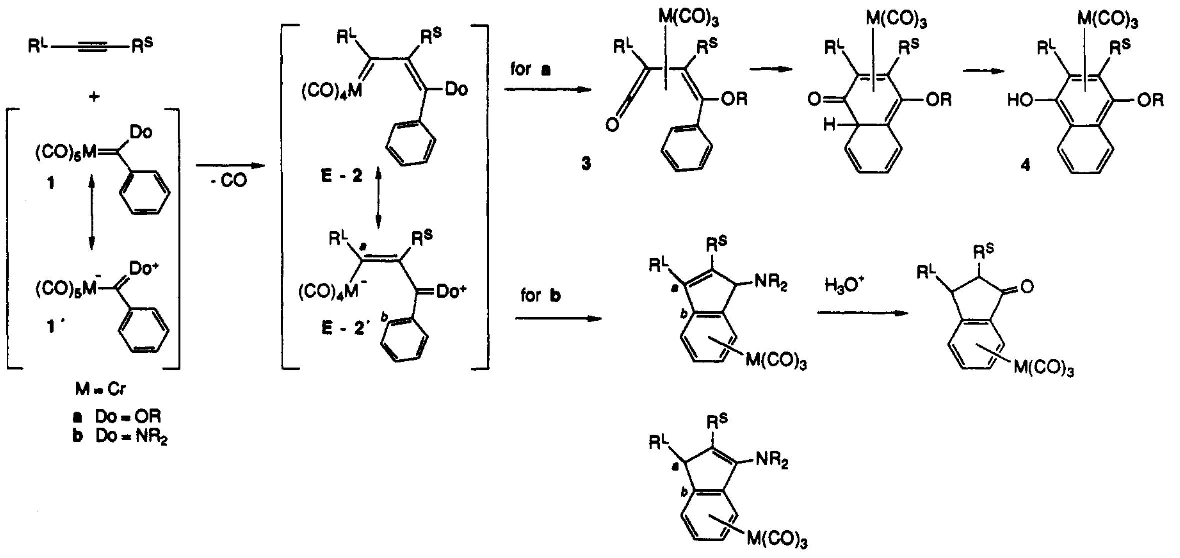
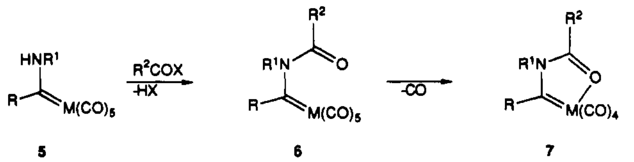
**Scheme I. Carbene–Alkyne Annelation**



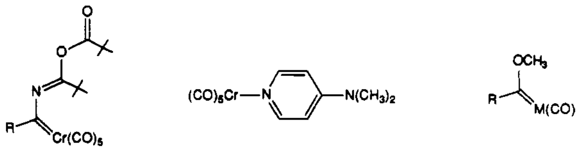
**Scheme II**



5 6 7

$R^2 = CH_3, OC(CH_3)_3$
$X = Cl\ , O_2COC(CH_3)_3$

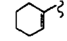
**Chart I**



8 a:R = p-Tol b:R = Ph

9

10

| 10 | R | M |
|---|---|---|
| a | p-Tol | Cr |
| b |  | Cr |
| c | $CH_3$ | Cr |
| d | p-Tol | Mo |
| e | $2\text{-}CH_3O\text{-}C_6H_4$ | Mo |
| f | Ph | W |
| g | Ph | Mo |

atom, which led us to compare the C=M(CO)$_5$ moiety with a C=O group. With such an analogy in mind, we sought reagents which had been shown to acylate carboxylic acid amides, preferably under the mildest possible conditions (e.g., at room temperature or below) to avoid further reactions or even destruction of the products. In this regard, many of the known acylations of carboxylic acid amides[16a] to produce imides seemed to proceed under harsh conditions. We found that in our first attempt to synthesize chromium (acylamino)carbene complexes **6** or **7**, the amino(4-methylphenyl)carbene complex **5a** did not react to a detectable extent with $(CH_3)_3CCOCl$ (1.10 equiv) in the presence of $Et_3N$ (1.18 equiv) within 5 min; however, as we recently noted,[17] addition of the potent acylation catalyst 4-(*N*,*N*-dimethylamino)pyridine (DMAP)[18] to the mixture led within 5 min to the production of considerable quantities of a new orange complex, as seen on TLC. However, even after an additional 3 h, the reaction had not progressed further. Full consumption of **5a** could be effected only by adding additional $(CH_3)_3CCOCl$ (0.9 equiv) along with $Et_3N$ (1.2 equiv) and DMAP (0.03 equiv); subsequent column chromatography afforded the orange complex, which to our surprise (but consistent with the requirement of 2 equiv of acid chloride) turned out to be the bisacylated compound **8a** (81%) and a more polar, dark red product (ca. 10%), the IR spectroscopic properties of which, in particular, led to its tentative identification as chelate complex **7** (see Table I). When this reaction was repeated with greater initial quantities of $(CH_3)_3CCOCl$ (2.2 equiv) and $Et_3N$ (2.2 equiv), clean formation of **8a** (87%) occurred within 2 h, **7** being undetectable in the crude reaction mixture. The catalytic effect of DMAP in this transformation is dramatically illustrated by the report that 57% of pentacarbonyl[amino(phenyl)methylene]chromium is recovered (and 41% of **8b** is isolated) after treatment with $(CH_3)_3CCOCl$ (2.5 equiv) and $Et_3N$ (3.0 equiv) for 15 h at 50 °C[14] (Chart I).

It was obvious from our first result that the reactivity of the acylating agent had to be modulated to allow selective monoacylation. In that event, further experimentation with the carboxylic acid anhydride $(CH_3CO)_2O$ as acylating agent for **5a** under DMAP catalysis revealed that the dark red acetaminocarbene chelate **7a** (42–60%) was the only isolated carbene-containing product even in the presence of 2 equiv of $(CH_3CO)_2O$. A similar reaction of the molybdenum analogue **5d** gave **7g** (63%). Compound **7a** as well as the other chelate complexes of chromium described below as solids can be handled briefly in air at room temperature and show unexceptional analytical data, except that at room temperature the three signals expected for the four carbonyl ligands are utterly absent in the $^{13}C$ NMR spectrum. The molybdenum analogues are more thermolabile but their four CO ligands do not interchange on the NMR time scale. Monitoring of the acetylation reaction by TLC showed the rapid consumption of yellow **5a** to give a new orange compound which we presume to be the pentacarbonyl[acetamino(4-methylphenyl)methylene]chromium complex. Even before all of **5a** was consumed, however, red **7a** had already appeared in the mixture. Toward the end of the decarbonylation reaction

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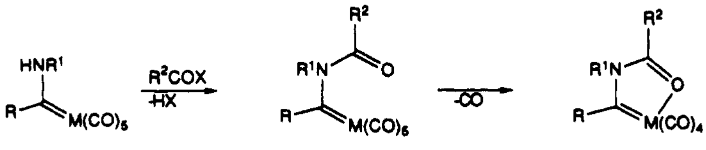
[16] See references in: March, J. D. *Advanced Organic Chemistry*, 3rd Ed.; Wiley: New York, 1985; (a) p 379, (b) pp 346, 370.

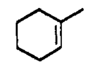
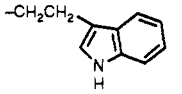
[17] Dötz, K. H.; Grotjahn, D. B.; Harms, K. *J. Organomet. Chem.* 1989, *375*, C47.

[18] Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 569.

Table I. Monoacylation of Aminocarbene Complexes



**5** **6** **7**

| start. mat. | metal M | R | R¹ | R² | condition[a] | acylation product | yield, % |
|---|---|---|---|---|---|---|---|
| **5a** | Cr | *p*-Tol | H | $CH_3$ | A | **7a** | 60 |
| **5a** | Cr | *p*-Tol | H | $OC(CH_3)_3$ | B | **7b** | 83 |
| **5b** | Cr | Ph | $CH_3$ | $OC(CH_3)_3$ | C | **7c** | 57 |
| **5b** | Cr | Ph | $CH_3$ | $CH_3$ | D | *d* | |
| **5c** | Cr | $CH_3$ | H | $OC(CH_3)_3$ | E | **6a** | 80 |
| **10**[b] | Cr | *p*-Tol | $CH_2Ph$ | $OC(CH_3)_3$ | B | **7d** | 76 |
| **10a** | Cr | *p*-Tol | $C(CH_3)_3$ | $OC(CH_3)_3$ | B | *c* | |
| **10b** | Cr |  | $CH_2Ph$ | $OC(CH_3)_3$ | B | **7e** | 76 |
| **10c** | Cr | $CH_3$ |  | | F | 11 | 54 |
| **10c** | Cr | $CH_3$ | $CH_2Ph$ | | A | *c* | |
| **5d** | Mo | *p*-Tol | H | $OC(CH_3)_3$ | G | **7f** | 33 |
| **5d** | Mo | *p*-Tol | H | $CH_3$ | H | **7g** | 63 |
| **5e** | Mo | *p*-Tol | $CH_3$ | $OC(CH_3)_3$ | G | **7h** | 27 |
| **5f** | Mo | Ph | $CH_3$ | $OC(CH_3)_3$ | G | **7i** | 50 |
| **5g** | Mo | Ph | $C(CH_3)_3$ | $OC(CH_3)_3$ | I | *c* | |
| **10d** | Mo | *p*-Tol | $CH_2Ph$ | $OC(CH_3)_3$ | G | **7j** | 44 |
| **10e** | Mo | 2-$CH_3O$–$C_6H_4$ | $CH_3$ | $OC(CH_3)_3$ | G | **7k** | 48 |
| **10**[f] | W | Ph | $CH_2Ph$ | $OC(CH_3)_3$ | J | **6b** | 71 |

[a] A = $(CH_3CO)_2O$ (1.49 equiv), $Et_3N$ (1.46 equiv), DMAP (0.1 equiv), $Et_2O$, 5.5 h; B = $BOC_2O$ (2–2.5 equiv), DMAP (0.1 equiv), $Et_2O$, room temperature, 8–16 h; C = same a B but with only 1.3 equiv of $BOC_2O$; D = same as A but 2 weeks; E = same as B but in $CH_2Cl_2$ under 2 atm of CO; F = same as B but with twice as much reagent and total time 3 days; G = same as B but at −15 to 0 °C; H = $(CH_3CO)_2O$ (1.23 equiv), *i*-$Pr_2NEt$ (1.54 equiv), DMAP (0.1 equiv), $Et_2O$, −15 °C for 7 h, 0 °C for 3 h; I = same as G but allowed to warm to room temperaure. J = same as B but with 0.06 equiv of DMAP and within 1.5 h. [b] Aminolysis of **10** carried out with the appropriate amine to give crude **5**, suitable for acylation; yields are for both steps. [c] No evidence of acylation after 12 h. [d] No evidence of acylation after 2 weeks. [e] No evidence of acylation at −15 °C, and **5g** was destroyed after warming to room temperature. [f] **10f** = $(CO)_5WC(OC_2H_5)C_6H_5$.

minor amounts of a yellow compound were seen, which after its isolation was tentatively identified by $^1H$ NMR and IR spectral data as DMAP·$Cr(CO)_5$ (**9**).

Subsequent to the completion of this work a similar reaction of pentacarbonyl[amino(phenyl)methylene]chromium was reported to give an acetaminocarbene complex of type **6**.[13a] However, from the reported color, IR absorption frequencies, mass spectral fragmentation, and combustion data for the product, we concluded (and the authors have since concurred)[19] that the product was in fact the tetracarbonyl chelate of type **7**. In reactions related to the conversion of **5** to **8**, Wulff's group observed the formation of **9** as well and suggested that the carbene ligand is displaced from the metal by DMAP after N-acylation.

Our attempts to extend the scope of the acetylation reaction to *N*-alkyl-substituted aminocarbene complexes have failed. The reluctance of such complexes to undergo acetylation was dramatically underscored by the observation by TLC that a mixture of yellow **5b**, $(CH_3CO)_2O$ (1.5 equiv), $Et_3N$ (1.5 equiv), and DMAP (0.11 equiv) in $CH_2Cl_2$ showed no signs of giving orange or red-to-brown products of the type **6** or **7**, respectively, even after 2 weeks at room temperature. That the acylation reagent was still active after this time was demonstrated qualitatively by allowing an aliquot of the mixture to react with a sample of **5a**; by TLC the pentacarbonyl[acetamino(4-methylphenyl)methylene]chromium complex and the chelate **7a** could be seen within 0.5 h.

Clearly, we required a different acylating agent. We were intrigued by the *tert*-butoxycarbonyl (BOC) function because facile monoacylation of $RCONH_2$ using $(BOC)_2O$ under DMAP catalysis had been reported.[20] Furthermore, BOC groups could be expected to be easily removed from the amino nitrogens in the cyclization products.[21] Indeed, as most conveniently monitored by TLC, treatment of a wide variety of **5**[22] with 2 equiv of $(BOC)_2O$ and 0.1 equiv of DMAP at room temperature led to consumption of starting material within 3–6 h in the case of the chromium compounds and within 1.5 h in the case of the one tungsten analogue examined. The origin of this difference in reactivity is unclear. Because of the expected greater thermolability of the products the corresponding molybdenum analogues were acylated between −15 and 0 °C (within 3–6 h). Table I summarizes the synthetic results.

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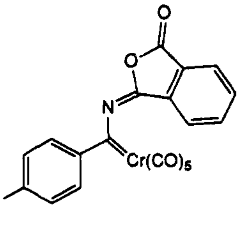
(19) Wulff, W. D. Personal communication.

(20) Grehn, L.; Gunnarsson, K.; Ragnasson, U. *Acta Chem. Scand., Ser. B* **1986**, 745.

(21) Carpino, L. A. *Acc. Chem. Res.* **1973**, *6*, 191.

(22) (a) A kinetic investigation of the reaction of amines with alkoxycarbene complexes **10** to give **5** in nonpolar solvents revealed that the rate of the aminolysis reaction is third-order in amine.[22b] Perhaps because of this result most workers have used up to 10-fold excesses of amine to make **5**, an untenable situation when one considers the synthesis of aminocarbene complexes bearing precious *N*-alkyl groups. We found that the aminolysis reaction of methoxycarbene complexes **10** (ca. 1 M in $Et_2O$) is complete within minutes either at room or dry ice temperatures using as little as 1.02 equiv of amine. Removal of solvent and the 1 equiv of $CH_3OH$ presumably released in this reaction under vacuum leave **5** in a form suitable for subsequent acylation. Moreover, we find that as in the acylation of amines under Schotten–Baumann conditions[16b] aqueous solutions of small, volatile amines can be conveniently used in aminolysis of alkoxycarbene complexes. (b) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367.

Chart II



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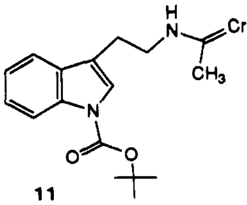

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Optimization of the acylation in the chromium series suggested that the utilization of less $(BOC)_2O$ or DMAP at the beginning of the reaction usually resulted in incomplete acylation of **5**, which could not be rectified by addition of more of the acylating reagents. We speculate that **7** or perhaps **6** once formed reacts[13a] readily with DMAP to give **9**, and thus efficient acylation requires relatively large amounts of $(BOC)_2O$ and DMAP at the outset. In all cases except that of **5c** and the one example of the tungsten series, TLC showed that even before all **5** had been acylated to **6**, considerable amounts of **7** were present in the mixture. In both exceptions mentioned above, acylation of **6a** or **6b**, respectively, proceeded smoothly, especially under CO atmosphere to suppress formation of the corresponding chelate complexes **7**. Attempts to force decarbonylation of **6a** or **6b** to go to completion led at best to production of the corresponding $M(CO)_6$, as identified by IR spectroscopy, and to low yields of unstable dark red or brown products tentatively identified as the presumed chelate complexes of type **7**.

Even $(BOC)_2O$/DMAP fails to acylate certain kinds of **5**. For example, substitution of the nitrogen with the bulky $(CH_3)_3C-$ group made it impossible to acylate (*tert*-butylamino)carbene complexes such as **5g**. This compound did not react to a detectable extent at −15 to 0 °C within 1 h, conditions under which all other molybdenum analogues of **5** were already acylated to a significant degree, and was destroyed when the mixture was stirred at room temperature. The chromium analogue showed no sign of being acylated after 12 h at room temperature. Furthermore, the methylcarbene complex **5c** underwent readily N-acylation whereas its N-alkylated cousins bearing an *N*-benzyl or *N*-3-indolylethyl side chain did not to any detectable extent. In these intractable cases, the sluggishness of acylation can be readily ascribed to steric hindrance about the nitrogen atom.[23] However, it is not so clear why N-benzylated compounds such as derived from **10a** or **10b** react readily with $(BOC)_2O$/DMAP whereas the (*N*-benzylamino)(methyl)carbene complex accessible from **10c** does not.[24] Attempts to increase the nucleophilicity of this aminocarbene complex by N-deprotonation with NaH or tertiary amines did not result in acylation.

We briefly screened other acylation reagents. A mixture of **5a** and $1,2\text{-}(COCl)_2C_6H_4$ (1.16 equiv) in THF retained the yellow color of **5a** for 15 min, but as $Et_3N$ (2.2 equiv) was added, the reaction mixture began to assume a red color which deepened in the ensuing 16 h. While the product of this reaction could not be isolated in a pure form because of apparent instability to chromatography,[25] on the basis of IR absorption of the reaction mixture ($A_1$ band at 2055 $cm^{-1}$, no peak in the vicinity of 2020 $cm^{-1}$) and in analogy with the reaction of aminocarbene complexes with monofunctional acid chlorides,[13,18,19] we formulate the compound as **12** (Chart II). The interaction of **5a** with $(COCl)_2$/catalytic DMF or $4\text{-}CH_3C_6H_4SO_2Cl$ at room temperature or with $C_6H_5NCO$/catalytic DMAP in THF at room temperature then under reflux led to destruction of the carbene complex without production of identifiable products. In summary, the $(BOC)_2O$/DMAP system remained the reagent of choice for the formation of chelate complexes **7**.

**Spectroscopic Characterization.** First indications on the nature of acylation products **7** came from comparison of the IR spectra with those of other tetracarbonyl carbene chelate complexes;[26] a particularly diagnostic peak is the moderately strong $A_1$ absorption, which for the closely related pair **6a** and its tetracarbonyl chelate analogue **7l** appears at 2062 and 2023 $cm^{-1}$, respectively. The bonding of the amide carbonyl oxygen to the metal also reduces the C=O bond order, as evidenced by absorptions of **6a** and **7l** at 1771 and 1673 $cm^{-1}$, respectively.[27]

In all cases studied so far, chelation occurs via the acylamino moiety. Although chelation of the oxygen atom in (2-methoxyphenyl)methylene complexes is well-knwon,[26] the chemical shift of the methoxy protons in **7k** ($\delta$ 3.83 ppm) indicates that the methoxy function is uncoordinated. Unchelated complexes **6a** and **6b** each exist as two rotamers in ratios of 1.2 and 6 to 1, respectively, as determined by integration of their $^1H$ NMR spectra.

However, the $^{13}C$ NMR spectra data for **7** were most informative for structural identification and evaluation of chemical reactivity. At temperatures between −30 and +40 °C a sharp signal for the carbene carbon appears in the range $\delta$ 311–330 ppm for chromium complexes and 302–313 ppm for the molybdenum analogues. These chemical shifts are downfield from those of corresponding aminocarbene complexes ($\delta$ ca. 280) and shifted toward those of alkoxy analogues ($\delta$ 330–350),[28] which is consistent with a reduced donor capacity of the nitrogen upon acylation. The distribution of the four CO ligands into two unique CO ligands trans to carbene and carbonyl oxygen and two equivalent CO ligands cis to each of these ligands was revealed by the appearance of three signals in the intensity ratio of ca. 1:1:2 with chemical shifts $\delta$ 231–237 (M = Cr) and 225–228 (M = Mo) for the trans CO ligands and 216–217 (M = Cr) and 207.1–208.3 (M = Mo) for the cis CO ligands. Other resonances at $\delta$ 161, 90, and 28 ppm could be readily assigned to the $NCO_2C(CH_3)_3$ moiety.

Surprisingly, at temperatures near 0 °C the three peaks for the $Cr(CO)_4$ fragment in **7** are quite broad and near room temperature they are invisible, whereas all other signals remain sharp. For the corresponding molybdenum analogues even at room temperature all $^{13}C$ resonances were sharp, although the *heights* of the three signals for the $Mo(CO)_4$ fragment were noticeably less than at −30 °C. Even at 60 °C the spectrum of **7d** in $C_6D_5CD_3$ showed no signal in the region $\delta$ 200–240 ppm other than a small but growing sharp resonance at 211 ppm, attributable to the ubiquitous decomposition product $Cr(CO)_6$. However, by stirring a sample of **7d** for 2 days under 1 atm of $^{13}CO$, we could obtain approximately 20-fold enrichment over nat-

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[23] Aminolysis of alkoxycarbene complexes of chromium is hampered by the increasing bulk of the amine: Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578.

[24] Cf. conformational analysis of phenyl-, vinyl-, methylcyclohexenes: Eliel, E. L.; Manoharan, M. *J. Org. Chem.* **1981**, *46*, 1959.

[25] (a) Isophthalimides are known to be much more readily cleaved by nucleophiles than phthalimides:[25b] (b) Kukolja, S.; Lambert, S. R. *J. Am. Chem. Soc.* **1975**, *97*, 5582.

[26] (a) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267. (b) Dötz, K. H.; Erben, H.-G.; Staudacher, W.; Harms, K.; Müller, G.; Riede, J. *Ibid.* **1989**, *355*, 177.

[27] Robinson, N. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *349*, 209.

[28] Mann, B. E.; Taylor, B. F. $^{13}C$-NMR Data for Organometallic Compounds; Academic Press: London, 1981.

**Table II. Bond Lengths (Å) and Bond Angles (deg) of 7b**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cr1–O1 | 2.1439 (27) | Cr1–C1 | 1.9851 (36) | Cr1–C14 | 1.8830 (49) | Cr1–C15 | 1.8063 (40) |
| Cr1–C16 | 1.8918 (50) | Cr1–C17 | 1.8761 (48) | O1–C9 | 1.2296 (51) | O2–C9 | 1.3110 (48) |
| O2–C10 | 1.4841 (52) | O3–C14 | 1.1441 (59) | O4–C15 | 1.1636 (48) | O5–C16 | 1.1393 (62) |
| O6–C17 | 1.1465 (60) | N1–C1 | 1.3739 (47) | N1–C9 | 1.3626 (58) | C1–C2 | 1.4639 (54) |
| C2–C3 | 1.3817 (53) | C2–C7 | 1.3806 (58) | C3–C4 | 1.3792 (65) | C4–C5 | 1.3613 (70) |
| C5–C6 | 1.3779 (68) | C5–C8 | 1.5063 (69) | C6–C7 | 1.3744 (60) | C10–C11 | 1.5098 (72) |
| C10–C12 | 1.4955 (62) | C10–C13 | 1.5064 (68) | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O1–Cr1–C1 | 77.76 (12) | O1–Cr1–C14 | 94.51 (16) | O1–Cr1–C15 | 178.59 (1) |
| O1–Cr1–C16 | 94.10 (16) | O1–Cr1–C17 | 92.15 (17) | C1–Cr1–C14 | 86.13 (1) |
| C1–Cr1–C15 | 100.83 (16) | C1–Cr1–C16 | 90.24 (16) | C1–Cr1–C17 | 169.57 (2) |
| C14–Cr1–C15 | 85.42 (19) | C14–Cr1–C16 | 169.74 (18) | C14–Cr1–C17 | 92.11 (2) |
| C15–Cr1–C16 | 85.83 (19) | C15–Cr1–C17 | 89.26 (20) | C16–Cr1–C17 | 93.14 (2) |
| Cr1–O1–C9 | 112.18 (26) | C9–O2–C10 | 122.89 (32) | C1–N1–C9 | 116.74 (3) |
| Cr1–C1–N1 | 113.56 (26) | Cr1–C1–C2 | 132.75 (24) | N1–C1–C2 | 113.47 (3) |
| C1–C2–C3 | 119.84 (35) | C1–C2–C7 | 122.52 (35) | C3–C2–C7 | 117.44 (3) |
| C2–C3–C4 | 120.15 (39) | C3–C4–C5 | 122.68 (43) | C4–C5–C6 | 116.91 (4) |
| C4–C5–C8 | 122.14 (45) | C6–C5–C8 | 120.95 (44) | C5–C6–C7 | 121.42 (4) |
| C2–C7–C6 | 121.28 (41) | O1–C9–N1 | 119.70 (36) | O1–C9–O2 | 126.25 (4) |
| N1–C9–O2 | 114.04 (36) | O2–C10–C11 | 109.03 (38) | O2–C10–C12 | 102.64 (3) |
| O2–C10–C13 | 108.62 (34) | C11–C10–C12 | 112.30 (40) | C11–C10–C13 | 112.20 (4) |
| C12–C10–C13 | 111.55 (41) | Cr1–C14–O3 | 173.14 (43) | Cr1–C15–O4 | 177.92 (4) |
| Cr1–C16–O5 | 172.49 (40) | Cr1–C17–O6 | 175.80 (44) | | |

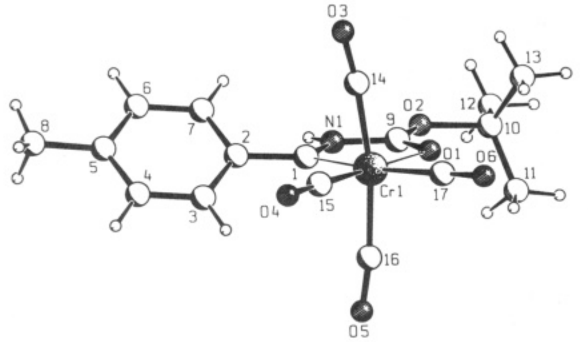


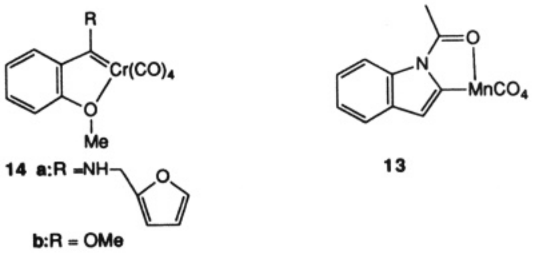
**Figure 1.** Crystal structure of **7b**.

ural abundance,[29] which allowed us to detect the broadened carbon resonances for the $Cr(CO)_4$ fragment near the coalescence point, before deterioration of **7d** became significant.

**Crystallographic Study of 7b.** An X-ray crystal structure of the aminocarbene chelate complex **7b** (Figure 1, Table II) shows a planar five-membered chelate ring (C1–N1–C9–O1–Cr1) (none of the five atoms deviates more than 0.017 Å from the best plane), thus resembling those complexes in which the chelated heteroatom is an oxygen.[26] The directly bonded atoms of the substituents on the ring all lie close to the plane; the biggest deviation is found for C17, which is 0.124 Å out of the chelate plane. Unfortunately, we have no good model compound with which to compare the length of the C═O bond in the acylamino group [1.230 (5) Å], but this value is in line with that for the *N*-acylindole–$Mn(CO)_4$ complex **13**[27] (Chart III).

Focusing on the metal, the ligands on chromium are in a distorted octahedral environment, as illustrated by the C1–Cr–O1 angle of 77.8°. The Cr–carbene bond length (1.985 (4) Å) is rather short (cf. in **10** 2.00–2.05 Å,[30] in **5** >2.08 Å,[30] in **14** 2.00–2.06 Å[26]). These comparisons point to a relatively weak donation of the carbene moiety to the metal, as a result of N-acylation. The effect of the carbene on the bonding of the CO trans to it is slight: The Cr–C17 distance of 1.876 (5) Å is not significantly shorter than the Cr–C14 and Cr–C16 bond lengths. On the other hand, the relatively strong σ-donor character of the acylamino substituent is revealed by the short Cr–C15 distance of 1.806 (4) Å. The distance between acylamino oxygen O1 and the metal (2.144 (3) Å) is greater than the Cr–O bond length in $(CO)_5Cr(THF)$ [2.123 (3) Å][31] but shorter than those in **14a** [2.173 (2) Å] or **14b** [2.183 (2) Å],[26] suggesting a moderately weak Cr–O bond.

**Chart III**



**Reactivity of (Acylamino)carbene Chelates 7 toward Alkynes.** Our observation by $^{13}C$ NMR spectroscopy that the chelate ring in chromium derivatives **7** opens readily suggested that the binding of added alkynes should be facile, leading to **2** (Scheme I). Furthermore, the relatively downfield chemical shifts of the carbene carbons in **7** intimated that at the stage of **2** CO insertion should take place, leading ultimately to amino derivatives of **4**. In the experiment, N-unalkylated complex **7b** reacted with 3-hexyne (2.0 equiv) in THF within 2 h at 55 °C, conditions comparable to those for annelations involving alkoxycarbene complexes of chromium.[2,5] IR spectroscopy of the crude reaction mixture revealed the presence of an intense absorption attributable to $Cr(CO)_6$, and TLC indicated that one colorless major organic product was present, suggesting that at this point arene–$Cr(CO)_3$ complexes were absent. At this point in our investigation we were somewhat concerned about the potential sensitivity of electron-rich phenols such as **15** toward oxidation, and thus, before product isolation, we attempted to protect the phenolic moiety[32] by acetylation, most conveniently carried out under DMAP catalysis.[12] Under conditions under which phenols such as **19a**, **21a**, and **23a** were acylated (vide infra) the major organic product remained unchanged and so column chromatography of the resulting mixture was carried out to give oily **16a** (54%) as the only iden-

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(29) Casey, C. P.; Cesa, M. C. Organometallics **1982**, *1*, 87.

(30) Schubert, U. In *Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983.

(31) Schubert, U.; Friedrich, P.; Orama, O. *J. Organomet. Chem.* **1978**, *144*, 175.

(32) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981; pp 101–2.

Scheme III

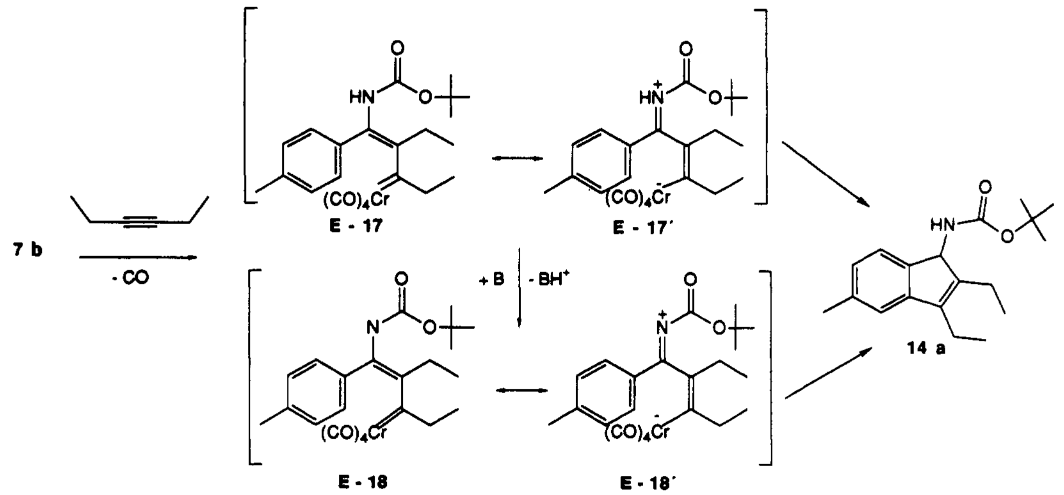
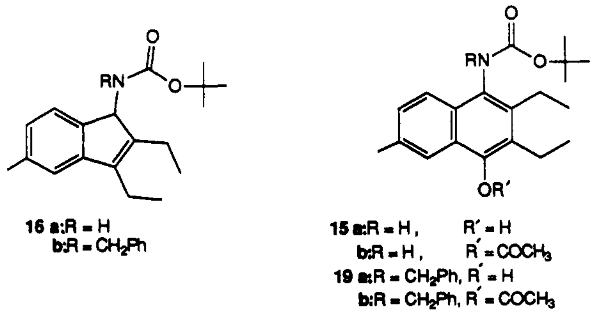


Chart IV



tifiable product[33] (Chart IV). The $^1H$ NMR spectrum of the compound showed sharp singlets for the $C(CH_3)_3$ and $CH_3$ groups and one broad signal for the NH proton. In the aromatic region three signals were visible with coupling patterns diagnostic for a 1,2,4-substituted benzene ring. These data and the appearance of two triplets at $\delta$ 0.54 and 1.01 ppm, corresponding to two $CH_2CH_3$ groups, clearly indicated that the carbene ligand of **7b** had been annelated by 3-hexyne. However, the parent ions in low- and high-resolution mass spectra of the compound were consistent with a combination of carbene and alkyne moieties *without* incorporation of CO, focusing our attention on structure **16a**. In the $^1H$ NMR spectrum of the product five one-proton signals, all but one well-resolved, remained unassigned. Most notable of these was a doublet of doublets ($J$ = 4.2 and 5.4 Hz) at $\delta$ 3.26 ppm, which was coupled to two mutually coupled ($J$ = 14.7 Hz) resonances at $\delta$ 1.85 and 1.64, which were each in turn coupled to the triplet at 0.54 ppm. We ascribe the signal at 3.26 ppm to the methine hydrogen of **16a**, which apparently enters into (an unusually large)[34] long-range coupling with the two diastereotopic protons of one of the two ethyl groups.

The reaction of **7b** with 3-hexyne indeed proceeded under conditions much milder than those necessary for other aminocarbene complexes; however, the obtention of **16a** and not **15** as a major product was contrary to our hopes. It occurred to us (Scheme III) that either the electron-withdrawing ability of the BOC function was insufficient to reduce back-bonding from Cr to CO (**17′**) or perhaps the pronounced electron-donating capability of the amino function that we wanted to suppress was restored by deprotonation at nitrogen (**18**) (Scheme III). An ideal way to block the latter pathway appeared to use N-alkylated substrates such as **7d**. Reaction of **7d** with 3-hexyne (2.0 equiv) in $C_6H_5CH_3$ at 55–60 °C was complete in 3 h. As determined by TLC, four major products had been formed; two of these were colorless, one was pale yellow and the fourth one was pale orange. IR spectroscopic examination of the mixture showed absorptions ascribable to arene–$Cr(CO)_3$ moieties and to $Cr(CO)_6$. On the assumption that the two colored compounds were $Cr(CO)_3$ complexes of the two colorless substances, we decided to simplify product isolation by intentionally demetalating residual complexes, for example by oxidation with Fe(III) reagents[5d] after protecting the OH moiety by acetylation. Thus, DMAP-catalyzed acetylation[12] and subsequent oxidation with $FeCl_3 \cdot 1.5DMF$[35] afforded two colorless products in a ratio of 5 to 1, as determined by NMR spectroscopy before radial chromatography.

The major product (56%) contained acetate and carbamate functions, as indicated by IR absorptions at 1759 and 1696 $cm^{-1}$, respectively, and showed a parent ion of the proper mass for CO insertion product **19b**. The NMR spectra of the major product were consistent with the assigned structure but showed two notable features. First, many peaks were doubled: for example, in the $^1H$ NMR spectrum of **19b** in $C_6D_6$, two singlets (ratio 8 to 1) ascribable to the $OC(CH_3)_3$ group could be seen at $\delta$ 1.14 and 1.34 ppm, respectively. This observation is consistent with the presence of two isomeric forms, presumably rotamers about the N–C bond of the amide linkage. Compounds **16b**, **19a,b**, **21a,b**, and **23a,b** all showed similar doubling of many NMR signals which precluded full assignments of overlapping peaks. A second feature presented by the $^1H$ NMR spectrum of **19b** gave additional structural insights. The $NCH_2Ph$ protons did not appear as two singlets in the region $\delta$ 4–5 ppm as expected of two rotamers of a planar structure. Rather, the signals for these protons appeared as two pairs of doublets, all with $J$ = ca. 14 Hz, at $\delta$ 5.05 and 4.43 for the major rotamers and 4.72 and 4.30 ppm for the minor rotamer. These data show that **19b** contains a stereogenic center. Inspection of molecular models suggests that for steric reasons the acetoxynaphthyl ring prefers to be orthogonal to the plane defined by the nitrogen and the carbonyl and methylene carbons. This

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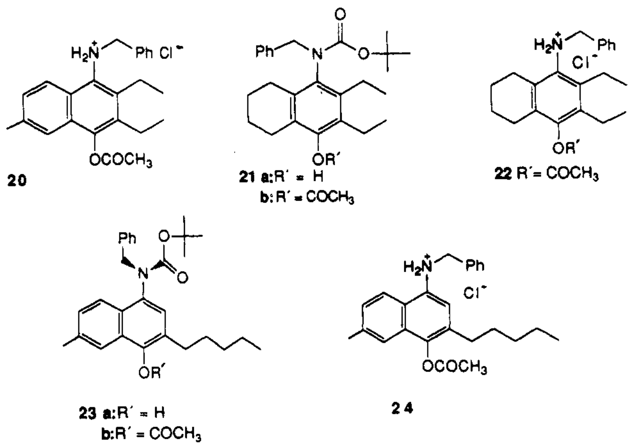
[33] Traces of other compounds could be seen by TLC in these and other reactions to be described in this section, but these compounds were never isolated in sufficient quantity and purity to allow their identification; we estimate that as much as 10% of the product could escape our analytical and purification procedures.

[34] Robinson, B. *Chem. Rev.* **1969**, *69*, 227.

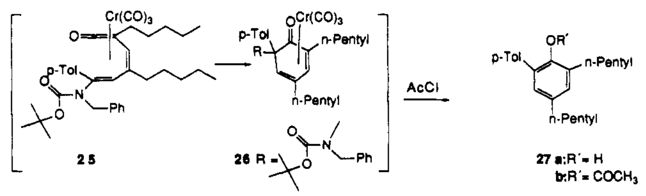
[35] Tobinaga, S.; Kotani, E. *J. Am. Chem. Soc.* **1972**, *94*, 309.

[36] Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

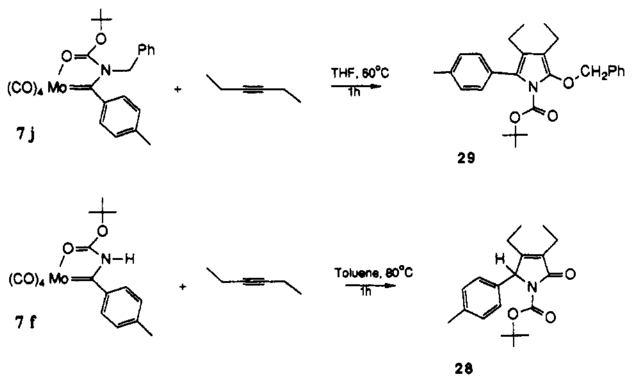
Chart V



Scheme IV



Scheme V



crowded situation may explain the ready loss of metal under the annelation reaction conditions. Treatment of **19b** with HCl in $Et_2O$[21] led to **20** in 79% yield. In stark contrast to the relatively complicated NMR spectra presented by **19b**, compound **20**, in which the BOC function is absent, displays only one set of $^1H$ NMR signals, most notably a two-proton singlet at $\delta$ 4.66 ppm attributable to the $NCH_2Ph$ moiety.

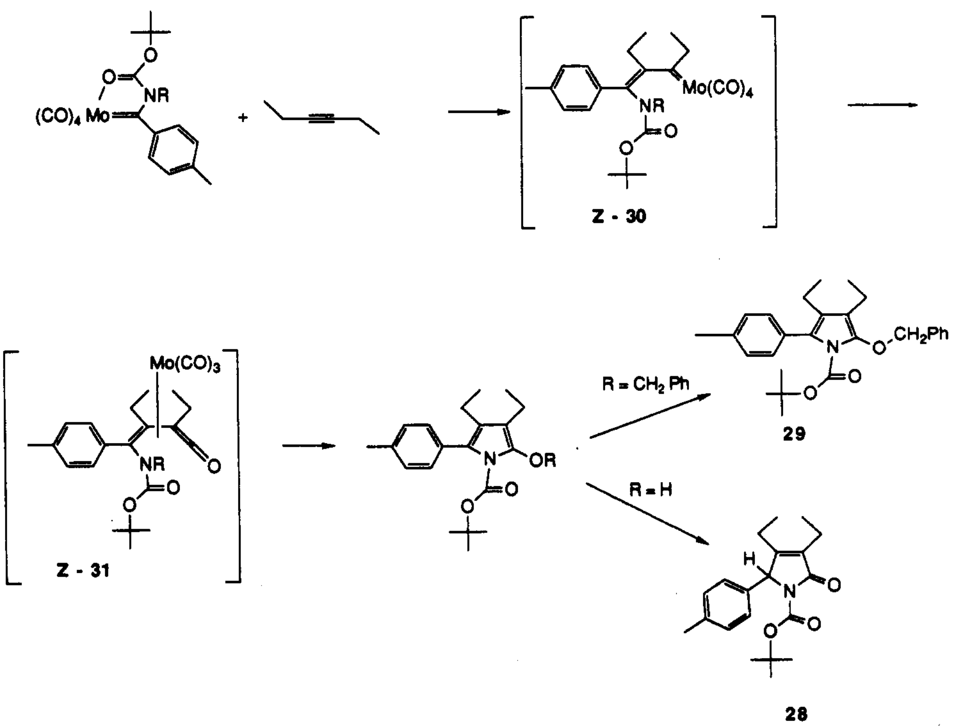
To see if annelation of **7** bearing alkenyl groups was possible, cyclohexenylcarbene complex **7e** was treated with 3-hexyne. As evidenced by TLC, two products were formed; the major one (in one experiment isolated and shown to be **21a**) was colorless whereas the minor one was pale yellow. Acetylation and oxidation of the mixture led to the isolation of only colorless oily acetate **21b** (67%).[33] The NMR spectral data for **21b** indicated that it, like **19b** (vide supra) existed as two amide rotamers (3:1 ratio), each in an "orthogonal" conformation. Congestion about the nitrogen was relieved by HCl cleavage[21] of the BOC group, giving salt **22**, the $^1H$ NMR spectrum showed a two-proton singlet at $\delta$ 4.51 attributable to the $NCH_2Ph$ moiety.

Reactions of $(CO)_5Cr$–carbene complexes with terminal alkynes proceed with high regioselectivity.[3] When **7d** was allowed to react with 1-heptyne two colorless oily products were obtained in 46 and 19% yields, respectively, after acetylation, oxidation, and chromatographic workup. The combustion and high-resolution mass spectral data for the major product were in accord with the expected structure **23b**, in which the position of the $(CH_2)_4CH_3$ group on the naphthalene ring is assumed on the basis of the analogous cyclizations of alkoxycarbene complexes.[3] However, the $^1H$ NMR spectra of **23b** in $CDCl_3$ were more complicated than those of **19b** and **21b** and allowed only confirmation of the presence of $CH_3CO_2$– and $CH_3$–aryl groups (singlets at $\delta$ 2.49 and 2.55), a BOC group (singlet at 1.46), and a $(CH_2)_4CH_3$ group. In the region $\delta$ 4.0–7.0 ppm broadened signals not readily ascribable to the orthogonal conformers suggested for **19b** and **21b** were seen. Comparison of molecular models of **23b** with those of **19b** and **21b** suggests that in **23b** the absence of an alkyl group on the naphthalene ring next to the bulky BOC–N–$CH_2Ph$ substituent may allow the latter to more easily adopt a coplanar conformation than in **19b** and **21b**. As in the case of **19b** and **21b**, HCl cleavage of **23b** led to salt **24**, the NMR spectra of which were considerably simplified (Chart V).

The $^1H$ NMR spectrum of the minor compound curiously lacked any peaks ascribable to any portion of the BOC–N–$CH_2Ph$ fragment and showed two mutually coupled two-proton doublets at $\delta$ 7.24 and 7.04 ppm, characteristic of the $CH_3C_6H_4$ moiety. From these data it was clear that the carbene ligand had been incorporated into the product with loss of the amino substituent and without annelation onto the aryl group. Two three-proton singlets at 2.15 and 1.90 ppm were consistent with the presence of $CH_3C_6H_4$– and $CH_3CO_2$– groups. The remaining signals, in particular two one-proton singlets at 7.19 and 7.12 and two two-proton triplets at 2.58 and 2.55 ppm suggested that *two* molecules of 1-heptyne had been incorporated into the product, forming an aromatic ring bearing two hydrogens meta or para to each other. Mechanistic considerations (Scheme IV) aided final identification of the product. Two successive regioselective[3] insertions of 1-heptyne into the metal–carbene bond of **7d** followed by CO insertion could lead to **25**. Pericyclic ring closure to **26** and reduction of the cyclohexadienone (probably by Cr(0)[3b]) may afford **27b** via acetylation of the intermediate phenol **27a**.

**Molybdenum (Acylamino)carbene Complexes.** The synthetic procedure which has been used in the preparation of chromium-based (acylamino)carbene complexes can be extended to the molybdenum series as well. Following this route the pentacarbonyl complexes **5d–g** have been modified into the tetracarbonyl chelates **7f–k**. The yields of the molybdenum chelate formation are significantly lower than those observed for analogous chromium complexes. To explore the role of the metal in carbene/alkyne coupling reactions complexes **7f** and **7j** have been allowed to react with 3-hexyne. The reaction occurs with cyclization of the alkyne, the carbene, and a carbonyl ligand and, after oxidative and chromatographic workup, affords moderate yields of dihydropyrrolone **28** and (benzyloxy)pyrrole **29**, respectively (Scheme V). In contrast to the reaction of chromium analogues with alkynes described above, no carbene annelation has occurred, as evidenced by $^1H$ NMR spectra which indicate a 1,4-disubstituted arene ring. For **28** two multiplets are observed for the methylene groups arising from the alkyne at $\delta$ 1.74–1.81 and 1.41–1.51 ppm, which indicates a stereogenic center, while a pair of well-resolved quartets and triplets for the ethyl substituents of **29** is compatible with the structure of a nonchiral compound. The formation of the pyrrole skeleton can be rationalized in terms of a primary alkyne insertion into the metal–carbene bond of **7j** to give **30**. The alkyne/carbene coupling appears to be stereoselective.

Scheme VI



While an *E*-alkenylcarbene intermediate is expected to finally undergo carbene annelation according to Scheme I, the *Z* isomer obviously leads to vinylketene *Z*-31 upon subsequent carbene/CO coupling. Finally, ring closure may afford pyrrole 29 or dihydropyrrolone 28, respectively (Scheme VI).

## Experimental Section

**General Considerations.** All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether were distilled from benzophenone ketyl. Dichloromethane and petroleum ether (bp 40–60 °C) were distilled from 5-Å molecular sieves and, when used for chromatography of complexes, were degassed by rapidly bubbling nitrogen through the solvent for 10 min. Toluene was washed with $H_2SO_4$, $H_2O$, and aqueous $NaHCO_3$, dried over $MgSO_4$, and distilled from $CaH_2$ under nitrogen. Most reactions were carried out in Schlenk tubes evacuated and filled with nitrogen that had been passed through molecular sieves (3–4 Å) and BTS catalyst. All reactions of 7 which required heating or prolonged reaction times were carried out in thick-walled glass tubes with stopcocks and teflon-lined screw-tops. These reaction mixtures were deoxygenated by applying the freeze–pump–thaw method (liquid nitrogen to room temperature) three times. Column chromatography of complexes was carried out in jacketed columns at temperatures of −40 to −20 °C using Merck silica gel, 0.063–0.200 mm. Radial chromatography was performed on a Chromatotron from Harrison Research, Inc.

Infrared spectra were measured on a Bruker IFS 88 FT-IR or on a Perkin-Elmer Model 281 spectrometer. Electron-impact mass spectra were recorded on a Varian Match 7A instrument, whereas high-resolution mass spectra were obtained from a Varian MAT 711. $^1$H and $^{13}$C NMR spectra were recorded on Bruker 300 or 400 MHz instruments operating at 300.1/400.1 or 75.5/100.6 MHz, respectively, in the indicated solvents using the residual protonated solvent resonance as a reference. Elemental analyses were carried out at the Fachbereich Chemie.

**Tetracarbonyl[(*N*-acetylamino)(4-methylphenyl)methylene-*C*,*O*]chromium (7a).** DMAP (36 mg, 0.30 mmol) was added to a solution of pentacarbonyl[amino(4-methylphenyl)methylene]chromium (**5a**)[37] (0.950 g, 3.05 mmol), $(CH_3CO)_2O$ (0.43 mL, 4.55 mmol), and $Et_3N$ (0.62 mL, 4.45 mmol) in ether (15 mL). TLC ($SiO_2$, $CH_2Cl_2$/petroleum ether, 2:1) after 5.5 h indicated that the reaction was complete, and the mixture was chromatographed (2.5 × 30 cm $SiO_2$, −30 °C) to give **7a** (0.59 g, 60%) as a deep red powder: IR (KBr) 3348 (NH), 2012, 1913, 1816 [$Cr(CO)_4$], 1645, 1601, 1454, 1232, 1139, 1117 cm$^{-1}$; MS (*m*/*z*) 325 (6%, M$^+$), 297 (5, M$^+$ − CO), 241 (17, M$^+$ − 3CO), 220 (29), 213 (100, M$^+$ − 4CO), 170 (20), 108 (38), 86 (38), 84 (47), 80 (64); $^1$H NMR ($CD_3COCD_3$, −40 °C, 400.1 MHz) δ 12.5 (br s, 1 H, NH), 7.78 (d, *J* = 7.6 Hz, 2 H) and 7.39 (d, *J* = 7.6 Hz, 2 H, Ar C*H*), 2.65 and 2.43 (two s, each 3 H, Ar C*H*$_3$ and NCOC*H*$_3$); $^{13}$C NMR ($CD_3COCD_3$, −40 °C, 100.6 MHz) δ 317.2 (C=Cr), 236.6, 233.3, 216.8 [intensity ca. 1:1:2, $Cr(CO)_4$], 184.6 (NCO), 144.7 and 144.0 (Ar *C*), 130.1 and 127.5 (Ar CH), 21.7 and 21.5 (Ar $CH_3$ and $NCOCH_3$).

**Tetracarbonyl[(((2,2-dimethylethoxy)carbonyl)amino)(4-methylphenyl)methylene-*C*,*O*]chromium (7b).** Pentacarbonyl[amino(4-methylphenyl)methylene]chromium (**5a**)[37] (1.39 g, 4.47 mmol) was allowed to react with $(BOC)_2O$ (1.61 g, 7.38 mmol) and DMAP (25 mg, 0.20 mmol) in THF (10 mL) for 24 h; chromatography (3 × 40 cm $SiO_2$, −30 °C, $CH_2Cl_2$/petroleum ether) afforded **7b** (1.42 g, 83%) as fine brown needles: IR (KBr) 3281 (NH), 2014, 1939, 1924, 1804 [$Cr(CO)_4$], 1672 (NC=O), 1459, 1445, 1249, 1138, 1120 cm$^{-1}$; MS (*m*/*z*) 383 (3%, M$^+$), 355 (3, M$^+$ − CO), 299 (12, M$^+$ − 3CO), 271 (21, M$^+$ − 4CO); $^1$H NMR ($CD_3COCD_3$, −40 °C, 400.1 MHz) δ 12.07 (br s, 1 H, NH), 7.75 (d, *J* = 7.8 Hz, 2 H) and 7.37 (d, *J* = 7.8 Hz, 2 H, aryl C*H*), 2.40 (s, 3 H, Ar C*H*$_3$), 1.54 [s, 9 H, OC(C*H*$_3$)$_3$]; $^1$H NMR ($C_6D_6$, 25 °C, 400.1 MHz) δ 8.22 (br s, 1 H, NH), 7.23 (d, *J* = 8.0 Hz) and 6.79 (d, *J* = 8.0 Hz, Ar C*H*), 1.95 (s, 3 H, Ar C*H*$_3$), 1.01 (s, 9 H, C(C*H*$_3$)$_3$); $^{13}$C NMR ($CD_3COCD_3$, −40 °C, 100.6 MHz) δ 317.0 (C=Cr), 234.6, 231.6, 216.2 (intensity ca. 1:1:2, $Cr(CO)_4$), 161.8 (NCO), 144.1, 143.7, 129.7 and 127.4 (Ar CH), 88.0 [O*C*(CH$_3$)$_3$], 27.5 [OC(*C*H$_3$)$_3$], 21.4 (Ar *C*H$_3$). Anal. Calcd for $C_{17}H_{17}CrNO_6$: C, 53.27; H, 4.47; N, 3.66. Found: C, 53.21; H, 4.53; N, 3.70.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-methylamino)(phenyl)methylene-*C*,*O*]chromium (7c).** DMAP (29 mg, 0.24 mmol) was added to a solution of pentacarbonyl[(*N*-methylamino)(phenyl)methylene]chromium[38] (**5b**) (1.42 g, 4.74 mmol) and $(BOC)_2O$ (1.347 g, 6.17 mmol) in ether (20 mL). TLC indicated that after 5.5 h some starting material remained, and additional DMAP (29 mg, 0.24 mmol) was added. After further reaction overnight column chromatography (3 × 45 cm $SiO_2$, −30 °C, $CH_2Cl_2$/petroleum ether, 1:2 to 1:1) afforded

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[37] Fischer, E. O.; Kollmeier, J. *Chem. Ber.* **1971**, *104*, 1339.

[38] Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599.

**7c** (1.17 g, 64%) as a brown solid containing some starting material and pentacarbonyl(DMAP)chromium (**9**), as shown by TLC. Recrystallization from $CH_2Cl_2$/petroleum ether gave pure **7c** (1.03 g, 57%) as fine brown needles: IR (KBr) 2012, 1898, 1849 [Cr(CO)$_4$], 1663 (NC=O), 1357, 1328, 1233, 1150 cm$^{-1}$; MS (*m/z*) 383 (4%, M$^+$), 355 (4, M$^+$ - CO), 299 (10, M$^+$ - 3CO), 271 (23, M$^+$ - 4CO), 220 (18), 215 (66), 108 (22), 80 (33); $^1$H NMR ($CD_3COCD_3$, -40 °C, 400.1 MHz) δ 7.53 (t, *J* = 7.7 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.22 (d, *J* = 7.2 Hz, 2 H), 3.33 (s, 3 H, $NCH_3$), 1.59 [s, 9 H, OC($CH_3$)$_3$]; $^{13}$C NMR ($CD_3COCD_3$, -40 °C, 100.6 MHz) δ 324.3 (C=Cr), 235.2, 230.8, 216.0 [intensity ca. 1:1:2, Cr(CO)$_4$], 161.1 (NCO), 148.3, 128.8, 122.6 (one signal lacking), 89.2 [*OC*($CH_3$)$_3$], 37.9 ($NCH_3$), 27.5 [OC($CH_3$)$_3$]. Anal. Calcd for $C_{17}H_{17}CrNO_6$: C, 53.27; H, 4.47; N, 3.66. Found: C, 53.31; H, 4.54; N, 3.68.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-(phenylmethyl)amino)(4-methylphenyl)methylene-*C*,*O*]chromium (7d).** Phenylmethanamine (0.412 mL, 3.77 mmol) was added dropwise to a stirred solution of pentacarbonyl[methoxy(4-methylphenyl)methylene]chromium (**10a**)[36] (1.20 g, 3.68 mmol) in ether (4 mL). By the end of the addition the solution boiled gently and within 5 min the color had faded from deep red to orange-yellow. After 30 min the mixture was concentrated under high vacuum and the thick oily residue of pentacarbonyl[benzylamino(4-methylphenyl)methylene]chromium (**5h**) was dissolved in ether (10 mL) with $(BOC)_2O$ (1.64 g, 7.51 mmol). After addition of DMAP (45 mg, 0.37 mmol) the mixture slowly evolved gas and became darker. TLC ($SiO_2$, ether/petroleum ether 1:3) indicated that the aminocarbene complex **5h** (yellow spot, $R_f$ = 0.34) was consumed within 3–6 h to give a new orange spot (presumably the N-acylated pentacarbonyl complex) ($R_f$ = 0.43). Even before **5h** was fully consumed, substantial amounts of the final product **7d** (brown-red, $R_f$ = 0.29) were to be seen; toward the end of the reaction pentacarbonyl(DMAP)chromium (**9**) could also be detected as a yellow spot, $R_f$ = 0.1. After 16 h the mixture was chromatographed ($SiO_2$, -20 °C, ether/petroleum ether, 1:4 → 1:2) to give **7d** (1.33 g, 76%) as fine brown needles: IR (KBr) 2014, 1951, 1893, 1863 [Cr(CO)$_4$], 1660 (NC=O), 1372, 1348, 1223, 1146, 1126 cm$^{-1}$; MS (*m/z*) 473 (1.7%, M$^+$), 361 (6, M$^+$ - 4CO), 262 (13), 220 (37), 151 (24), 150 (22), 108 (40), 91 (20); $^1$H NMR ($CD_3COCD_3$, -40 °C, 400.1 MHz) δ 7.05–7.4 (m, 5 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 7.07 (d, *J* = 7.3 Hz, 2 H), 5.09 (s, 2 H, $NCH_2Ph$), 2.33 (s, 3 H, Ar $CH_3$), 1.32 [s, 9 H, OC($CH_3$)$_3$]; $^{13}$C NMR ($CD_3COCD_3$, -40 °C, 100.6 MHz) δ 326.0 (C=Cr), 235.5, 230.6 and 216.0 [intensity ca. 1:1:2, Cr(CO)$_4$], 161.0 (NC=O), 145.5, 139.2, 137.1, 129.5, 129.4, 128.2, 126.7, 123.0, 89.5 [*OC*($CH_3$)$_3$], 53.4 ($NCH_2Ph$), 27.3 [OC($CH_3$)$_3$]. Anal. Calcd for $C_{24}H_{23}CrNO_6$: C, 60.88; H, 4.89; N, 2.96. Found: C, 60.86; H, 5.19; N, 3.02.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-(phenylmethyl)amino)(cyclohex-1-en-1-yl)methylene-*C*,*O*]chromium (7e).** Phenylmethanamine (0.300 mL, 2.75 mmol) was added dropwise to a stirred solution of pentacarbonyl[methoxy(cyclohex-1-en-1-yl)methylene]chromium (**10b**)[39] in ether (6 mL) which was in a Schlenk tube cooled in dry ice/acetone. After 10 min the cooling bath was removed, and after 0.5 h the solution was concentrated. Further operations as in the synthesis of **7d** gave **7e** (0.95 g, 76%) as a fine dark brown powder: IR (KBr) 2012, 1948, 1884, 1853 [Cr(CO)$_4$], 1661 (NC=O), 1373, 1341, 1227, 1146 cm$^{-1}$; MS (*m/z*) 463 (13%, M$^+$), 435 (4, M$^+$ - CO), 379 (17, M$^+$ - 3CO), 351 (100, M$^+$ - 4CO), 295 (83), 220 (25), 160 (21), 159 (32), 108 (19), 91 (40); $^1$H NMR ($CD_3COCD_3$, 25 °C, 300.1 MHz) δ 7.2–7.4 (m, 5 H), 7.15 (d, *J* = 7.4 Hz, 2 H), 5.36–5.42 (m, 1 H, *H*C=C), 5.16 (s, 2 H, $NCH_2Ph$), 1.9–2.3 (m, partly obscured by acetone peaks), 1.6–1.85 (m), 1.3–1.5 (m), 1.34 [s, 9 H, OC($CH_3$)$_3$]; $^{13}$C NMR ($CD_3COCD_3$, 0 °C, 100.6 MHz) δ 330.1 (C=Cr), 235.0, 232.1, 216.6 [Cr(CO)$_4$], 160.9 (NC=O), 147.4, 137.7, 129.5, 128.3, 127.0, 117.2, 89.7 [*OC*($CH_3$)$_3$], 53.3 ($NCH_2Ph$), 27.9 ($CH_2$), 27.5 [OC($CH_3$)$_3$], 24.8, 22.7, 22.3 (3 $CH_2$). Anal. Calcd for $C_{23}H_{25}CrNO_6$: C, 59.61; H, 5.44; N, 3.02. Found: C, 59.52; H, 5.34; N, 3.10.

**Pentacarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)amino)(methyl)methylene]chromium (6a).** DMAP (15 mg, 0.12 mmol) was added to a solution of pentacarbonyl[amino(methyl)methylene]chromium (**5c**)[38] (270 mg, 1.15 mmol) and $(BOC)_2O$ (552 mg, 2.53 mmol, 2.20 equiv) in $CH_2Cl_2$ (5 mL) in a screw-top glass tube with a stopcock bearing sidearm. During the next 5 min carbon monoxide was rapidly bubbled through the resulting solution before the tube was closed under 2 atm of CO pressure. After 4 h TLC revealed the complete absence of starting material and the presence of only traces of decarbonylation product **7l**. Solvent was removed and the residue was chromatographed (2 × 20 cm $SiO_2$, -30 °C, $CH_2Cl_2$/petroleum ether, 1:1 as eluent) to give **6a** as an orange powder (0.31 g, 80%), containing two rotamers in a ratio of ca. 1.2 to 1, as determined by $^1$H NMR spectroscopy: IR (KBr) 3354 (NH), 2062, 1987, 1943, 1912, 1898, 1771 (NC=O), 1474, 1229, 1143, 645 cm$^{-1}$; MS (*m/z*) 335 (18%, M$^+$), 307 (5, M$^+$ - CO), 279 (2, M$^+$ - 2CO), 251 (4, M$^+$ - 3CO), 223 (31, M$^+$ - 4CO), 196 (15), 195 (69, M$^+$ - 5CO), 167 (15), 140 (16), 139 (100); $^1$H NMR ($CD_3COCD_3$, -40 °C, 400.1 MHz) for major rotamer δ 12.5 (br s, 1 H, NH), 3.34 (s, 3 H, $CH_3$), 1.47 [s, 9 H, OC($CH_3$)$_3$]; $^1$H NMR ($CD_3COCD_3$, -40 °C, 400.1 MHz) for minor rotamer δ 12.0 (br s, 1 H, NH), 3.09 (s, 3 H, $CH_3$), 1.53 [s, 9 H, OC($CH_3$)$_3$]; $^{13}$C NMR ($CD_3COCD_3$, -40 °C, 100.6 MHz) for major rotamer δ 317.6 (C=Cr), 255.1 and 217.4 [intensity ca. 1:4, Cr(CO)$_5$], 145.6 (NC=O), 84.4 [*OC*($CH_3$)$_3$], 43.3 ($CH_3CCr$), 27.4 [OC($CH_3$)$_3$]; $^{13}$C NMR ($CD_3COCD_3$, -40 °C, 100.6 MHz) for minor rotamer δ 311.1 (C=Cr), 226.6 and 217.8 [intensity ca. 1:4, Cr(CO)$_5$], 151.8 (NC=O), 84.7 [*OC*($CH_3$)$_3$], 46.6 ($CH_3CCr$), 27.4 [OC($CH_3$)$_3$]. Anal. Calcd for $C_{12}H_{13}CrNO_7$: C, 42.99; H, 3.91; N, 4.18. Found: C, 42.83; H, 4.09; N, 4.12.

**Tetracarbonyl[(((2,2-dimethylethoxy)carbonyl)amino)(methyl)methylene-*C*,*O*]chromium (7l).** Isolated in 20% yield as a dark red solid when a mixture as described in the synthesis of **6a** was stirred 1 day under a nitrogen atmosphere: IR (KBr) 3301 (NH), 2023, 1940, 1900, 1791 [Cr(CO)$_4$], 1673 (NC=O), 1470, 1224, 1142 cm$^{-1}$; Anal. Calcd for $C_{11}H_{13}CrNO_6$: C, 43.00; H, 4.27; N, 4.56. Found: C, 42.30; H, 4.29; N, 4.38.

**Pentacarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-(phenylmethyl)amino)(phenyl)methylene]tungsten (6b).** According to the procedure used for **7d**, to a solution of pentacarbonyl[methoxy(phenyl)methylene]tungsten (**10f**) (1.70 g, 3.81 mmol) in ether was added phenylmethanamine (0.425 mL, 3.89 mmol). The crude aminocarbene complex remaining after concentration under vacuum was dissolved in ether (10 mL) with $(BOC)_2O$ (1.30 g, 5.96 mmol), and the resulting solution was saturated with carbon monoxide before DMAP (25.6 mg, 0.21 mmol) was added. After 5 min TLC ($SiO_2$, ether/petroleum ether 1:3) showed considerable conversion of the aminocarbene complex (light yellow spot, $R_f$ = 0.20) to the product (orange spot, $R_f$ = 0.40). After 10 min the product began to crystallize out of the mixture as a bright yellow powder, and after a total of 1.5 h TLC indicated that all light yellow aminocarbene complex was gone, and only traces of dark brown presumed decarbonylation product ($R_f$ = 0.17) were present. Petroleum ether (15 mL) was added and after 0.5 h the mixture was filtered through a glass frit and the retained yellow powder was washed with ether/petroleum ether. Storage under high vacuum left **6b** (1.68 g, 71%) as a bright yellow powder, the NMR data for which indicated that it existed as two rotamers in a ratio of 6 to 1: IR (KBr) 2064, 1972, 1938, 1899 [W(CO)$_5$], 1758 (NC=O), 1452, 1432, 1255, 1146 cm$^{-1}$; $^1$H NMR ($CD_3COCD_3$, -40 °C, 400.1 MHz) for the major rotamer δ 7.3–7.6 (m, 7 H), 7.26 (td, *J* = 1.2, 7.5 Hz, 1 H), 7.09 (dd, *J* = 1.2, 8.4 Hz), 5.74 (s, 2 H, $NCH_2Ph$), 0.69 [s, 9 H, OC($CH_3$)$_3$]; signals readily attributable to the minor rotamer δ 4.83 (s, 2 H, $NCH_2Ph$), 1.27 [s, 9 H, OC($CH_3$)$_3$]; partial $^{13}$C NMR ($CD_3COCD_3$, 0 °C, 100.6 MHz) of major rotamer δ 261.3 (C=W), 205.0 and 198.3 [intensity ca. 1:4, W(CO)$_5$], 86.9 [*OC*($CH_3$)$_3$], 66.3 ($NCH_2Ph$), 26.0 [OC($CH_3$)$_3$]. Anal. (of a sample recrystallized from $CH_3COCH_3$). Calcd for $C_{24}H_{21}NO_7W$: C, 46.55; H, 3.42; N, 2.26. Found: C, 46.42; H, 3.32; N, 2.32.

**Pentacarbonyl[(methylamino)(phenyl)methylene]molybdenum (5f).** Gaseous methanamine was condensed into a cooled (ethanol/dry ice) and stirred solution of pentacarbonyl[methoxy(phenyl)methylene]molybdenum (**10g**)[40] (0.65 g, 1.82 mmol) in ether. Within 2 min the color changed from red to yellow. The solvent was removed under reduced pressure.

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Chromatography ($SiO_2$, −20 °C, petroleum ether/$CH_2Cl_2$ 2:1) yielded **5f** (0.4 g, 62%) as a yellow powder, the NMR spectra of which indicated that it existed as a mixture of *E* and *Z* isomers: IR (NaCl, petroleum ether) 2068, 1983, 1946, 1923 cm$^{-1}$; MS (*m/z*) 353 (6%, M$^+$); $^1$HNMR ($CDCl_3$, −10 °C, 400.1 MHz) (*E*/*Z* 1.6:1) δ 9.07 (s, 1 H, *E*), 8.65 (s, 1 H, *Z*), 7.44–7.33 (m, 6 H, *E* + *Z*), 7.07–7.04 (m, 2 H, *E*), 6.84–6.82 (m, 2 H, *Z*), 2.97 (d, *J* = 5.11 Hz, 3 H, *E*), 3.71 (d, *J* = 5.02 Hz, 3 H, *Z*); $^{13}$C NMR ($CDCl_3$, −10 °C, 100.6 MHz) (*E*/*Z* 1.6:1) δ 275.08 (*Z*), 272.59 (*E*), 214.01, 213.75, 206.23, 206.17, 154.3, 149.21, 128.46, 128.58, 126.69, 128.06, 121.53, 119.18, 41.49, 37.25. Anal. Calcd for $C_{13}H_9NO_5Mo$: N, 3.95; C, 43.96; H, 2.54. Found: N. 3.78; C, 44.24; H, 2.83.

**Pentacarbonyl[amino(4-methylphenyl)methylene]molybdenum (5d).** Into a cooled and stirred solution of pentacarbonyl[methoxy(4-methylphenyl)methylene]molybdenum (**10d**)[41] (1.23 g, 3.32 mmol) was condensed gaseous ammonia. Further operations as described for the synthesis of **5f** gave **5d** (0.42 g, 36%): IR (NaCl, petroleum ether) 2077, 1988, 1953, 1934 cm$^{-1}$; MS (*m/z*) 357 (9%, M$^+$); $^1$H NMR ($CDCl_3$, −25 °C, 400.1 MHz) δ 8.66 (s, 1 H), 8.41 (s, 1 H), 7.26 (s, 4 H), 2.41 (s, 3 H); $^{13}$C NMR ($CDCl_3$, −25 °C, 100.6 MHz) δ 282.87, 213.36, 206.26, 148.51, 141.09, 129.3, 123.99, 21.41. Anal. Calcd for $C_{13}H_9NO_5Mo$: N, 3.95; C, 43.96; H, 2.54. Found: N. 3.95; C, 43.67; H, 2.37.

**Pentacarbonyl[((2,2-dimethylethyl)amino)(phenyl)methylene]molybdenum (5g).** (2,2-Dimethylethyl)amine (0.5 mL, 4.77 mmol) was added dropwise to a stirred and cooled (−75 °C) solution of pentacarbonyl[methoxy(phenyl)methylene]molybdenum (**10g**)[40] (0.3 g, 4.77 mmol). The color faded from red to yellow. Chromatography ($SiO_2$, −20 °C, petroleum ether/$CH_2Cl_2$ 5:1) afforded **5g** (328 mg, 98%) as a white powder: IR (NaCl, petroleum ether) 2066, 1984, 1946, 1921 cm$^{-1}$; MS (*m/z*) 399 (20%, M$^+$); $^1$H NMR ($CD_3COCD_3$, −10 °C, 400.1 MHz) (one isomer) δ 10.53 (s, 1 H), 7.39–7.35 (m, 2 H), 7.16–7.13 (m, 1 H), 6.99–6.96 (m, 2 H), 1.25 (s, 9 H); $^{13}$C NMR ($CD_3COCD_3$, −10 °C, 100.6 MHz) δ 268.88, 215.54, 207.25, 151.76, 129.19, 126.29, 120.39, 64.94, 30.73. Anal. Calcd for $C_{16}H_{15}NO_5Mo$: N, 3.52; C, 48.37; H, 3.78. Found: N, 3.53; C, 48.36; H, 3.72.

**Pentacarbonyl[(2-methoxyphenyl)(methylamino)methylene]molybdenum (5i).** Pentacarbonyl[(2-methoxyphenyl)(methoxy)methylene]molybdenum (**10e**)[26b] (0.92 g, 2.36 mmol) was allowed to react with methylamine in ether. Subsequent operations as described for the synthesis of **5f** gave **5i** (0.66 g, 72%): IR (NaCl, petroleum ether) 2065, 1973, 1952, 1925 cm$^{-1}$; MS (*m/z*)) 387 (13%, M$^+$); $^1$H NMR ($CDCl_3$, −20 °C, 400.1 MHz) (*E*/*Z* 3.4:1) δ 9.11 (s, 1 H, *E*), 8.76 (s, 1 H, *Z*), 7.25–7.21 (m, 2 H, *E* + *Z*), 7.06–7.02 (m, 1 H, *E*), 7.01–6.97 (m, 1 H, *Z*), 6.94–6.89 (m, 2 H, *E* + *Z*), 6.8–6.78 (m, 1 H, *E*), 6.76–6.74 (m, 1 H, *Z*), 3.83 (s, 3 H, *E* + *Z*), 2.95 (d, *J* = 5.05 Hz, 3 H, *E*), 3.73 (d, *J* = 5.00 Hz, 3 H, *Z*); $^{13}$C NMR ($CDCl_3$, −20 °C, 100.6 MHz) δ 272.03 (*Z*), 271.98 (*E*), 214.48, 214.07, 206.27, 206.3, 150.28, 148.53, 142.17, 137.39, 128.35, 127.98, 121.77, 120.98, 120.08, 120.62, 110.65, 110.53, 55.01, 55.19, 41.29, 37.04. Anal. Calcd for $C_{14}H_{11}NO_6Mo$: N, 3.64; C, 43.66; H, 2.88. Found: N, 3.70; C, 43.63; H, 2.86.

**Tetracarbonyl[(((2,2-dimethylethoxy)carbonyl)amino)(4-methylphenyl)methylene-*C*,*O*]molybdenum (7f).** Aminocarbene complex **5d** (1.1 g, 3.09 mmol) was treated with $(BOC)_2O$ (0.75 mL, 3.28 mmol) and DMAP (40 mg, 0.33 mmol) at 0 °C in ether (10 mL). Chromatography ($SiO_2$, −25 °C, $CH_2Cl_2$) after 3 h afforded **7f** (0.44 g, 33%) as a dark powder: IR (NaCl, $CH_2Cl_2$) 2027, 1927, 1842, 1678 cm$^{-1}$; MS (*m/z*) 427 (100%, M$^+$); $^1$H NMR ($CD_3COCD_3$, −30 °C, 400.1 MHz) δ 12.19 (s, 1 H), 7.89–7.87 (m, 2 H), 7.46–7.39 (m, 2 H), 2.4 (s, 3 H), 1.59 (s, 9 H); $^{13}$C NMR ($CD_3COCD_3$, −30 °C, 100.6 MHz) δ 303.24, 226.1, 225.67, 207.72, 162.53, 145.50, 143.24, 129.94, 129.03, 88.68, 27.65, 21.5. Anal. Calcd for $C_{17}H_{17}NO_6Mo$: N, 3.28; C, 47.79; H, 4.01. Found: N. 3.24; C, 47.56; H, 3.62.

**Tetracarbonyl[(*N*-acetylamino)(4-methylphenyl)methylene-*C*,*O*]molybdenum (7g).** To a stirred solution of **5d** (0.4 g, 1.12 mmol) in ether (3 mL) at −15 °C were added $(CH_3CO)_2O$ (0.13 mL, 1.38 mmol), *i*-$Pr_2NEt$ (0.31 mL, 1.73 mmol), and DMAP (13.7 mg, 0.112 mmol). After 3 h the solution was warmed to 0 °C and the reaction continued for 4 h. Chromatography ($SiO_2$, −25 °C, $CH_2Cl_2$) afforded **7g** (0.26 g, 63%) as a dark red powder: IR (NaCl, $CH_2Cl_2$) 2036, 1941, 1872, 1625 cm$^{-1}$; $^1$H NMR ($CD_3COCD_3$, −30 °C, 400.1 MHz) δ 12.69 (s, 1 H), 7.91–7.88 (m, 2 H), 7.40–7.38 (m, 2 H), 2.69 (s, 3 H), 2.34 (s, 3 H); $^{13}$C NMR ($CD_3COCD_3$, −30 °C, 100.6 MHz) δ 302.73, 227.38, 227.18, 207.94, 184.32, 145.21, 144.29, 130.09, 128.85, 21.9, 21.52. Anal. Calcd for $C_{14}H_{11}NO_5Mo$: N, 3.79; C, 45.55; H, 3.00. Found: N, 3.80; C, 45.53; H, 2.95.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-methylamino)(4-methylphenyl)methylene-*C*,*O*]molybdenum (7h).** A mixture of crude pentacarbonyl[(*N*-methylamino)(4-methylphenyl)methylene]molybdenum (**5e**) (1.2 g, 3.25 mmol) and $(BOC)_2O$ (1.05 mL, 4.6 mmol) in ether (15 mL) was cooled to 0 °C, and DMAP (24 mg, 0.198 mmol) was added. After 3 h column chromatography ($SiO_2$, −25 °C, $CH_2Cl_2$) yielded **7h** (0.39 g, 27%): IR (NaCl, $CH_2Cl_2$) 2030, 1940, 1850, 1658 cm$^{-1}$; MS (*m/z*) 443 (100%, M$^+$); $^1$H NMR ($CD_3COCD_3$, −30 °C, 400.1 MHz) δ 7.33–7.31 (m, 2 H), 7.19–7.17 (m, 2 H), 3.42 (s, 3 H), 2.36 (s, 3 H), 1.65 (s, 9 H); $^{13}$C NMR ($CD_3COCD_3$, −30 °C, 100.6 MHz) δ 313.35, 227.30, 225.17, 207.49, 161.79, 145.49, 139.71, 129.35, 124.24, 89.99, 38.45, 27.59, 21.21. Anal. Calcd for $C_{18}H_{19}NO_6Mo$: N, 3.17; C, 49.00; H, 4.34. Found: N, 3.19; C, 48.55; H, 4.32.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-methylamino)(phenyl)methylene-*C*,*O*]molybdenum (7i).** DMAP (34 mg, 0.28 mmol) was added to an ice-cooled solution of **5f** (1.0 g, 2.8 mmol) and $(BOC)_2O$ (1.28 mL, 5.6 mmol) in ether (6 mL). The reaction was finished in 4 h. Column chromatography ($SiO_2$, −25 °C, $CH_2Cl_2$) afforded **7i** (0.6 g, 50%) as a brown powder: IR (NaCl, $CH_2Cl_2$) 2030, 1928, 1855, 1650 cm$^{-1}$; MS (*m/z*) 429 (100%, M$^+$); $^1$H NMR ($CD_3COCD_3$, −30 °C, 400.1 MHz) δ 7.52–7.44 (m, 2 H), 7.39–7.33 (m, 2 H), 7.24–7.22 (m, 2 H), 3.39 (s, 3 H), 1.65 (s, 9 H); $^{13}$C NMR ($CD_3COCD_3$, −30 °C, 100.6 MHz) δ 313.09, 227.32, 225.1, 207.39, 161.79, 148.18, 129.15, 128.79, 123.35, 90.04, 38.45, 27.59. Anal. Calcd for $C_{17}H_{17}NO_6Mo$: N, 3.28; C, 47.79; H, 4.01. Found: N, 3.31; C, 47.92; H, 4.00.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-(phenylmethyl)amino)(4-methylphenyl)methylene-*C*,*O*]molybdenum (7j).** Crude pentacarbonyl[(*N*-phenylmethylamino)(4-methylphenyl)methylene]molybdenum prepared from pentacarbonyl[methoxy(4-methylphenyl)methylene]molybdenum (**10d**) (1.5 g, 3.87 mmol) and benzylamine (1.6 mL, 14.6 mmol) was treated with DMAP (50 mg, 0.4 mmol) and $(BOC)_2O$ (3.3 mL, 14.6 mmol) at 0 °C in 10 mL of ether. After chromatography ($SiO_2$, −25 °C, ether/petroleum ether 1:1) the black product was crystallized from ether at −78 °C. It afforded **7j** as black needles (1.05 g, 44%). $^1$H NMR ($CD_3COCD_3$, −30 °C, 400.1 MHz) δ 7.40–7.37 (m, 3 H), 7.36–7.29 (m, 2 H), 7.22–7.20 (m, 2 H), 7.10–7.08 (m, 2 H), 5.18 (s, 2 H), 2.33 (s, 3 H), 1.39 (s, 9 H); $^{13}$C NMR ($CD_3COCD_3$, −30 °C, 100.6 MHz) δ 314.63, 227.52, 224.91, 207.29, 161.63, 145.49, 139.69, 137.13, 129.48, 128.29, 126.69, 123.72, 90.29, 53.93, 27.30, 21.14. Anal. Calcd for $C_{24}H_{23}NO_6Mo$: N, 2.71; C, 55.72; H, 4.48. Found: N, 2.72; C, 55.39; H, 4.45.

**Tetracarbonyl[(*N*-((2,2-dimethylethoxy)carbonyl)-*N*-methylamino)(2-methoxyphenyl)methylene-*C*,*O*]molybdenum (7k).** An aqueous solution of methylamine (4.95 g, 40%) was added dropwise to a solution of pentacarbonyl[methoxy(2-methoxyphenyl)methylene]molybdenum (**10e**)[26b] (1.2 g, 3.1 mmol) in ether (30 mL) at −70 °C. The reaction was finished within 1 min. After removal of the solvent the crude aminolysis product **5i** was redissolved in ether (20 mL) and treated with $(BOC)_2O$ (1.4 mL, 6.06 mmol) and DMAP (38 mg, 0.31 mmol) at 0 °C. Chromatography ($SiO_2$, −25 °C, ether) and crystallization from ether afforded **7k** (0.68 g, 48%) as black needles: IR (NaCl, ether) 2029, 1929, 1869 cm$^{-1}$; MS (*m/z*) 468 (100%, M$^+$); $^1$H NMR ($CD_3COCD_3$, −30 °C, 400.1 MHz) δ 7.39–7.34 (m, 1 H), 7.15–7.08 (m, 3 H), 3.83 (s, 3 H), 3.25 (s, 3 H), 1.67 (s, 9 H); $^{13}$C NMR ($CD_3COCD_3$, −30 °C, 100.6 MHz) δ 313.37, 227.89, 225.37, 208.25, 207.12, 161.63, 150.1, 137.17, 130.55, 126.39, 121.12, 111.85, 90.3, 55.83, 37.72, 27.79. Anal. Calcd for $C_{18}H_{19}NO_7Mo$: N, 3.06; C, 47.28; H, 4.19. Found: N, 3.19; C, 47.16; H, 4.19.

**Enrichment of 7d with $^{13}$CO.** A Schlenk tube (internal volume 35 mL) was charged with **7d** (0.2 g) and $C_6H_5CH_3$ (4 mL), a magnetic stir bar was added, and the system was capped with a rubber septum. The resulting solution was degassed by three freeze–pump–thaw cycles before the stopcock was closed, and 35 mL of 99% $^{13}$CO (MSD Isotopes) was injected by syringe while the tube was under vacuum and the contents were still frozen.

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**Table III. Atomic Coordinates and Equivalent Isotropic Temperature Factors**

| atom | $x/a$ | $y/b$ | $z/c$ | $U$(eq),[a] Å$^2$ |
|---|---|---|---|---|
| Cr1 | 0.37167 (3) | 0.34727 (6) | 0.05959 (4) | 0.0628 (2) |
| O1 | 0.3453 (1) | 0.2721 (2) | 0.1658 (2) | 0.070 (1) |
| O2 | 0.3377 (1) | 0.3246 (2) | 0.3013 (2) | 0.071 (1) |
| O3 | 0.2524 (2) | 0.4780 (3) | −0.0409 (2) | 0.110 (2) |
| O4 | 0.4097 (1) | 0.4534 (3) | −0.0853 (2) | 0.097 (1) |
| O5 | 0.5056 (2) | 0.2733 (3) | 0.1415 (2) | 0.118 (2) |
| O6 | 0.3309 (2) | 0.1305 (3) | −0.0633 (3) | 0.138 (2) |
| N1 | 0.3744 (2) | 0.4547 (3) | 0.2250 (2) | 0.061 (1) |
| C1 | 0.3898 (2) | 0.4799 (3) | 0.1501 (2) | 0.054 (2) |
| C2 | 0.4116 (2) | 0.6025 (3) | 0.1495 (2) | 0.054 (1) |
| C3 | 0.4566 (2) | 0.6259 (4) | 0.1142 (2) | 0.069 (2) |
| C4 | 0.4747 (2) | 0.7420 (5) | 0.1083 (3) | 0.081 (2) |
| C5 | 0.4475 (2) | 0.8379 (5) | 0.1313 (3) | 0.080 (2) |
| C6 | 0.4027 (2) | 0.8142 (4) | 0.1667 (3) | 0.083 (2) |
| C7 | 0.3855 (2) | 0.6991 (4) | 0.1765 (3) | 0.071 (2) |
| C8 | 0.4653 (3) | 0.9645 (4) | 0.1196 (3) | 0.122 (3) |
| C9 | 0.3517 (2) | 0.3434 (4) | 0.2285 (3) | 0.063 (2) |
| C10 | 0.3173 (2) | 0.2065 (4) | 0.3228 (3) | 0.073 (2) |
| C11 | 0.3676 (2) | 0.1159 (5) | 0.3349 (4) | 0.128 (3) |
| C12 | 0.3076 (2) | 0.2304 (5) | 0.4106 (3) | 0.104 (2) |
| C13 | 0.2580 (2) | 0.1731 (5) | 0.2462 (3) | 0.117 (3) |
| C14 | 0.2955 (2) | 0.4236 (4) | −0.0009 (3) | 0.075 (2) |
| C15 | 0.3945 (2) | 0.4139 (4) | −0.0282 (3) | 0.070 (2) |
| C16 | 0.4542 (2) | 0.2942 (4) | 0.1132 (3) | 0.077 (2) |
| C17 | 0.3463 (2) | 0.2102 (4) | −0.0139 (3) | 0.092 (2) |

The contents of the tube were stirred at room temperature for 2 days before the mixture was chromatographed to give 0.08 g of $^{13}$C-enriched **7d** in which the three $^{13}$C NMR signals for the $Cr(CO)_4$ fragment were approximately 20 times as tall as those in the natural-abundance sample.

**Crystallographic Data for Tetracarbonyl[(((2,2-dimethylethoxy)carbonyl)amino)(4-methylphenyl)methylene-*C*,*O*]chromium (7b)**: Monoclinic, space group $C2/c$ (No. 15), $a$ = 23.355 (5) Å, $b$ = 11.187 Å, $c$ = 15.629 Å, $\beta$ = 111.66 (1)°, $V$ = 3795 Å$^3$, $M_r$ = 303.32, $\rho_{calcd}$ = 1.342 g cm$^{-3}$, $F(000)$ = 1504 e, $\mu$(Cu K$\alpha$) = 53.0 cm$^{-1}$. A crystal (0.3 × 0.3 × 0.5 mm) was measured at room temperature on an Enraf-Nonius CAD4 diffractometer (Cu K$\alpha$ radiation, graphite monochromator). A total of 2429 reflections ($\psi$ scans, 2–55°) were measured, 2120 of which were unique; 1864 with $F_o > 4\sigma(F_o)$ were regarded as observed. The structure was solved by the automatic Patterson method in SHELX–86[42] and refined with SHELX–76;[43] H atoms with fixed isotropic temperature factors, with the exception of N–H, were refined at calculated positions; all other atoms were treated anisotropically, R = 0.042, $R_w$ = 0.034 ($w = 1/\sigma^2$), 241 parameters. The absorption was corrected empirically with DIFABS.[44] All calculations were carried out on a MICRO-VAX II computer.[45–47]

Atomic coordinates and equivalent isotropic temperature factors are given in Table III.

**Pentacarbonyl[(*N*-(1-((2,2-dimethylethoxy)carbonyl)-indolyl-3-ethyl)amino)(methyl)methylene]chromium (11).** A solution of pentacarbonyl[methoxy(methyl)methylene]chromium (**10c**) (0.58 g, 2.3 mmol) in $Et_2O$ (5 mL) was treated with indole-3-ethanamine (0.34 g, 2.12 mmol) as described above to give the crude aminocarbene complex which was acylated with $BOC_2O$ (3.0 g, 13.7 mmol) and DMAP (56 mg, 0.46 mmol). After 3 h the mixture had assumed a wine red color and an aliquot readily acylated a sample of **5a** but, according to IR and TLC, acylation at the non-indolic nitrogen had not taken place to a detectable extent. After 3 days this situation remained unchanged and the mixture was purified by chromatography to give 1.14 g of pale yellow oily impure product. Crystallization from petroleum ether/ether afforded 11 (0.55 g, 54%) as a pale yellow solid, the NMR spectra of which showed only one rotamer to be present: IR (KBr) 3341 (N–H), 2055, 1967, 1890, 1715 (NC=O) cm$^{-1}$; MS ($m/z$) 478 (10%, M$^+$), 394 (18, M$^+$ − 3CO), 338 (38, M$^+$ − 5CO), 282 (100, M$^+$ − 5CO − $C_4H_8$), 238 (28), 237 (22), 130 (39); $^1$H NMR ($C_6D_6$, 300.1 MHz) $\delta$ 8.5 and 8.1 (two br s, each 1 H, N*H*), 7.1–7.4 (m, obscured by solvent resonance), 2.46 (q, $J$ = 6.5 Hz, 2 H, C*H*$_2$NH), 2.03 (t, $J$ = 6.5 Hz, 2 H, Ar C*H*$_2$), 1.79 (s, 3 H, C*H*$_3$), 1.43 [s, 9 H, OC(C*H*$_3$)$_3$]. Anal. Calcd for $C_{22}H_{22}CrN_2O_7$: C, 55.23; H, 4.63; N, 5.85. Found: C, 55.51; H, 4.60; N, 5.87.

***N*-(2,3-Diethyl-5-methyl-1*H*-inden-1-yl)carbamic Acid 2,2-Dimethylethyl Ester (16a).** A solution of **7b** (0.192 g, 0.500 mmol) and 3-hexyne (0.114 mL, 1.00 mmol) in THF (10 mL) was deoxygenated, and the glass tube containing the solution was heated in an oil bath maintained at 55 °C for 2 h. Complex **7b** was no longer detectable by TLC. At room temperature the mixture was treated with $Et_3N$ (0.155 mL, 1.11 mmol), $(CH_3CO)_2O$ (0.095 mL, 1.00 mmol), and DMAP (3.5 mg, 0.029 mmol). After 0.5 h the reaction mixture was concentrated and the residue was chromatographed over $SiO_2$ (25 g) using normal, undeoxygenated petroleum ether/$CH_2Cl_2$, to give **16a** (0.082 g, 54%) as a viscous pale yellow oil: IR (NaCl, $CH_2Cl_2$) 2969, 2933, 1699 (NC=O), 1480, 1457, 1391, 1245, 1160 cm$^{-1}$; MS ($m/z$) 302.2090 (5%, calcd for M$^+$ + 1 = $^{12}C_{18}{}^{13}C^1H_{27}{}^{14}N^{16}O_2$: 302.2105), 301.2059 (26%, calcd for M$^+$ = $^{12}C_{19}{}^1H_{27}{}^{14}N^{16}O_2$: 301.2076), 246 (21), 245 (69, M$^+$ − $C_4H_8$), 216 (54, M$^+$ − $C_4H_8$ − Et), 184 (66), 172 (54), 57 (100, $C_4H_9^+$); $^1$H NMR ($C_6D_6$, 300.1 MHz) $\delta$ 7.08 (d, $J$ = 7.6 Hz, 1 H) and 7.00 (d, $J$ = 7.5 Hz, 1 H) (H6 and H7), 7.05 (s, 1 H, H4), 5.6 (br s, 1 H, N*H*), 3.26 (dd, $J$ = 4.2, 5.4 Hz, 1 H, C*H*N), 2.52 (dq, $J$ = 7.5, 15 Hz, 1 H), 2.25 (s, 3 H, Ar C*H*$_3$), 2.0–2.2 (m, 1 H), 1.85 (ddq, $J$ = 4.2, 7.4, 14.7 Hz, 1 H), 1.64 (ddq, $J$ = 5.4, 7.4, 14.7 Hz, 1 H), 1.42 [s, 9 H, OC(C*H*$_3$)$_2$], 1.01 (t, $J$ = 7.5 Hz, 3 H) and 0.54 (t, $J$ = 7.4 Hz, 6 H) (2 CH$_2$C*H*$_3$); $^{13}$C NMR and multiplicity test ($C_6D_6$, 75.5 MHz) $\delta$ 153 (br, N*C*=O), 145.2 (C), 141.7 (C), 140.9 (C), 134.0 (C), 127.3 (CH), 123.8 (CH), 118.3 (CH), 79.5 [O*C*(CH$_3$)$_3$], 48.2 (*C*HN), 28.4 [C(*C*H$_3$)$_3$], 22.8 (CH$_2$), 21.6 (Ar *C*H$_3$), 19.9 (CH$_2$), 13.6 (CH$_3$), 8.5 (CH$_3$).

***N*-(4-Acetoxy-2,3-diethyl-6-methylnaphthalen-1-yl)-*N*-(phenylmethyl)carbamic Acid 2,2-Dimethylethyl Ester (19b) and *N*-(2,3-diethyl-5-methyl-1*H*-inden-1-yl)-*H*-(phenylmethyl)carbamic Acid 2,2-Dimethylethyl Ester (16b).** In analogy to the reaction of **7b** above, **7d** (0.377 g, 0.796 mmol) and 3-hexyne (0.182 mL, 1.60 mmol) in $C_6H_5CH_3$ (3.2 mL) were warmed for 3 h at 55–60 °C. During this time TLC ($SiO_2$, $CH_2Cl_2$/petroleum ether 1:1) showed that **7b** (brown spot, $R_f$ = 0.64) gave way to presumed phenol **19a** and indene **16b** (colorless spots, $R_f$ = 0.15 and 0.41, respectively) and their presumed $Cr(CO)_3$ complexes (pale orange and yellow spots with $R_f$ = 0.20 and 0.35, respectively). When **7b** was no longer detectable, the mixture was allowed to cool to room temperature and $Et_3N$ (0.223 mL, 1.60 mmol), $Ac_2O$ (0.135 mL, 1.43 mmol), and DMAF (4.8 mg, 0.04 mmol) were added. After 2 h $FeCl_3 \cdot 1.5$ DMF (1.5 g, 5.5 mmol) was added, and after 0.5 h chromatography over 1.5 × 40 cm $SiO_2$ (using first $CH_2Cl_2$/petroleum ether 1:1 and 2:1 and then pure $CH_2Cl_2$ as eluents) afforded first the indene derivative **16b** (0.0348 g, 11%) as a viscous oil, the NMR data for which indicated that it exists as two rotamers in a ratio of 2.5 to 1: IR (NaCl, $CH_2Cl_2$) 2973, 2934, 1693 (NC=O), 1456, 1391, 1367, 1330, 1299, 1243, 1166, 1133 cm$^{-1}$; MS ($m/z$) 391 (20%, M$^+$), 336 (57), 335 (69), 302 (46), 244 (56), 184 (78), 91 (94, $C_7H_7^+$), 84 (100); $^1$H NMR ($C_6D_6$, 300.1 MHz) signals readily attributable to major rotamer $\delta$ 5.35 and 4.32 (two d, both $J$ = 14.1 Hz, each 1 H, NC*H*$_2$Ph), 3.30 (t, $J$ = 4.5 Hz, 1 H, H1 for both rotamers), 2.27 (s, 3 H, Ar C*H*$_3$), 1.39 [s, 9 H, OC(C*H*$_3$)$_3$]; signals readily attributable to minor rotamer $\delta$ 5.18 and 4.45 (two d, both $J$ = 14.0 Hz, each 1 H, NC*H*$_2$Ph), 3.30 (t, $J$ = 4.5 Hz, H1), 2.24 (s, 3 H, Ar C*H*$_3$), 1.39 [s, 9 H, OC(C*H*$_3$)$_3$], 0.43 (t, $J$ = 7.4 Hz, 3 H, CH$_2$C*H*$_3$).

Further elution gave **19b** (0.2058 g, 56%) as a colorless viscous oil, the NMR data for which revealed that it exists as two rotamers in a ratio of 8 to 1: IR (NaCl, $CH_2Cl_2$) 2977, 2935, 2876, 1771 (OC=O), 1696 (NC=O), 1391, 1366, 1334, 1207, 1191, 1124, 1101 cm$^{-1}$; MS ($m/z$) 461 (48%, M$^+$), 419 (30, M$^+$ − $CH_2CO$), 363 (73), 272 (30), 151 (31), 150 (32), 91 (83, $C_7H_7^+$), 57 (100); $^1$H NMR

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($\mathrm{C_6D_6}$, 300.1 MHz) major rotamer δ 7.46–7.51 (m, 2 H), 6.85–7.00 and 7.05–7.10 (two m, no first-order patterns seen), 5.05 and 4.43 (two d, both *J* = 13.9 Hz, each 1 H, $\mathrm{NC}H_2\mathrm{Ph}$), 2.09 (s, 3 H, about half as tall as the signal at 1.85 presumably because of unresolved coupling to H on the naphthalene ring, Ar $\mathrm{C}H_3$), 1.85 (s, 3 H, $\mathrm{O_2CC}H_3$), 2.4–2.7 (two m, total 3 H), 2.26 (qd, *J* = 7.5, 14.8, 1 H, Ar $\mathrm{C}H\mathrm{HCH_3}$), 1.14 [s, 9 H, $\mathrm{OC(C}H_3)_3$], 1.07 and 0.95 (two t, both *J* = 7.5 Hz, each 3 H, two $\mathrm{CH_2C}H_3$); signals attributable to minor rotamer δ 4.72 and 4.30 (two d, both *J* = 14.4 Hz, each 1 H, $\mathrm{NC}H_2\mathrm{Ph}$), 1.34 [s, 9 H, $\mathrm{OC(C}H_3)_3$]; $^{13}$C NMR ($\mathrm{C_6D_6}$, 75.5 MHz) signals ascribable to major rotamer δ 168.5 ($\mathrm{O_2}C\mathrm{CH_3}$), 156.2 ($\mathrm{N}C{=}\mathrm{O}$), 144.4, 138.8, 138.3, 135.6, 135.0, 132.5, 130.3, 129.2, 128.5, 128.4, 127.2, 124.1, 120.9 (one peak in the arene region is presumedly obscured by benzene peaks), 79.6 [$\mathrm{O}C\mathrm{(CH_3)_3}$], 54.6 ($\mathrm{N}C\mathrm{H_2Ph}$), 28.4 (Ar $C\mathrm{H_3}$), 28.0 [$\mathrm{OC(}C\mathrm{H_3)_3}$], 22.2, 21.6, 21.1, 20.0, 14.7, 14.6. Anal. Calcd for $\mathrm{C_{29}H_{35}NO_4}$: C, 75.46; H, 7.64; N, 3.03. Found: C, 75.53; H, 7.82; N, 3.13.

***N*-(Phenylmethyl)-*N*-(4-acetoxy-2,3-diethyl-6-methylnaphthalen-1-yl)ammonium Chloride (20).** A solution of **19b** (0.1068 g, 0.231 mmol) in ether (5 mL) saturated with HCl gas was stored at room temperature for 3 h and then overnight in a freezer. The supernatant was removed and the remaining solid was stored under vacuum to leave **20** (0.0728 g, 79%) as an off-white solid: $^1$H NMR ($\mathrm{CD_3OD}$, 300.1 MHz) δ 7.97 (d, *J* = 8.7 Hz, 1 H), 7.60 (s, 1 H), 7.54 (d, *J* = 8.7 Hz, 1 H), 7.23–7.44 (m, 3 H), 7.09 (d, *J* = 7 Hz, 2 H), 4.66 (s, 2 H, $\mathrm{NC}H_2\mathrm{Ph}$), 2.54–2.72 (m, 2 H, Ar $\mathrm{C}H_2$), 2.53 and 2.51 (two s, each 3 H, Ar $\mathrm{C}H_3$ and $\mathrm{O_2CC}H_3$), 2.42 (q, *J* = 7.5 Hz, 2 H, Ar $\mathrm{C}H_2$), 1.11 and 1.04 (two d, each *J* = 7.5 Hz, each 3 H, two $\mathrm{CH_2C}H_3$). Anal. Calcd for $\mathrm{C_{24}H_{28}ClNO_2}$: C, 72.44; H, 7.09; N, 3.52. Found: C, 71.50; H. 7.00; N, 3.78.

***N*-(4-Acetoxy-2,3-diethyl-5,6,7,8-tetrahydronaphthalen-1-yl)-*N*-(phenylmethyl)carbamic Acid 2,2-Dimethylethyl Ester (21b).** A degassed (three freeze–pump–thaw cycles, −196 °C to room temperature) solution of **7e** (0.189 g, 0.408 mmol) and 3-hexyne (0.093 mL, 0.82 mmol) in $\mathrm{PhCH_2}$ (1.6 mL) was heated in a screw-top tube with a stopcock-bearing sidearm in a 55 °C oil bath for 4 h. During this time TLC ($\mathrm{SiO_2}$, $\mathrm{CH_2Cl_2}$) showed that **7e** (brown spot, $R_f$ = 0.6) gave way to phenol **21a** (for characterization, see below; colorless spot, $R_f$ = 0.18) and its presumed $\mathrm{Cr(CO)_3}$ complex (pale yellow spot, $R_f$ = 0.27). IR spectroscopy of aliquots showed the presence of bands at 1986, 1955, and 1870 cm$^{-1}$, suggestive of $\mathrm{Cr(CO)_6}$ and $\mathrm{Cr(CO)_3}$–arene moieties. At room temperature the reaction mixture was treated with $\mathrm{Et_3N}$ (0.114 mL, 0.82 mmol), $\mathrm{Ac_2O}$ (0.069 mL, 0.73 mmol), and DMAP (4.8 mg, 0.020 mmol). After 3.5 h $\mathrm{FeCl_3 \cdot 1.5\,DMF}$ (0.6 g, 2.2 mmol) was added, and 20 min later the dark mixture was filtered through $\mathrm{SiO_2}$ using ether/petroleum ether 1:1 as eluent. Radial chromatography ($\mathrm{SiO_2}$, ether/petroleum ether 1:3) afforded **21b** (0.123 g, 67%) as a viscous oil, homogeneous by TLC and $^1$H NMR spectroscopy. NMR data indicated that **21b** exists as two rotamers in a ratio of 3 to 1: IR (NaCl, $\mathrm{CH_2Cl_2}$) 2974, 2934, 1759 ($\mathrm{OC{=}O}$), 1696 ($\mathrm{NC{=}O}$), 1391, 1367, 1204, 1170 cm$^{-1}$; MS (*m*/*z*) 451 (6%, $\mathrm{M^+}$), 395 (62), 353 (100), 91 (46, $\mathrm{C_7H_7^+}$), 57 (49); $^1$H NMR ($\mathrm{C_6D_6}$, 300.1 MHz) of the major rotamer δ 7.25–7.3 and 7.0–7.2 (m, 5 H, $\mathrm{CH_2C_6}H_5$), 4.71 and 4.61 (two d, *J* = 13.9 Hz, each 1 H, $\mathrm{NC}H_2\mathrm{Ph}$), 2.0–2.8 (m, 8 H, Ar $\mathrm{C}H_2$), 1.85 (s, 3 H, $\mathrm{O_2CC}H_3$), 1.35 [s, 9 H, $\mathrm{C(C}H_3)_3$], 1.3–1.6 (m, 4 H), 1.15 and 1.07 (two t, *J* = 7.5 Hz, each 3 H, 2 $\mathrm{CH_2C}H_3$). The following signals for the minor rotamer could be recognized: δ 4.47 and 4.44 (two d, *J* = 14.5 Hz, each 1 H, $\mathrm{NC}H_2\mathrm{Ph}$), 1.85 (s, 3 H, $\mathrm{O_2CC}H_3$), 1.54 [s, 9 H, $\mathrm{C(C}H_3)_3$]. Partial $^{13}$C NMR and multiplicity test ($\mathrm{CDCl_3}$, 75.5 MHz): of major rotamer δ 169.0 ($\mathrm{O}C{=}\mathrm{O}$), 155.7 ($\mathrm{N}C{=}\mathrm{O}$), 147.0 (C), 79.7 [$\mathrm{O}C\mathrm{(CH_3)_3}$], 53.9 ($\mathrm{N}C\mathrm{H_2Ph}$), 28.4 [$\mathrm{OC(}C\mathrm{H_3)_3}$], 25.6 ($\mathrm{CH_2}$), 23.6 ($\mathrm{CH_2}$), 22.4 ($\mathrm{CH_2}$), 22.3 ($\mathrm{CH_2}$), 21.5 ($\mathrm{CH_2}$), 20.7 ($\mathrm{CH_3}$), 20.5 ($\mathrm{CH_2}$), 14.9 ($\mathrm{CH_3}$), 14.7 ($\mathrm{CH_3}$); corresponding peaks of minor rotamer δ 169.0, 154.5, 147.3, 80.2, 54.7, 28.6, 25.2, 23.7, 22.1, 21.8, 21.5, 20.7, 20.5, 14.9, 14.7. Anal. Calcd for $\mathrm{C_{28}H_{37}NO_4}$: C, 74.47; H, 8.26; N, 3.10. Found: C, 74.41; H, 8.34; N, 3.24.

In one attempt, the acylation step was inadvertently not allowed to go to completion (compounds **21a** and **21b** absorb very weakly at 254 nm), leading to the isolation of **21a** as a viscous oil, the NMR data for which revealed that it exists as two rotamers in a ratio of ca. 3 to 1: MS (*m*/*z*) 409 (12%, $\mathrm{M^+}$), 353 (100, $\mathrm{M^+ - C_4H_8}$), 262 (27), 244 (10), 217 (12), 204 (16), 202 (16), 91 (35, $\mathrm{C_7H_7^+}$); $^1$H NMR ($\mathrm{C_6D_6}$, 300.1 MHz) signals readily attributable to major rotamer δ 4.82 and 4.61 (two d, both *J* = 13.8 Hz, each 1 H, $\mathrm{NC}H_2\mathrm{Ph}$), 4.56 (br s, 1 H, $\mathrm{O}H$), 1.40 [s, 9 H, $\mathrm{OC(C}H_3)_3$], 1.22 and 1.12 (two t, both *J* = 7.5 Hz, each 3 H, two $\mathrm{CH_2C}H_3$); $^1$H NMR ($\mathrm{C_6D_6}$, 300.1 MHz) signals readily attributable to minor rotamer δ 4.91 (br s, 1 H, $\mathrm{O}H$), 4.62 and 4.47 (two d, both *J* = 14.4 Hz, each 1 H, $\mathrm{NC}H_2\mathrm{Ph}$), 1.56 [s, 9 H, $\mathrm{OC(C}H_3)_3$].

***N*-(Phenylmethyl)-*N*-(4-acetoxy-2,3-diethyl-5,6,7,8-tetrahydronaphthalen-1-yl)ammonium Chloride (22).** A solution of **21b** (0.1229 g, 0.272 mmol) in ether (3 mL) at 0 °C was treated with a sample of ether (3 mL) that had been saturated with HCl gas at 0 °C. After storage of the reaction mixture at room temperature for 4 h the ether was removed in vacuo; the salt **22** was the only compound detectable; recrystallization from ethanol/ether gave an analytical sample of **22** (yield undetermined) as a white solid: $^1$H NMR ($\mathrm{CD_3OD}$, 300.1 MHz) δ 7.36–7.44 (t, *J* = ca. 7 Hz, 1 H), 7.31 (t, *J* = ca. 7 Hz, 2 H), 7.14 (dd, *J* = 1 and 7 Hz, 2 H), 4.51 (s, 2 H, $\mathrm{NC}H_2\mathrm{Ph}$), 2.2–2.8 (m, Ar $\mathrm{C}H_2$) and 2.32 (s, $\mathrm{O_2CC}H_3$) (total 11 H), 1.5–1.8 (m, 4 H), 1.08 and 1.00 (two t, *J* = 7.5 and 7.4 Hz, each 3 H, 2 $\mathrm{CH_2C}H_3$). Anal. Calcd for $\mathrm{C_{23}H_{30}ClNO_2}$: C, 71.21; H, 7.79; N, 3.61. Found: C, 71.20; H, 7.70; N, 3.55.

***N*-(4-Acetoxy-3-pentyl-6-methylnaphth-1-yl)-*N*-(phenylmethyl)carbamic Acid 2,2-Dimethylethyl Ester (23b) and Acetic Acid 2,4-Dipentyl-6-(4-methylphenyl)phenol Ester (27b).** A degassed solution of **7d** (0.3517 g, 0.743 mmol) and 1-heptyne (0.194 mL, 1.48 mmol) in $\mathrm{C_6H_5CH_3}$ (15.8 mL) was stirred at 55–60 °C for 2.5 h, until **7d** was no longer detectable by TLC ($\mathrm{SiO_2}$, $\mathrm{CH_2Cl_2}$). As in the previous two experiments the reaction mixture was treated at room temperature with $\mathrm{Et_3N}$ (0.207 mL, 1.49 mmol), $\mathrm{Ac_2O}$ (0.126 mL, 1.33 mmol), and DMAP (4.5 mg, 0.04 mmol) for 1 h, followed by $\mathrm{FeCl_3 \cdot 1.5\,DMF}$ (0.90 g, 3.3 mmol) for 20 min. Column chromatography led to isolation of the less polar **27b** (0.0521 g, 19%) as a colorless viscous oil: MS (*m*/*z*) 367.2600 (20%, calcd *m*/*z* for $\mathrm{^{12}C_{24}{}^{13}C^1H_{34}{}^{16}O_2}$: 367.2608), 366.2578 (71%, calcd *m*/*z* for $\mathrm{^{12}C_{25}{}^1H_{34}{}^{16}O_2}$: 366.2597), 325 (100), 267 (81), 197 (45); $^1$H NMR ($\mathrm{C_6D_6}$, 300.1 MHz) δ 7.24 and 7.04 (two d, both *J* = 8.0 Hz, each 2 H, $\mathrm{CH_3C_6}H_4$–), 7.19 and 7.12 (two s, each 1 H, H3 and H5 on phenolic ring), 2.58 and 2.55 (two t, *J* = 8 Hz, total 4 H, Ar $\mathrm{C}H_2$), 2.15 and 1.90 (two s, each 3 H, $\mathrm{O_2C}H_3$ and $\mathrm{C}H_3\mathrm{C_6H_4}$), 1.4–1.65 (m, 4 H), 1.18–1.3 (m, 4 H), 1.05–1.15 (m, 4 H), 0.78–0.88 (m, 3 H), 0.70–0.78 (m, 3 H); $^{13}$C NMR ($\mathrm{CDCl_3}$, 100.6 MHz, tentative multiplicity assignments made when possible based on intensities) δ 169.7 ($\mathrm{O_2}C\mathrm{CH_3}$), 147.9 (C1 of phenolic ring), 139.5 (C), 139.3 (C), 138.5 (C), 136.3 (C), 131.8 (CH, C3 or C5 of phenolic ring), 131.3 (C), 129.2 and 128.9 (both CH on 4-methylphenyl group), 122.3 (CH, C5 or C3 of phenolic ring), 32.6, 31.7, 31.6, 30.7, 29.7, 29.6, 22.4, 22.3, 21.2, 21.0, 14.0, 13.9.

Further elution afforded **23b** (0.1624 g, 46%) as a colorless viscous oil: MS (*m*/*z*) 475.2735 (33%, calcd for $\mathrm{^{12}C_{30}{}^1H_{37}{}^{14}N^{16}O_4}$: 475.2748), 419 (10), 377 (100, $\mathrm{M^+ - CH_2CO - C_4H_8}$), 333 (35), 332 (21), 286 (22), 150 (12), 91 (61, $\mathrm{C_7H_7^+}$), 57 (81); $^1$H NMR ($\mathrm{CDCl_3}$, 300.1 MHz) δ 7.63 (d, *J* = 8.6 Hz, 0.7 H), 7.45 (s, 0.7 H), 7.2–7.35 (m, 7 H), 6.74 (br s, 0.3 H), 5.35 (br d, *J* = ca. 14 Hz, 0.7 H), 4.92 (br s, 0.3 H), 4.20–4.35 (m, 2 H), 2.49 and 2.45 (two s, total 6 H), 1.1–1.7 (m) and 1.46 (s) [total 19 H, $\mathrm{C(C}H_3)_3$ and $(\mathrm{C}H_2)_5$], 0.86 [t, *J* = 7 Hz, 3 H, $\mathrm{(CH_2)_5C}H_3$]; partial $^{13}$C NMR and multiplicity test ($\mathrm{CDCl_3}$, 75.5 MHz) δ 169.0 ($\mathrm{O_2}C\mathrm{CH_3}$), 156.3 ($\mathrm{N}C{=}\mathrm{O}$). Anal. Calcd for $\mathrm{C_{30}H_{37}NO_4}$: C, 75.76; H, 7.84; N, 2.95. Found: C, 75.64; H, 7.60; N, 3.20.

***N*-(Phenylmethyl)-*N*-(4-acetoxy-3-pentyl-6-methylnaphthalen-1-yl)ammonium Chloride (24).** A solution of **23b** (0.1428 g, 0.300 mmol) in ether (3 mL) at 0 °C was treated with ether (3 mL) saturated with HCl gas at 0 °C. The ice bath was removed and the solution was stored at room temperatures for 4 h. Workup occurred as described for the isolation of **20** and **22**.

**[3,4-Diethyl-2,3-dihydro-5-(4-methylphenyl)-*N*-((2,2-dimethylethoxy)carbonyl)]-1*H*-pyrrol-2-one (28).** 3-Hexyne (0.137 mL, 1.2 mmol) was added dropwise to a solution of **7f** (430 mg, 1.0 mmol) in 10 mL of THF. The mixture was kept for 1 h at 60 °C then stirred on air for 12 h, and finally filtered over $\mathrm{SiO_2}$. Radial chromatography using petroleum ether/ether 10:1 afforded **28** (39 mg, 11%) as a viscous oil. MS (*m*/*z*) 329 (2.99%, $\mathrm{M^+}$), 273 (92.54, $\mathrm{M^+ - H_2C{=}C(CH_3)_2}$), 229 (96.08), 214 (63.68), 200 (90.87), 91 (30.24, $\mathrm{C_7H_7^+}$), 57 (100, $\mathrm{H_2C{=}C(CH_3)_2^+}$), 29 (31.17, COH, Et); $^1$H NMR ($\mathrm{C_6D_6}$, 300.1 MHz) 6.92–6.80 (m, 4 H), 5.02 (s, 1 H), 2.16–2.11 (m, 2 H), 1.95 (s, 3 H), 1.81–1.74 (m, 1 H), 1.51–1.41 (m, 1 H), 1.25 (s, 9 H), 1.01 (t, $J$ = 7.48 Hz, 3 H), 0.51 (t, $J$ = 7.6 Hz, 3 H); $^{13}$CNMR ($C_6D_6$, 75.5 MHz) 169.20, 157.48, 149.69, 137.75, 135.01, 132.98, 129.54, 127.30, 81.53, 65.01, 28.06, 21.01, 19.74, 17.22, 13.56, 12.70.

**[2-(Benzyloxy)-3,4-diethyl-5-(4-methylphenyl)-*N*-((2,2-dimethylethoxy)carbonyl)]pyrrole (29).** A solution of **7j** (432 mg, 0.835 mmol) and 3-hexyne (0.115 mL, 1.00 mmol) in 15 mL of toluene was kept at 80 °C for 1 h. After oxidation (3 h, air) and filtration over $SiO_2$ the residue was chromatographed with petroleum ether/ether 9:1 to 1:1. The last band afforded **29** as viscous yellow oil (46 mg, 13%). MS ($m/z$) 419 (–%, $M^+$), 347 (90.67, $M^+ - H_2C{=}C(CH_3)_2$), 91 (100, $C_7H_7^+$), 57 (21.87, $H_2C{=}C(CH_3)_2$), 28 (44.06); $^1$H NMR ($CDCl_3$, 300.1 MHz) 7.29–7.08 (m, 9 H), 5.38 (s, 2 H), 2.60 (q, $J$ = 7.41 Hz, 2 H), 2.43 (q, $J$ = 7.55 Hz, 3 H), 2.39 (s, 3 H), 1.13 (t, $J$ = 7.43 Hz, 3 H), 0.97 (s, 9 H), 0.84 (t, $J$ = 7.47 Hz, 3 H); $^{13}$C NMR ($C_6D_6$, 75.5 MHz) 162.45, 151.45, 149.5, 137.55, 136.92, 134.01, 132.07, 128.81, 128.32, 127.54, 126.97, 126.85, 114.19, 86.29, 46.38, 28.82, 23.36, 21.22, 20.81, 14.25, 13.68.

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**Supplementary Material Available:** Tables of atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles (3 pages). Ordering information is given on any current masthead page.

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# Photochemistry of Acyldisilanes

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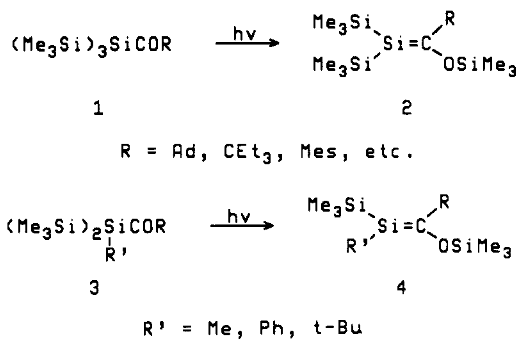
The new acyldisilanes $Me_3SiSiR'_2COAd$ (R′ = Ph, Mes) were prepared by coupling of the appropriate disilyl lithium or potassium reagent with adamantylcarbonyl chloride. Photolyses of the compounds in deuteriobenzene and in the presence of methanol were studied. In the presence of methanol the phenyl compound gave products from the trapping of the anticipated silene and disiloxycarbene, as well as products of radical recombination. Photolysis in $C_6D_6$ gave three dimers, two of which were a cis–trans pair of alkenes resulting from the initially formed silene undergoing cycloaddition with its parent unphotolyzed acyldisilane, followed by rearrangement. The third dimer was relatively unstable, being the head-to-head dimer of the silene. At room temperature, the dimesitylacyldisilane gave only a silaindane, even in the presence of methanol, while at –78 °C in addition to the silaindane, products of radical recombination and from trapping of a disiloxycarbene were obtained. Under no circumstances was the expected silene or its methanol-trapping product observed. These results are interpreted.

The photolysis of tris(trimethylsilyl)acylsilanes $(Me_3Si)_3SiCOR$ (1) gave rise to the first "stable" isolated silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$[1] (2) and to a family of related relatively stable silenes, which differed only in the R group attached to the $sp^2$-hybridized carbon atom, as shown in Scheme I. It is important to establish how the chemistry of the silicon–carbon double bond is influenced by the substituents on the ends of the double bond, i.e. by the $Me_3Si$ and $OSiMe_3$ groups. Attempts were made to clarify this by replacing one of the $Me_3Si$ groups on silicon by a hydrocarbon group, i.e. Me, Ph, or *t*-Bu.[2] The silenes $(Me_3Si)R'Si{=}C(OSiMe_3)Ad$ (4) prepared (Scheme 1) showed similar chemistry to 2 (e.g. addition of MeOH, [2 + 4] cycloadditions with dienes, etc.), but when R′ = Me or Ph, they tended to dimerize and/or rearrange. For R′ = *t*-Bu, the silene was relatively stable, surviving in solution for days like its $Me_3Si$ analogue, although it rearranged on further photolysis.[2]

Scheme I



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