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CARBENE COMPLEXES IN INTRAMOLECULAR DIELS-ALDER REACTIONS [1)]

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Abstract - Diene-dienophile functionalized Fischer type carbene complexes [(CO)$_5$W=C(R)R'] are accessible from hexacarbonyl tungsten by a tandem nucleophilic addition/substitution sequence. Either the diene or the dienophile functionality can be bonded directly to the carbene carbon atom. The synthetic potential of these complexes is demonstrated by furfurylamino(prop-2-enyl)-carbene and diallylamino(furyl)carbene complexes 2 and 11 which - in contrast to their amide analogues - undergo an intramolecular [4+2] cycloaddition under mild conditions. The cycloaddition occurs in a *trans* mode as is established by X-ray analyses.

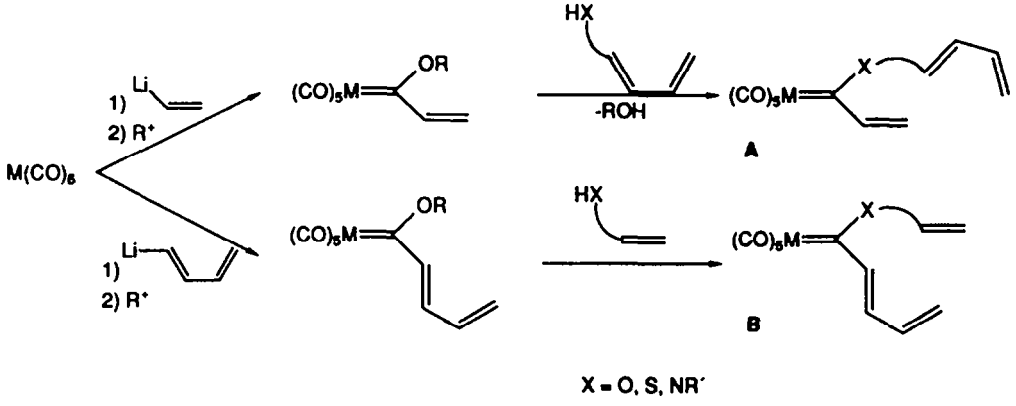
Fischer type carbene complexes [(CO)$_5$M=C(R)R'][2)] are useful reagents for cycloaddition reactions leading to carbocyclic or heterocyclic ring systems.[3)] For instance, carbene annulation reactions by alkynes[4)] leading to hydroquinones as well as the photochemically induced generation of ketene intermediates[5)] have been applied to the synthesis of natural products[6)]. These reactions have been shown to occur at the metal template. Moreover, cycloaddition reactions may proceed at the carbene ligand without the metal being directly involved. Due to their electrophilic nature Fischer type carbene complexes can be regarded as metal-tuned carbonyl compounds. According to the isolobal analogy of a (CO)$_5$M-fragment (M = Cr, Mo, W) and an oxygen atom[7)] alkoxy vinyl carbene complexes are analogous to acrylates. As a consequence complexes containing an α,ß-unsaturated carbene substituent can be used as dienophiles in [4+2] cycloaddition reactions[8)]. In particular the reaction rates and the *exo/endo*-selectivity of metal carbene based Diels-Alder reactions which occur at ambient temperature seem to be comparable to those observed for customary Lewis acid catalyzed reactions performed at -78°C. Pursuing our studies on metal carbene mediated cycloaddition reactions we fo-

cussed on the *intra*molecular version which is well known as a powerful tool for selective carbon-carbon bond formation[9]. A preliminary account of this work has appeared.[10]

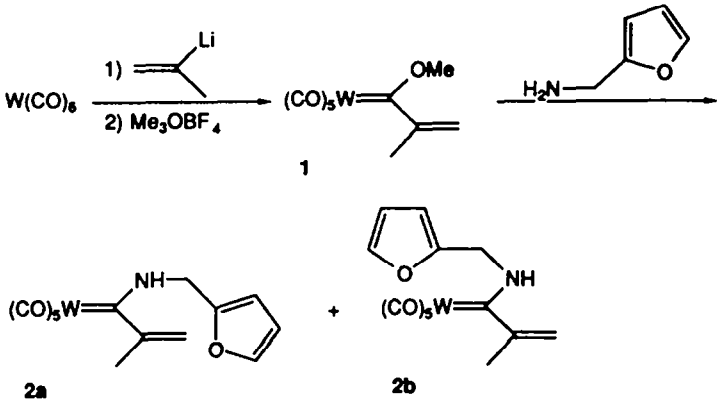
RESULTS AND DISCUSSION

DIENE-DIENOPHILE FUNCTIONALIZED CARBENE COMPLEXES

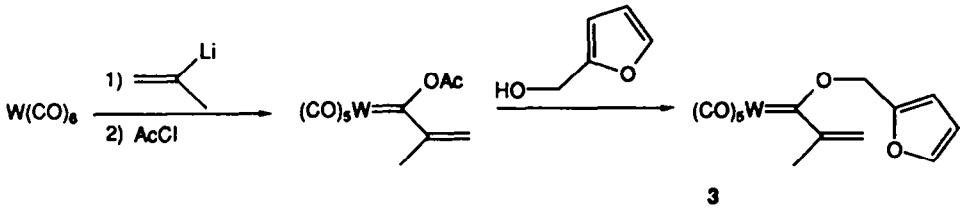
The *intra*molecular Diels-Alder reaction requires diene-dienophile substituted carbene complexes. Our strategy for the synthesis of such compounds is based on a tandem nucleophilic addition/substitution process starting from a metal carbonyl. Following this route two types of complexes (A and B) are accessible containing either the dienophile or the diene functionality bonded directly to the carbene carbon atom.



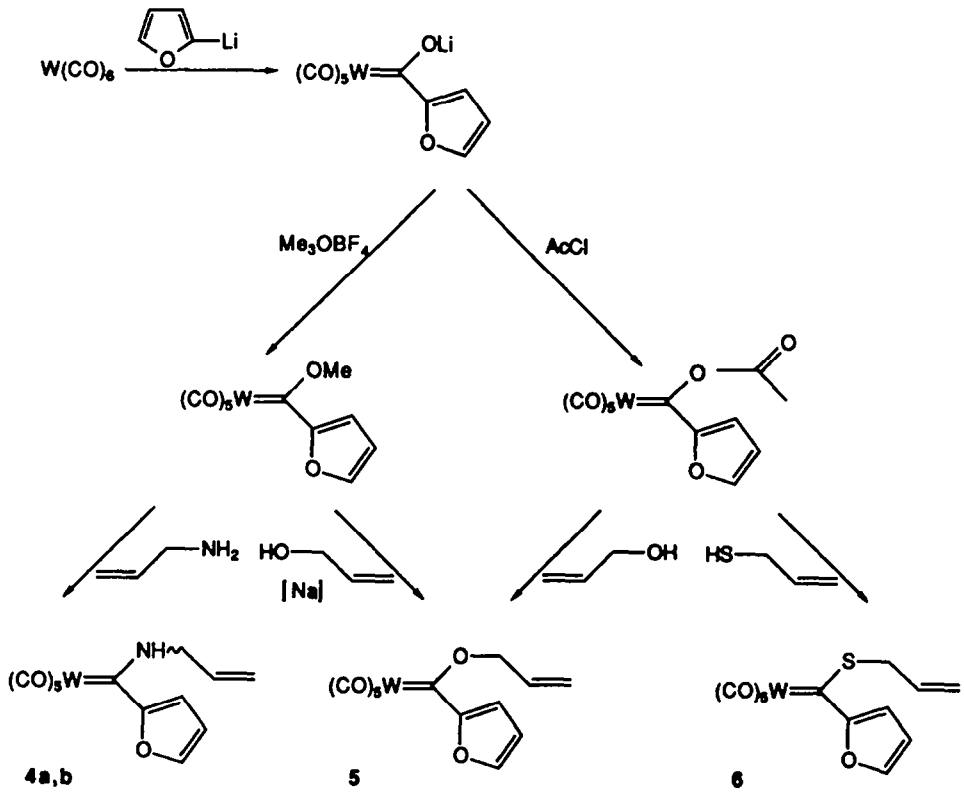
A characteristic example of type A compounds, pentacarbonyl[methoxy(prop-2-enyl)carbene]tungsten (1), is obtained by a one-pot sequential addition of 2-lithiopropene and trimethyloxonium-tetrafluoroborate across the C=O bond in hexacarbonyltungsten. Aminolysis of 1 with furfuryl amine leads to an *E/Z*-mixture (45/55) of aminocarbene complexes 2a and 2b in nearly quantitative yield. The existence of *E/Z*-stereoisomers configurationally stable at ambient temperature is due to a significant heteroatom to carbene π-bonding which is a characteristic feature of Fischer type carbene complexes. In general, the rotational barrier about the nitrogen to carbene bond in amino carbene complexes is >25 kcal/mol[11] indicating that the metal carbonyl fragment is a stronger acceptor than oxygen is in carboxylic amides[12].



The tandem nucleophilic addition/substitution methodology can be extended to alkoxy carbene analogues. The lower nucleophilicity of alcohols (compared to amines) requires a stronger metal carbene electrophile. This goal can be achieved by acylation of the lithium pentacarbonyl tungstate obtained by addition of 2-lithiopropene to hexacarbonyl tungsten. The resulting acyloxy carbene complex undergoes alcoholysis even at low temperatures to give the alkoxy carbene complex 3.

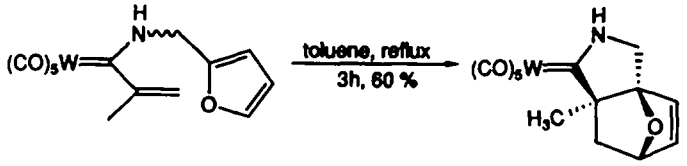


The exchange of diene and dienophile groups within the carbene ligand leads to type B complexes. Typical representatives are compounds 4 - 6 which are accessible from addition of 2-furyllithium to hexacarbonyltungsten followed by alkylation and aminolysis or by reaction with acetyl chloride and subsequent alcoholysis or thiolysis.



INTRAMOLECULAR CYCLOADDITION REACTIONS

An intramolecular Diels-Alder reaction in the furfurylamino carbene complex 2 requires an *E*-configuration at the nitrogen to carbene bond. Consequently, only 2a undergoes cycloaddition to give the isoindolylidene complex 7 when an *E/Z*-mixture 2a/b (45/55) is warmed in toluene to 80°C; the *Z*-isomer 2b remains unchanged under these conditions. If the same reaction is carried out in *refluxing* toluene the cycloadduct 7 is isolated in 60% yield based on the *E/Z*-mixture 2a,b. This indicates that prior to the cycloaddition reaction an *E/Z*-isomerization must occur. So far, no thermally induced isomerization has been reported for aminocarbene complexes below 140°C.[11] The cycloaddition occurs stereospecifically: Only *one* diastereomer characterized by a *trans* mode of ring fusion is observed and its structure has been elucidated by X-ray analysis *(vide infra)*.



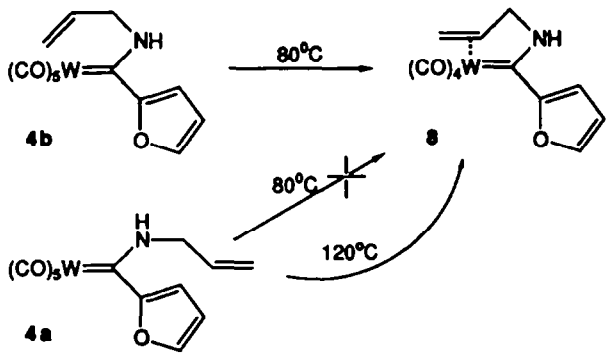
2a,b 7

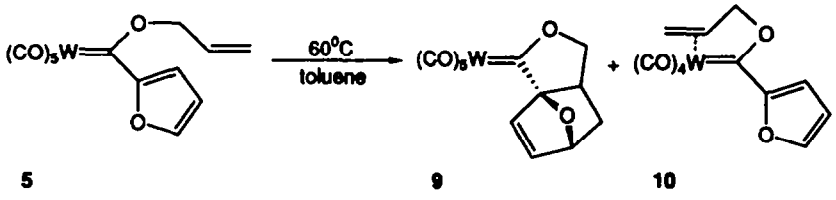
The Diels-Alder product 7 is obtained as light yellow crystals which can be shortly handled in air. It should be noted that secondary amides analogous to 2a,b failed to undergo a cycloaddition even in the presence of strong Lewis acids.[13] Comparable tertiary amides are in principle suitable for intramolecular Diels-Alder reactions[13], but the resulting lactams are often prone to cycloreversion[14]. In summary, the replacement of the oxygen atom in amides with the pentacarbonyl metal fragment enhances the rate of the cycloaddition and allows less severe reaction conditions. However, a general extension of this methodology to alkoxy carbene complexes is problematic. It is known that alkoxy carbene complexes are less stable with regard to thermal decarbonylation than their amino analogues. For instance, the furfuryloxy carbene complex 3 undergoes decomposition above 0°C in solution without detection of any cycloadduct.

The thermolyses of the allylamino, allyloxy and allylmercapto type B carbene complexes 4 - 6 lead to different products. The allylamino carbene complex 4 which is obtained from the aminolysis reaction as a mixture of *E/Z*-isomers (4a/4b = 45/55) eludes cycloaddition. Upon warming to 80°C in toluene the *Z*-isomer 4b undergoes a decarbonylation to yield the tetracarbonyl alkene carbene chelate complex 8 while the *E*-isomer 4a remains unchanged. Both compounds are separable by column chromatography. Further warming of isolated 4a to 120°C in a sealed Schlenk tube results in a combined *E/Z*-isomerization decarbonylation sequence producing again the carbene chelate 8. The chelation process even occurs under CO-atmosphere in a CO-saturated solvent.

No [4+2] cycloaddition has been reported so far for allyl dienyl carboxylates which are analogous to the allyloxy carbene complex 5[15]. This complex, however, reacts upon warming to 60°C in toluene to give the Diels-Alder product 9 which undergoes a facile cycloreversion, and thus can be isolated only in moderate yield. Again the alkene carbene chelate 10 is obtained as a by-product. Neither cycloaddition nor chelation could be observed for the allylthio carbene complex 6. No reaction occurs upon warming up to 60°C, and above this temperature decomposition, presumably arising from the cleavage of the

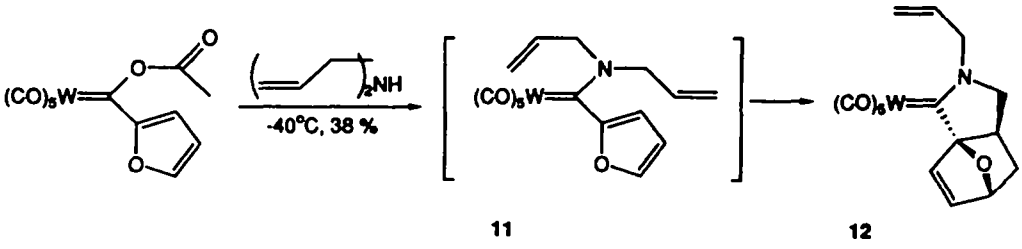
sulfur to carbene bond, may take place.



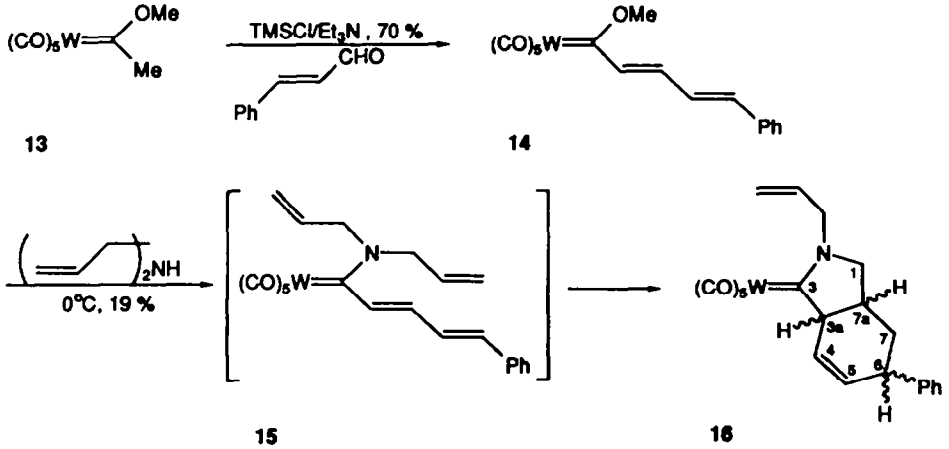


5 9 10

To avoid a trapping of the dienophile by chelation we have extended our studies to the diallylamino carbene complex 11. The diallylamino substituent can be introduced by nucleophilic substitution at an alkoxy or acyloxy carbene center; the latter reaction occurs faster and gives better yields. Following this strategy pentacarbonyl[acetoxy(2-furyl)carbene]tungsten was treated with an excess of diallylamine in dichloromethane at -40°C. Under these conditions no diallylamino carbene complex 11 could be isolated. Instead the desired Diels-Alder adduct 12 is directly obtained in 38% yield as a single diastereomer the structure of which has been determined by X-ray analysis *(vide infra)*. Obviously the entropy of activation for the cycloaddition is decreased by an additional N-substituent in the carbene complex. A similar enhancement of Diels-Alder reactivity has been observed for a series of analogous furyl carboxylic amides. However, these compounds require more vigorous conditions (80-140°C, 2-3 hours)[16] indicating again the more efficient activation of a [4+2] cycloaddition reaction by the metal carbonyl fragment.



To see if acyclic non-aromatic enophiles behave differently from furan in the metal carbene mediated [4+2] cycloaddition we synthesized complex 15. This compound forms upon aminolysis of the dienyl carbene complex 14 which is most conveniently prepared by a condensation reaction of the methyl carbene complex 13 and cinnamaldehyde.[17] As observed for 11 in the furyl series the diene-dienophile substituted complex 15 cannot be isolated. At 0°C it undergoes an *in situ* [4+2] cycloaddition to give the Diels-Alder product 16. In contrast to the cycloadducts 7 and 12 which are obtained as single diastereoisomers the bicyclic compound 16 is formed as a pair of stereoisomers in a 6:1 ratio as is evident from their NMR spectra. The spectral data do not allow an unequivocal distinction whether this is due only to a *cis* or *trans* ring fusion or also to diastereomers arising from the stereocenter next to the phenyl group. For analogous amides only a very poor diastereoselectivity for the *cis/trans* ring fusion (close to 1) has been reported.[18]



STRUCTURAL STUDIES

To elucidate the stereochemistry of the [4+2] cycloaddition the structures of the Diels-Alder products 7 and 12 were determined by X-ray diffraction (Figures 1,2). The relevant structural features are very similar for both molecules. For both compounds the *trans* mode of cyclization is confirmed. The five-membered rings containing the carbene carbon and the nitrogen atoms adopt an envelope conformation with C7 in 7 and C3 in 12 being out of the plane formed by the other four ring atoms (0.47 Å and 0.39 Å, respectively). The orientation of the oxanorbornene framework is along the bisector between two *cis* carbonyl ligands. The different connectivity between the oxanorbornene system and the five-membered ring containing the N and carbene C atoms in 7 and 12 results from the different location of the ene and the diene moieties for the Diels-Alder reaction in the starting materials. As generally encountered for metal carbene complexes[19] the π-bonding in the nitrogen to carbene bond is evident from the near planarity at N and from the short N-C distances [N1-C1 = 1.298(6) Å for 7 and 1.324(8) Å for 12], while the tungsten carbene bonds are rather long [2.227(4)Å for 7 and 2.213(6)Å for 12]. Although at the borderline of significance it is instructive to see that

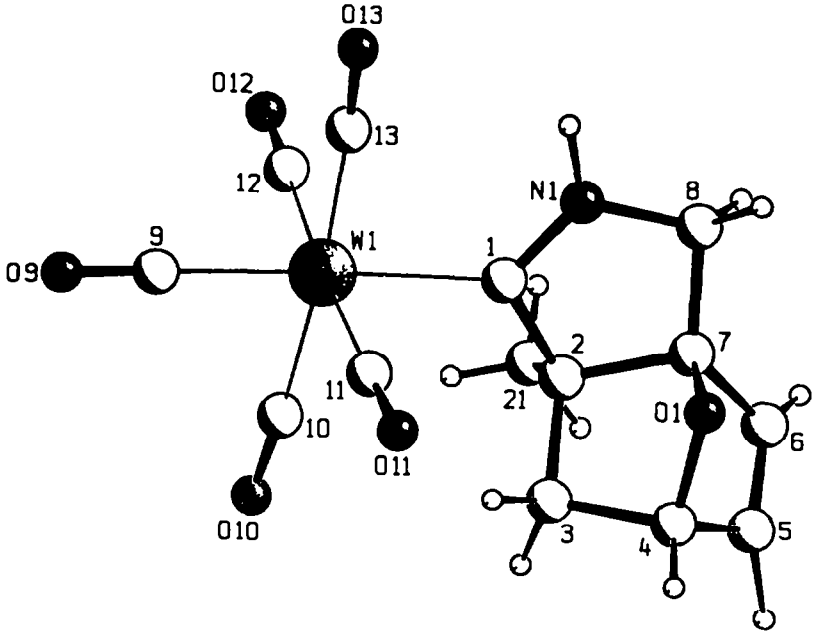


Figure 1. Molecular structure and atomic numbering scheme of 7 (SCHAKAL, atoms with arbitrary radii). Important distances (Å) and angles (°): W-C1 2.227(4), C1-C2 1.531(6), C1-N1 1.298(6), N1-C8 1.477(6); W-C1-C2 126.2(3), W-C1-N1 126.7(3), C2-C1-N1 107.1(4). Plane angles (°): C1,C2,N1,C8/C2,C7,C8 30.1; C7-C2-C3-C4/C4,O1,C7 118.6; C4,C5,C6,C7/C4,O1,C7 128.5. Torsion angle (°): C1-C2-C7-C8 29.3.

the longer N1-C1 bond in 12 corresponds to the shorter W-C1 carbene bond, while the opposite is true for 7. This indicates that the secondary amine function in 7 is slightly better suited for electron release onto the electrophilic carbene center than the tertiary amine in 12.

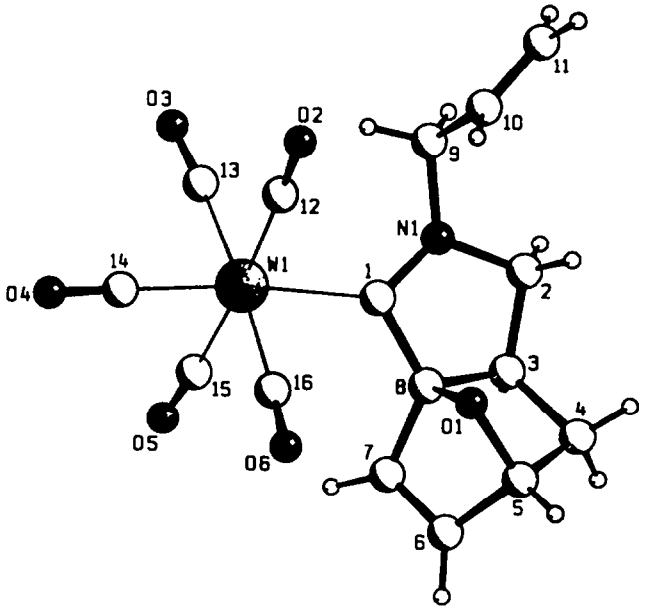
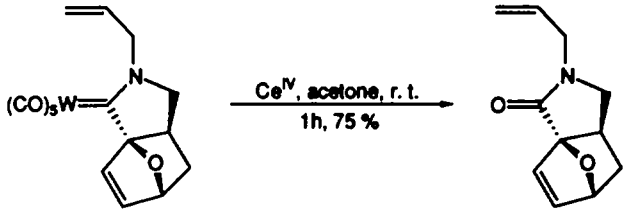


Figure 2. Molecular structure and atomic numbering scheme of 12 (SCHAKAL, atoms with arbitrary radii). Important distances (Å) and angles (°): W-C1 2.213(6), C1-C8 1.514(8), C1-N1 1.324(8), N1-C2 1.480(9); W-C1-C8 123.3(4), W-C1-N1 132.8(4), C8-C1-N1 103.8(5). Plane angles (°): C1,C8,N1,C2/C8,C3,C2 23.4(7); C5,C6,C7,C8/C8,O1,C5 128.1(6). Torsion angle (°): C1,C8,C3,C2 24.5.

CLEAVAGE OF THE METAL CARBENE BOND

As exemplified by the formation of 7, 12 and 16, aminocarbene complexes have a distinctly lower activation barrier for the [4+2] cycloaddition in comparison with analogous amides. Moreover, metal carbene derived Diels-Alder products are less prone to cycloreversion. These features can be attractive for synthetic applications only if mild and high-yield methods are available for the cleavage of the metal in the final step. A cleavage of the metal carbene bond can be achieved either by oxidation or by ligand substitution reactions.[3] Among a series of oxidizing agents best results have been obtained with cerium(IV) compounds. For instance, $(NH_4)_2Ce(NO_3)_6$ converts complex 12 at ambient temperature in acetone to lactam 17 in 75% yield.



12 17

EXPERIMENTAL

General technique

All reactions were carried out under an atmosphere of dried N_2. Solvents used for reactions were dried using standard methods, distilled, N_2-saturated and stored under N_2. The silica gel used for chromatography (type 60, E.Merck, Darmstadt, 0.063-0.2 mm) was dried at high vacuum and kept under N_2. The following instruments served for spectroscopic characterization: IR-spectrometers: Perkin Elmer 281 and 283b, Nicolet 5 DX; ^1H- and ^{13}C-NMR spectrometers: Jeol FX 270, Bruker AC 300, Bruker WH 400; mass spectrometers: Varian MAT 311 A and Varian MAT CH7A. NMR Data are reported in ppm using TMS as internal standard and abbreviations as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

Pentacarbonyl[methoxy(prop-2-enyl)carbene]tungsten (1). An equimolar amount of 2-lithiopropene [20] in 40 ml ether was added at -78°C to a solution of 6.50 g (18.5 mmol) $W(CO)_6$ in 80 ml ether. Within 2 h this mixture was warmed to room temp., and then the solvent was removed under reduced pressure. The dark brown residue was washed with pentane several times and finally dissolved in 30 ml H_2O. 4.00 g $[(CH_3)_3O][BF_4]$ (25.0 mmol) and 100 ml pentane were added, and the mixture was stirred vigorously. Extraction with pentane gave a dark red solution which was dried over Na_2SO_4. Removal of the solvent gave a deep red oil which was purified by chromatography over silica gel in pentane at -30°C affording a dark red oil. 6.00 g (80 %). IR (C_6H_{14}, ν(CO) cm^{-1}): 2072m, 1984w, 1959s, 1944vs. ^1H-NMR ($CDCl_3$, 300 MHz): δ 5.48 (s, br, 1H, =CH); 5.42 (s, br, 1H, =CH); 4.61 (s, 3H, OMe); 1.88 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 327.2 ($C_{carbene}$); 203.5 (CO_{trans}); 197.5 (CO_{cis}); 160.6 (C=); 121.5 (=CH_2); 69.6 (OMe); 19.2 (CH_3); MS: *m/z* 408 (M^+). (Found: C, 30.16; H, 2.12%; $C_{10}H_8O_6W$ requires: C, 29.44; H, 1.98%.)

Pentacarbonyl[(E/Z)-furfurylamino(prop-2-enyl)carbene]tungsten (2a,b). 1.0 ml (11.5 mmol) Furfuryl amine was added at -20°C to a solution of 2.64 g (6.5 mmol) 1 in 150 ml pentane, whereupon the colour immediately changed from dark red to yellow. After stirring for 3 h the solvent was removed, and the

remaining yellow oil was chromatographed on silica gel with pentane/CH_2Cl_2 (3:1) at -30°C. Bright yellow crystals were obtained from pentane/CH_2Cl_2 (4:1) at -78°C. 2.86 g (93 %). IR (C_6H_{14}, ν(CO) cm^{-1}): 2067m, 1978w, 1924s, 1946vs. ^{1}H-NMR (C_7D_8, 270 MHz): δ 8.12 (s, br, 1H, NH); 6.87 (d, 1.84 Hz, 1H, furyl-H_5); 5.92 (dd, 3.30 Hz, 1.84 Hz, 1H, furyl-H_4); 5.70 (d, 3.30 Hz, 1H, furyl-H_3); 4.32 (d, 1.46 Hz, 1H, =CHH); 4.19 (d, 1.46 Hz, 1H, =CHH); 3.66 (s) and 3.54 (s) (2H, *E*- and *Z*- NCH_2); 1.65 (s, 3H, CH_3). ^{13}C-NMR (CD_3COCD_3, 68.0 MHz): *E*-isomer: δ 257.9 ($C_{carbene}$); 204.1 (CO_{trans}); 199.5 (CO_{cis}); 159.5 (furyl-C_2); 149.3 (furyl-C_5 and C=); 144.2 (furyl-C_4); 111.7 (furyl-C_3); 104.9 (=CH_2); 53.2 (NCH_2); 20.0 (CH_3); *Z*-isomer: 257.3 ($C_{carbene}$); 203.9 (CO_{trans}); 199.1 (CO_{cis}); 159.5 (furyl-C_2); 149.3 (furyl-C_5 and C=); 144.2 (furyl-C_4); 111.7 (furyl-C_3); 106.0 (=CH_2); 46.9 (NCH_2); 21.4 (CH_3). MS: *m/z* 473 (M^+). (Found: C, 35.55; H, 2.45; N, 2.98; W, 38.70%; $C_{14}H_{11}NO_6W$ requires: C, 35.54; H, 2.34; N 2.96, W, 38.86%.)

Pentacarbonyl[furfuryloxy(prop-2-enyl)carbene]tungsten (3). An equimolar amount of 2-lithiopropene in 40 ml ether was added to a solution of 3.50 g $W(CO)_6$ (10.0 mmol) in 20 ml ether at -78°C. Within 2 h the mixture was warmed to room temp., and then the solvent was removed under reduced pressure. The dark brown oily residue was dissolved in 100 ml CH_2Cl_2 and cooled to -50°C. 1.0 ml (14.0 mmol) Acetyl chloride and 0.5 ml TMEDA were added, and the solution was stirred for 2 h at -40°C. After addition of 2.0 ml (23.0 mmol) furfuryl alcohol stirring was continued for 2 h at -40°C. Removal of the solvent gave a bright red oil which was purified by chromatography on silica gel at -40°C using petroleum ether/CH_2Cl_2 (5:2) as eluent. By recrystallization from petroleum ether bright red needles were obtained. 0.76 g (16%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2070m, 1956s,sh, 1946vs. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.53 (dd, 1.8 Hz, 0.8 Hz, 1H, furyl-H_5); 6.62 (d, br, 3.6 Hz, 1H, furyl-H_3); 6.46 (dd, 3.3 Hz, 1.8 Hz, 1H, furyl-H_4); 5.78 (s, 2H, OCH_2); 5.50 (s, br, 1H, =CHH); 5.31 (s, br, 1H, =CHH); 1.87 (dd, 3H, 1.4 Hz, 0.8 Hz, CH_3). ^{13}C-NMR ($CDCl_3$, 233 K, 100.6 MHz): δ 322.1 ($C_{carbene}$); 203.4 (CO_{trans}); 197.8 (CO_{cis}); 160.4 (furyl-C_2); 147.3 (C=); 144.3 (furyl-C_5); 137.1 (furyl-C_3); 112.5 (furyl-C_4); 110.9 (=CH_2); 77.1 (OCH_2); 19.0 (CH_3). MS: *m/z* 393 ($M^+-C_4H_3OCH_2$). (Found: C, 35.30; H, 2.20; W, 38.83%; $C_{14}H_{10}O_7W$ requires: C, 35.47; H, 2.13; W 38.78%.)

Pentacarbonyl[(E/Z)-allylamino(2-furyl)carbene]tungsten (4a,b). 1.24 g (2.8 mmol) Pentacarbonyl[2-furyl(methoxy)carbene]tungsten[21] were dissolved in 50 ml pentane and treated with an excess of allyl amine (3 - 5 equivalents) at -20°C. The colour immediately changed from dark red to yellow. After stirring for 30 min the solvent was removed and the crude product was chromatographed on silica gel at -30°C using pentane/CH_2Cl_2 (3:1) as an eluent. Yellow crystals were obtained from pentane/CH_2Cl_2 (5:1) at -78°C. 1.15 g (91%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2063m, 1933s,br. ^{1}H-NMR ($CDCl_3$, 300 MHz): in the spectrum appear two sets of signals, corresponding to the *E*- (**4a**) and the *Z*-isomer (**4b**) in a ratio of 45:55 : **4a**: δ 8.24 (s, br, 1H, NH); 7.74 (d, 1.8

Hz, 1H, furyl-H_5); 7.25 (d, 4.8 Hz, 1H, furyl-H_3); 6.63 (dd, 4.5 Hz, 1.8 Hz, 1H, furyl-H_4); 6.03 (ddt, 11.8 Hz, 16.7 Hz, 5.8 Hz, >1H, CH= [signal for both isomers]); 5.44 (m, 2H, $=CH_2$); 4.63 (dddd, 5.9 Hz, 5.9 Hz, 1.4 Hz, 1.4 Hz, 2H, NCH_2); **4b**: δ 9.09 (s, br, 1H, NH); 7.56 (d, 1.6 Hz, 1H, furyl-H_5); 7.45 (d, 3.6 Hz, 1H, furyl-H_3); 6.61 (dd, 3.7 Hz, 1.8 Hz, furyl-H_4); 5.40 (m, 2H, $=CH_2$); 4.36 (dddd, 5.7 Hz, 5.7 Hz, 1.5 Hz, 1.5 Hz, 2H, NCH_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): **4a**: δ 230.3 ($C_{carbene}$); 202.7 (CO_{trans}); 198.9 (CO_{cis}); 157.8 (furyl-C_2); 146.6 (furyl-C_5); 131.5 (CH=); 124.9 (furyl-C_3); 119.8 ($=CH_2$); 113.3 (furyl-C_4); 55.1 (NCH_2). **4b**: δ 225.1 ($C_{carbene}$); 202.2 (CO_{trans}); 198.3 (CO_{cis}); 159.3 (furyl-C_2); 144.4 (furyl-C_5); 131.6 (CH=); 126.7 (furyl-C_3); 120.1 ($=CH_2$); 113.9 (furyl-C_4); 57.3 (NCH_2). MS: *m/z* 459 (M^+). (Found: C, 34.12; H, 1.98; N, 3.09%; $C_{13}H_9NO_6W$ requires: C, 34.01; H, 1.98; N, 3.05%.)

Pentacarbonyl[allyloxy(2-furyl)carbene]tungsten (5) and ***pentacarbonyl[allylmercapto(2-furyl)carbene]tungsten*** (6). 3.50 g (10.0 mmol) $W(CO)_6$ were dissolved in 20 ml ether and cooled to -10°C. An equimolar amount of 2-lithiofuran[22] was added, and the solution was stirred for 1 h at room temp.. After removal of the solvent the dark brown residue was dissolved in CH_2Cl_2 and treated with 1.0 ml (14.0 mmol) acetyl chloride and 0.5 ml TMEDA at -40°C, whereupon the colour changed from dark brown to purple within 5 min. After stirring for 45 min 15.0 mmol of the nucleophile (allyl alcohol resp. allyl mercaptane) were added. After 1 h the solution was filtered through silica gel. The solvent was removed, and the products were purified by chromatography on silica gel using petroleum ether/CH_2Cl_2 as eluent.

5: Dark red crystals were obtained from petroleum ether. 1.58 g (35%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2069m, 1988w, 1959s, 1944vs. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.90 (d, 1.5 Hz, 1H, furyl-H_5); 7.18 (d, 3.6 Hz, 1H, furyl-H_3); 6.62 (dd, 3.7 Hz, 1.9 Hz, 1H, furyl-H_4); 6.18 (ddt, 16.2 Hz, 15.5 Hz, 4.8 Hz, 1H, CH=); 5.53 (dd, 15.4 Hz, 1.2 Hz, 1H, =CHH); 5.40 (d, 5.3 Hz, 2H, OCH_2); 5.39 (dd, 17.3 Hz, 1.2 Hz, 1H, =CHH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 284.9 ($C_{carbene}$); 203.3 (CO_{trans}); 197.3 (CO_{cis}); 166.4 (furyl-C_2); 150.3 (furyl-C_5); 131.5 (CH=); 119.9 ($=CH_2$); 115.2 (furyl-C_3); 113.6 (furyl-C_4); 82.5 (OCH_2). MS: *m/z* 460 (M^+). (Found: C, 33.29; H, 1.77; W, 39.50%; $C_{13}H_8O_7W$ requires: C, 33.94; H, 1.75; W 39.96%.)

6: Deep violet crystals were obtained from petroleum ether. 4.07 g (85%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2061m, 1990w, 1943vs,br. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, 1.5 Hz, 1H, furyl-H_5); 7.59 (d, 3.7 Hz, 1H, furyl-H_3); 6.77 (dd, 4.0 Hz, 1.9 Hz, 1H, furyl-H_4); 5.95 (ddt, 17.1 Hz, 13.3 Hz, 7.2 Hz, 1H, CH=); 5.43 (dd, 16.9 Hz, 1.2 Hz, 1H, =CHH); 5.35 (dd, 14.7 Hz, 1.2 Hz, 1H, =CHH); 4.12 (d, 7.3 Hz, 2H, SCH_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 273 ($C_{carbene}$); 206.1 (CO_{trans}); 197.9 (CO_{cis}); 165.5 (furyl-C_2); 149.7 (furyl-C_5); 130.2 (CH=); 127.9 (furyl-C_3); 121.3 ($=CH_2$); 116.2 (furyl-C_4); 52.5 (SCH_2). MS: *m/z* 448 (M^+-CO). (Found: C, 32.63; H, 1.78; W, 39.08%; $C_{13}H_8O_6SW$ requires: C, 32.80; H, 1.69; W, 38.62%.)

Alternative procedure for the synthesis of **5.** 2.0 ml (29.4 mmol) Allyl alcohol were dissolved in 20 ml ether, treated with 0.02 g (1.0 mmol) sodium and stirred at room temp. until all of the sodium was consumed. Then the mixture was added dropwise to a solution of 0.44 g (1 mmol) pentacarbonyl[2-furyl(methoxy)carbene]tungsten in ether. Molecular sieve (4 Å) was added, and stirring was continued for 24 h at 0°C. Workup as above. 0.20 g (43%).

Pentacarbonyl(5,7a-epoxy-1,3,3a,4,5,7a-hexahydro-3a-methyl-isoindol-3-ylidene)tungsten **(7).** A solution of 0.50 g (1.1 mmol) of an isomeric mixture of **2a** and **2b** in 100 ml toluene was refluxed for 3 h. The solvent was removed at high vacuum, and the crude product was chromatographed at ambient temp. on silica gel in toluene/ether (1:2). Light yellow crystals were obtained from toluene at -30°C. 0.30 g (60%). IR ($C_2H_5OC_2H_5$, ν(CO) cm^{-1}): 2063m, 1968w, 1932vs, 1916vs. ^{1}H-NMR (C_6D_6, 270 MHz): δ 7.19 (s, br, 1H, NH); 5.77 (d, 5.9 Hz, 1H, =CH); 5.64 (dd, 5.9 Hz, 1.8 Hz, 1H, =CH); 4.35 (dd, 4.8 Hz, 1.8 Hz, 1H, $CH_{bridgehead}$); 2.83 (dd, 11.7 Hz, 1.8 Hz, 1H, CHH); 2.61 (d, 12.1 Hz, 1H, NCHH); 2.42 (dd, 11.7 Hz, 4.8 Hz, CHH); 1.01 (d, 12.1 Hz, 1H, NCHH); 0.58 (s, 3H, CH_3). ^{13}C-NMR (C_6D_6, 68.0 MHz): δ 263.1 ($C_{carbene}$); 202.5 (CO_{trans}); 198.7 (CO_{cis}); 138.4 (=C); 131.4 (=C); 92.8 (7a-C); 79.0 (5-C); 73.1 (3a-C); 54.9 (NCH_2); 38.8 (4-C); 22.0 (CH_3). MS: *m/z* 473 (M^+). (Found: C, 35.50; H, 2.32; N, 3.13; O, 20.32; W, 38.88%; $C_{14}H_{11}NO_6W$ requires: C, 35.54; H, 2.34; N, 2.96; O, 20.29; W 38.86%.)

cis-Tetracarbonyl[η^2-allylamino(2-furyl)carbene]tungsten **(8).** A solution of 0.88 g (1.92 mmol) of an isomeric mixture of **4a,b** in 50 ml toluene was warmed to 80°C for 10 h. After removal of the solvent the crude product was chromatographed at ambient temp. on silica gel in petroleum ether/CH_2Cl_2 (3:1). The first yellow band contained the pure *E*-aminocarbene complex **4a**, the second orange band the chelate complex **8**. Recrystallization from petroleum ether /CH_2Cl_2 (10:1) gave orange crystals (0.30 g). The residue of the first band was dissolved again in 30 ml toluene and heated to 120°C in a sealed Schlenk tube for another 10 h. After chromatography and recrystallization another 0.25 g **8** were obtained. Total yield 0.55 g (66%). IR ($C_2H_5OC_2H_5$, ν(CO) cm^{-1}): 2023m, 1963vs, 1929vs, 1885m. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.03 (s, br, 1H, NH); 7.45 (d, 1.6 Hz, 1H, furyl-H_5); 7.34 (d, 3.6 Hz, 1H, furyl-H_3); 6.47 (dd, 1.6 Hz, 3.6 Hz, 1H, furyl-H_4); 4.61 (m, 1H, =CH); 4.37 (d, 14 Hz, 1H, NCHH); 4.12 (dd, 14.1 Hz, 4.8 Hz, 1H, NCHH); 3.15 (dd, 9.0 Hz, 1.0 Hz, 1H, =CHH); 2.97 (d, 3.1 Hz, 1H, =CHH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 233.0 ($C_{carbene}$); 215.2 and 205.5 (CO_{trans}); 204.7 and 204.2 (CO_{cis}); 157.3 (furyl-C_2); 145.0 (furyl-C_5); 126.8 (furyl-C_3); 113.9 (furyl-C_4); 70.1 (=CH); 55.4 (NCH_2); 52.9 (=CH_2). MS: *m/z* 431 (M^+). (Found: C, 33.47; H, 2.00; N 3.23, W, 42.14%; $C_{12}H_9NO_5W$ requires: C, 33.44; H, 2.10; N, 3.25, W, 42.65%.)

Pentacarbonyl(3a,6-epoxy-1,3,3a,6,7,7a-hexahydroisobenzofuran-3-ylidene)tungsten **(9).** A solution of 0.20 g (0.4 mmol) **5** in 25 ml toluene was warmed to 60°C for 1.5 h, during which the dark red solution slowly lightened. The sol-

vent was removed under reduced pressure. A ^{1}H-NMR sample of the residue indicated that the starting material 5 had completely disappeared. However, chromatography on silica gel at -30°C using pentane/CH_2Cl_2 (4:1) as eluent gave first 5 and then a second orange band containing chelate complex 10. Further elution with ether yielded cycloadduct 9. 0.02 g 9 (10%) and 0.01 g 10 (5%). 9: IR (C_6H_{14}, ν(CO) cm^{-1}): 2073m, 1954s, 1944vs. ^{1}H-NMR (C_6D_6, 270 MHz): δ 6.78 (d, 3.3 Hz, 1H, =CH); 5.81 (dd, 3.6 Hz, 1.8 Hz, =CH); 5.00 (m, 2H, OCH_2); 3.30 (dt, 6.6 Hz, 1.7 Hz, 1H, H_6); 2.13 (m, 1H, H_{7a}); 1.42 (m, 2H, CH_2). 10: IR (C_6H_{14}, ν(CO) cm^{-1}): 2025m, 1948s, 1932vs, 1885s. MS: *m/z* 432 (M^+).

Pentacarbonyl(N-allyl-3a,6-epoxy-1,3,3a,6,7,7a-hexahydroisoindol-3-ylidene)-tungsten (12). To a solution of pentacarbonyl[acetoxy(2-furyl)carbene]tungsten in methylene chloride obtained from 3.50 g (10.0 mmol) $W(CO)_6$ as described for the synthesis of 5 and 6 were added dropwise 4.0 ml (30.0 mmol) diallylamine. Chromatographic workup on silica gel at -30°C using petroleum ether/CH_2Cl_2 (3:2) as an eluent followed by recrystallization from petroleum ether/CH_2Cl_2 (4:1) gave 12 as pale yellow rhombic crystals (m.p. 103°C). 1.91 g (38%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2067w, 1940s, 1931vs. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.86 (d, 5.9 Hz, 1H, =CH); 6.44 (dd, 5.9 Hz, 1.6 Hz, 1H, =CH); 5.91 (dddd, 16.4 Hz, 8.9 Hz, 10.3 Hz, 8.5 Hz, 1H, allyl-CH=); 5.36 (m, 2H, allyl-CH_2=); 5.20 (dd, 4.4 Hz, 1.7 Hz, 1H, H_6); 4.65 (dd, 6.0 Hz, 14.7 Hz, 1H, cyclic-NCHH); 4.57 (dd, 14.8 Hz, 6.3 Hz, 1H, cyclic-NCHH); 3.90 (dd, 12.5 Hz, 8.7 Hz, 1H, allyl-NCHH); 3.45 (dd, 8.6 Hz, 12.5 Hz, 1H, allyl-NCHH); 2.18 (dddd, 3.1 Hz, 10.8 Hz, 7.5 Hz, 7.9 Hz, 1H, H_{7a}); 1.95 (ddd, 4.3 Hz, 7.2 Hz, 11.8 Hz, 1H, CHH); 1.60 (dd, 11.8 Hz, 7.8 Hz, 1H, CHH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 243.6 ($C_{carbene}$); 202.6 (CO_{trans}); 198.4 (CO_{cis}); 136.3, 135.8 and 131.2 (=CH); 120.7 (allyl-CH_2=); 111.5 (C_{3a}); 80.6 (C_6); 65.7 (cyclic NCH_2); 59.9 (allyl-NCH_2); 39.8 (C_{7a}); 32.0 (C_7). MS: *m/z* 499 (M^+). (Found: C, 38.28; H, 2.26; N, 2.88; W, 36.92%; $C_{16}H_{13}NO_6W$ requires: C, 38.50; H, 2.63; N, 2.81; W, 36.83%.)

Pentacarbonyl[methoxy(E,E-4-phenyl-buta-1,3-dienyl)carbene]tungsten (14). A solution of 2.00 g (5.0 mmol) 13[23] in 35 ml ether was treated with 0.6 ml (5.0 mmol) cinnamaldehyde, 2.3 ml (15.0 mmol) trimethylsilyl chloride and 2.8 ml (20.0 mmol) triethylamine and stirred at room temp. for 3 days. Then the dark red solution was filtered through silica gel, and the solvent was removed at reduced pressure. After chromatography on silica gel at -30°C using petroleum ether/ether (4:1) as eluent and recrystallization from petroleum ether 14 was obtained as a dark red powder. 1.73 g (70%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2062m, 1981w, 1945vs,br. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.35 - 7.53 (m, 6H, C_6H_5 and =CH); 7.00 - 7.14 (m, 2H, =CH); 6.78 - 6.87 (m, 1H, =CH); 4.59 (s, 3H, OMe). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 305.5 ($C_{carbene}$); 203.9 (CO_{trans}); 191.2 (CO_{cis}); 147.0, 144.9, 136.3, 135.1, 129.7, 129.0, 128.1 and 127.5 (C_6H_5 and olefinic C's); 68.8 (OMe). MS: *m/z* 496 (M^+). (Found: C, 41.12; H, 2.24%; $C_{17}H_{12}O_6W$ requires: C, 41.16; H, 2.44%.)

Pentacarbonyl(N-allyl-6-phenyl-1,3,3a,6,7,7a-hexahydroisoindol-3-ylidene)-tungsten **(16).** A solution of 0.70 g (1.4 mmol) **14** in 75 ml petroleum ether was treated with 2.5 ml (19.0 mmol) diallylamine at 0°C. After stirring at 0°C for 10 h the solvent was removed at reduced pressure, and the residue was chromatographed at -30°C on silica gel using petroleum ether/CH_2Cl_2 (3:1) as an eluent. The first band contained traces of starting material **14**. Further elution gave **16**. Recrystallization from petroleum ether afforded **16** as an orange powder. 0.15 g (19%). IR (C_6H_{14}, ν(CO) cm^{-1}): 2059m, 1935vs, 1925vs. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.11 - 7.31 (m, 5H, C_6H_5); 6.68 (dd, 10.1 Hz, 2.4 Hz, 1H) and 6.05 (dd, 10.2 Hz, 1.5 Hz, 1H)(H_4, H_5); 5.84 (ddt, 5.6 Hz, 10.4 Hz, 16.6 Hz, 1H, allyl-CH=); 5.37 (m, 2H, allyl-CH_2=); 4.76 (dd, 14.5 Hz, 5.7 Hz, 1H, cyclic NCHH); 4.44 (dd, 14.8 Hz, 8.0 Hz, 1H, cyclic NCHH); 3.86 (ddd, 10.2 Hz, 5.3 Hz, 2.3 Hz, 1H, H_6); 3.41 (m, 3H, H_{3a} and allyl-NCH_2); 2.58 (m, 1H, H_{7a}); 1.07 - 1.23 (m, 2H, CH_2). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 250.5 ($C_{carbene}$); 202.8 (CO_{trans}); 198.4 (CO_{cis}); 145.1, 128.8, 127.9 and 127.4 (C_6H_5); 133.7 (allyl-CH=); 131.9 and 126.0 (C_4,C_5); 121.3 (allyl-CH_2=); 66.9 (cyclic-NCH_2); 64.1 (allyl-NCH_2); 60.2 (C_6); 41.4 (C_{3a}); 36.2 (C_{7a}); 32.8 (C_7). MS: *m/z* 561 (M^+).

Oxidation of **12.** 0.60 g (1.1 mmol) $(NH_4)_2Ce(NO_3)_6$ were added to a solution of 0.35 g (0.7 mmol) **12** in 20 ml acetone. After stirring for 1 h at room temp. the solvent was removed, the residue was dissolved in 20 ml water and extracted with ether. The organic phase was dried over molecular sieve (4 Å), and evaporation of the solvent gave **17** as a pale yellow oil. 0.10 g (75%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.98 (d, 3.3 Hz, 1H, H_4); 6.38 (dd, 3.4 Hz, 1.7 Hz, 1H, H_5); 5.92 (m, 1H, allyl-CH=); 5.43 (m, 2H, allyl-CH_2=); 5.13 (m, 1H, H_6); 4.20-4.40 (m, 2H, cyclic-NCH_2); 3.89 (dd, 12.4 Hz, 8.8 Hz, 1H, allyl-NCHH); 3.46 (dd, 12.2 Hz, 7.1 Hz, 1H, allyl-NCHH); 2.14 (m, 1H, H_{7a}); 1.86 (m, 1H, CHH); 1.63 (m, 1H, CHH). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 191.0 (CO); 143.9 (=CH); 137.1 (C_4); 133.2 (C_5); 116.1 (=CH_2); 111.5 (C_{3a}); 81.5 (C_6); 68.0 (cyclic-NCH_2); 65.7 (allyl-NCH_2); 38.8 (C_{7a}); 29.5 (C_7).

X-Ray structure determinations.

Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator, Syntex $P2_1$ (7) and Enraf-Nonius CAD4 (12). Crystal structure data for **7**·1 toluene: $C_{21}H_{19}NO_6W$, M_r = 565.239, triclinic, space group P1 (No.2) with a = 8.886(1), b = 10.706(1), c = 12.807(1) Å, α = 109.50(1), ß = 108.06(1), γ = 98.94(1)°, V = 1045.4 Å^3, D_c = 1.796 g/cm^3, Z = 2, μ(Mo-K_α) = 56.8 cm^{-1}, F(000) = 548, T = -35°C. 3689 unique reflections, 3399 of which with $F_o \geq 4.0\sigma(F_o)$ deemed "observed" (hkl range: +10, ±12, ±15, $(\sin\vartheta/\lambda)_{max}$ = 0.595 $Å^{-1}$). R(R_w) = 0.027(0.032), w = $1/\sigma^2(F_o)$ for 268 refined parameters (anisotropic, CH_3 rigid groups, all other H atoms constant, SHELX-76). Residual electron density: +1.04/-1.15 e/Å^3.

Fig. 1 shows the molecular structure, Tab. 1 contains the final atomic coordinates. Crystal data for **12**: triclinic, space group P-1 with a = 6.110(2), b = 9.353(3), c = 14.739(4) Å, α = 82.96(3), ß = 83.11(2), γ = 85.40(2), V =

828.1(5) Å^3, D_c = 2.002 g/cm^3, Z = 2, μ(Mo-K_α) = 71.5 cm^{-1}, RT. 5830 reflections, of which 2911 were unique (R_{int} = 0.0264) and 2877 with $F > 4\sigma(F)$ "observed". R(wR) = 0.0318(0.0383), $w = 1/\sigma^2(F)$ for 217 refined parameters (non-H anisotropic, hydrogens on calculated positions with fixed isotropic thermal parameters, SHELX-76), empirical absorption correction with DIFABS. Fig. 2 shows the molecular structure, Tab. 2 contains the final atomic coordinates.[24]

Tab. 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for 7. (U(eq.) = (U1*U2*U3)$^{1/3}$, where U1, U2, U3 are the eigenvalues of the U(ij) matrix. E.s.d.'s in parantheses.

ATOM	X/A	Y/B	Z/C	U(eq.)
W	0.0613(1)	0.1742(1)	0.3699(1)	0.026
O1	0.1791(4)	-0.1332(3)	0.0604(3)	0.029
O9	-0.1040(6)	0.2424(5)	0.5603(4)	0.054
O10	0.3103(5)	0.0916(5)	0.5567(4)	0.046
O11	-0.1638(5)	-0.1386(4)	0.2308(4)	0.045
O12	0.2960(6)	0.4841(5)	0.4940(4)	0.057
O13	-0.2119(6)	0.2660(6)	0.2084(4)	0.055
N1	0.1542(6)	0.1476(4)	0.1445(4)	0.033
C1	0.1830(6)	0.1211(4)	0.2395(4)	0.025
C2	0.3191(5)	0.0487(5)	0.2466(4)	0.024
C3	0.2898(6)	-0.0884(5)	0.2623(4)	0.028
C4	0.2689(6)	-0.1936(5)	0.1367(5)	0.031
C5	0.4337(6)	-0.1675(5)	0.1252(5)	0.037
C6	0.4567(6)	-0.0520(5)	0.1084(5)	0.034
C7	0.3070(6)	-0.0050(5)	0.1134(4)	0.027
C8	0.2454(6)	0.0976(5)	0.0679(5)	0.033
C9	-0.0446(6)	0.2189(6)	0.4920(5)	0.042
C10	0.2236(6)	0.1201(5)	0.4868(4)	0.034
C11	-0.0845(6)	-0.0259(5)	0.2814(4)	0.030
C12	0.2128(8)	0.3735(6)	0.4490(5)	0.040
C13	-0.1109(6)	0.2326(6)	0.2640(5)	0.037
C21	0.4834(6)	0.1573(6)	0.3374(5)	0.037
CT1	-0.5469(6)	-0.4929(5)	0.1853(5)	0.037
CT2	-0.6555(8)	-0.5703(5)	0.0670(5)	0.037
CT3	-0.8240(8)	-0.5991(5)	0.0333(5)	0.040
CT4	-0.8927(8)	-0.5530(6)	0.1189(5)	0.041
CT5	-0.7864(9)	-0.4757(6)	0.2364(5)	0.046
CT6	-0.6160(9)	-0.4456(6)	0.2703(5)	0.041
CT7	-0.3640(9)	-0.4623(6)	0.2212(6)	0.054

Tab. 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for 12. (U(eq.) = 1/3 $\Sigma_{ij}(U_{ij}\ \underline{a}_i^*\cdot\underline{a}_j^*\cdot\underline{a}_i\cdot\underline{a}_j)$. E.s.d.'s in parantheses.

ATOM	X/A	Y/B	Z/C	U(eq.)
W1	0.03030(4)	0.06341(2)	0.25151(1)	0.0223(1)
O1	0.0336(7)	-0.3238(5)	0.1837(3)	0.033(2)
O2	-0.2451(9)	-0.0266(6)	0.4438(3)	0.052(2)
O3	0.347(1)	0.2133(6)	0.3609(4)	0.056(2)
O4	-0.2524(9)	0.3600(6)	0.2351(4)	0.055(2)
O5	0.3084(9)	0.1878(6)	0.0660(3)	0.050(2)
O6	-0.3261(8)	-0.0467(6)	0.1398(3)	0.045(2)
N1	0.3223(9)	-0.2338(6)	0.3098(3)	0.032(2)
C1	0.215(1)	-0.1498(6)	0.2484(4)	0.024(2)
C2	0.425(1)	-0.3734(8)	0.2830(5)	0.046(3)
C3	0.411(1)	-0.3587(7)	0.1787(4)	0.034(2)
C4	0.316(1)	-0.4837(7)	0.1390(5)	0.040(2)
C5	0.101(1)	-0.4087(8)	0.1083(5)	0.039(2)
C6	0.158(1)	-0.2914(8)	0.0309(5)	0.041(2)
C7	0.230(1)	-0.1863(7)	0.0681(4)	0.032(2)
C8	0.225(1)	-0.2390(7)	0.1687(4)	0.027(2)
C9	0.328(1)	-0.2079(8)	0.4054(4)	0.043(3)
C10	0.177(1)	-0.3011(8)	0.4694(5)	0.047(3)
C11	0.231(2)	-0.383(1)	0.5413(6)	0.073(4)
C12	-0.145(1)	0.0034(7)	0.3742(5)	0.034(2)
C13	0.238(1)	0.1542(8)	0.3215(5)	0.035(2)
C14	-0.151(1)	0.2502(8)	0.2421(4)	0.034(2)
C15	0.210(1)	0.1385(7)	0.1312(4)	0.031(2)
C16	-0.196(1)	-0.0119(7)	0.1794(4)	0.031(2)

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