Diene–Dienophile-functionalized Carbene Ligands: Synthons for the Intramolecular Diels–Alder Reaction[1]

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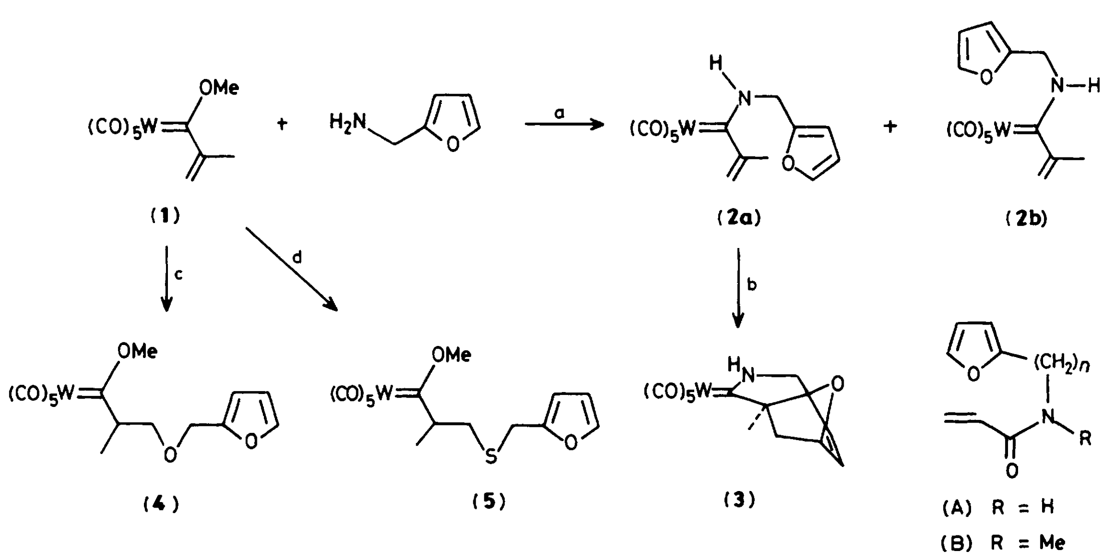
The diene–dienophile-substituted carbene complex pentacarbonyl(1-furfurylamino-2-methylprop-2-enylidene) tungsten undergoes a stereospecific intramolecular Diels–Alder reaction leading to a *trans*-fused hexahydroisoindolidene complex, the crystal structure of which has been determined.

The isolobal relation[2,3] has become an efficient basis for the use of transition metal complexes in organic synthesis. This principle has also been applied to Fischer-type carbene complexes which are known to react as metal-tuned carbonyl compounds.[4] For instance, the analogy of acrylates and alkoxy(vinyl)carbene complexes is demonstrated by facile [4 + 2] cycloaddition reactions.[5—7] Since Diels–Alder reactions, especially when carried out in an intramolecular fashion, provide a powerful tool in selective carbon–carbon bond formation, in, for example highly stereoselective syntheses of natural products,[8,9] we have focused on intramolecular Diels–Alder reactions effected at a metal carbene



Scheme 1. *Reagents and conditions:* a, hexane, −20 °C, 3 h, 93%; b, toluene, 80 °C, 24 h, 68%; c, furfuryl alcohol/sodium, ether/pentane, −70 °C to room temp., 2 h, 39%; d, furfuryl thiol/potassium, ether, −5 °C, 5 min, 87%.

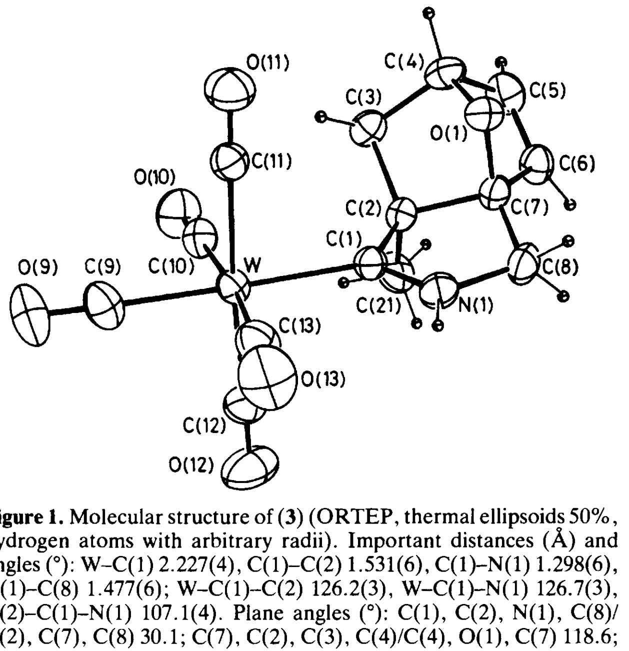


Figure 1. Molecular structure of (**3**) (ORTEP, thermal ellipsoids 50%, hydrogen atoms with arbitrary radii). Important distances (Å) and angles (°): W–C(1) 2.227(4), C(1)–C(2) 1.531(6), C(1)–N(1) 1.298(6), N(1)–C(8) 1.477(6); W–C(1)–C(2) 126.2(3), W–C(1)–N(1) 126.7(3), C(2)–C(1)–N(1) 107.1(4). Plane angles (°): C(1), C(2), N(1), C(8)/C(2), C(7), C(8) 30.1; C(7), C(2), C(3), C(4)/C(4), O(1), C(7) 118.6; C(4), C(5), C(6), C(7)/C(4), O(1), C(7) 128.5. Torsion angle (°): C(1)–C(2)–C(7)–C(8) 29.3.

template. This strategy is of general potential utility owing to the broad compatibility with group functionalization both in the carbene ligand and in the metal–coligand sphere.

We have used a two-step procedure which is based on the addition of nucleophiles to a carbene ligand and then to the carbonyl ligand formed therefrom. The propenylidene complex (**1**), obtained from a sequential addition of 2-lithiopropene and trimethyloxonium tetrafluoroborate to hexacarbonyltungsten reacts with furfurylamine to give a stereoisomeric mixture (which is not separable by chromatography) of aminocarbene complexes (**2a**) and (**2b**) (45 : 55). While the isomer (**2b**) remains unchanged upon warming of a toluene solution to 80 °C, the isomer (**2a**) undergoes cycloaddition to give (**3**)† (Scheme 1). In contrast, secondary amides analogous to (**2**), *e.g.* (A), fail to react. Tertiary amides such as (B) are required for Diels–Alder reactions;[10] the resulting lactams, however, are prone to cycloreversion.[11]

The *X*-ray analysis‡ of the cycloadduct (**3**) confirms the *exo*-mode of cyclization (Figure 1). A similar stereochemistry has been suggested for analogous tertiary amides on the basis of n.m.r. spectroscopy.[10] The five-membered ring containing the carbene carbon atom adopts an envelope conformation with C(7) being 0.47 Å above the best plane of the other four

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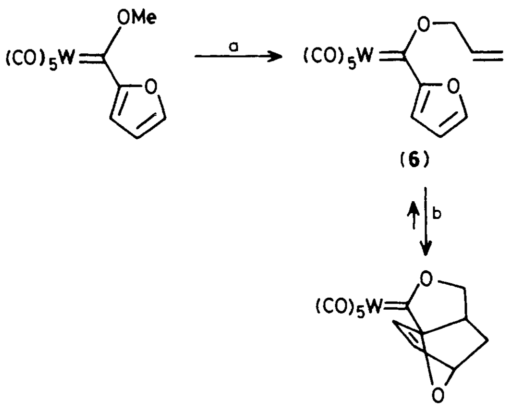
† *Selected spectroscopic data* (numbering system according to I.U.P.A.C. nomenclature): (**3**): i.r.: ν_{CO} (ether) 2063m, 1968w, 1932vs, and 1916vs cm^{-1}; ^{1}H n.m.r. δ (C_6D_6) 7.19 (br., NH), 5.77 (dd, =CH), 5.64 (d, =CH), 4.35 ('dd,' CH), 2.83 (dd, CH_2), 2.42 (dd, CH_2), 2.61 (d, NCH_2), 1.01 (d, NCH_2), and 0.58 (s, CH_3); ^{13}C n.m.r. δ (C_6D_6) 263.05 ($C_{carbene}$), 202.52 (CO_{trans}), 198.72 (CO_{cis}), 138.44 and 131.42 (=C), 92.83 (7a-C), 79.01 (5-C), 73.09 (3a-C), 54.88 (1-C), 38.75 (4-C), and 21.85 (CH_3).

(**4**): ν_{CO} (hexane) 2069w, 1952vs, and 1942s cm^{-1}; ^{1}H n.m.r. δ (C_6D_6) 6.70 (d, =CH), 5.60 (m, =CH), 3.95 (s, OCH_3), 3.92 (s, OCH_2), 3.13 (d, OCH_2), 2.23 (t, CH), 1.28 (d, CH_3).

(**5**): ν_{CO}, (hexane) 2074w and 1943vs.(br.) cm^{-1}; ^{1}H n.m.r. δ (C_6D_6) 7.00 (d, =CH), 5.95 (m, =CH), 3.90 (s, OCH_3), 3.35 (s, SCH_2), 3.10 (d, SCH_2), 1.80 (t, 1-H), and 1.40 (d, CH_3).

(**7**): ν_{CO} (hexane) 2073w, 1954s, and 1944s cm^{-1}; ^{1}H n.m.r. δ (C_6D_6) 6.78 (d, =CH), 5.81 (dd, =CH), 5.00 (m, OCH_2), 3.30 (dt, 6-H), 2.13 (m, 7a-H), and 1.42 (m, 7-H).

‡ *Crystal data* for (**3**)·PhMe: triclinic, space group $P1$, $a = 8.886(1)$, $b = 10.706(1)$, $c = 12.807(1)$ Å, $\alpha = 109.50(1)$, $\beta = 108.06(1)$, $\gamma = 98.94(1)°$, $U = 1045.4$ Å^3, $D_c = 1.796$ g cm^{-3}, $Z = 2$, μ (Mo-K_α) = 56.8 cm^{-1}, $T = -35$ °C. 3689 unique reflexions were recorded on a Syntex P2$_1$ diffractometer of which 3399 were 'observed' with $I \geqslant 2.0\,\sigma(I)$ [ω-scan, $\Delta\omega = 0.9°$, $(\sin\theta/\lambda)_{max.} = 0.595$, Mo-$K_\alpha$ radiation, $\lambda = 0.71069$ Å, graphite monochromator]. Lorentz polarization and empirical absorption corrections were applied (rel. transm.: 0.7—1.0). Solution was by Patterson methods. $R = 0.027$, $R_w = 0.032$, $w = 1/\sigma^2 (F_o)$ for 268 refined parameters (anisotropic, H atoms fixed, SHELX-76). $\Delta\rho_{fin.}$ (max./min.) = 1.0/−1.2 e/Å^3. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



(6)

(7)

Scheme 2. *Reagents and conditions*: a, allyl alcohol/sodium, molecular sieve (4 Å), 0 °C, 24 h, 43%; b, toluene, 60 °C, 90 min, 25%.

ring atoms. The aminocarbene atom N(1) has a planar sp^2 configuration which results in a short N–C$_{carbene}$ bond [1.298(6) Å] and a relatively long W–C$_{carbene}$ bond [2.227(4) Å].

In (**1**) the nucleophilic addition to the carbene carbon atom has to compete with the conjugate addition to the C=C bond. In the presence of catalytic amounts of potassium or sodium, furfuryl thiol or furfuryl alcohol undergo Michael addition leading to (**5**) and (**4**), respectively.

In principle, the diene and the dienophile can be exchanged within the carbene ligand. In the allyloxy furfurylidene complex (**6**) which is accessible from the methoxy carbene complex by base-induced alcoholysis, however, the reactivity of the diene is reduced by the adjacent electrophilic carbene carbon atom. The cycloadduct (**7**)† is obtained in an only moderate yield because of a facile cycloreversion (Scheme 2).

The diene–dienophile functionalization of carbene ligands offers a new means of stereocontrol for the Diels–Alder reaction by a metal template. In combination with well known procedures for the cleavage of the metal–carbene bond,[4] our further studies are aimed at the synthetic scope of this methodology which should further demonstrate the versatility of metal carbenes in cycloaddition reactions.[12]

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