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Synthesis and X-ray structure of two isomeric aminocarbene complexes of tungsten containing a free carbon–carbon double bond

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Abstract

The reaction of allylamine with $(CO)_5W{=}C(OCH_2CH_3)CH_3$ gives two isomeric aminocarbene complexes $(CO)_5W{=}C(NHCH_2CH{=}CH_2)CH_3$ **2***E* and **2***Z*. Refluxing of a solution of this mixture in benzene gives the complexes $(CO)_4W{=}C(\eta^2NHCH_2CH{=}CH_2)CH_3$ (**3**) and **2***E*, which have been separated. **2***E* was fully characterized by X-ray diffraction. Crystals of **2***E* are monoclinic, space group $P2_1/n$ with $Z = 4$, a 7.188(3), b 14.312(2), c 12.530(2) Å and β 91.06(3)°.

The same mixture when treated with lithium diisopropylamide (LDA) followed by allyl bromide gives a mixture of $(CO)_5W{=}C(N(CH_2CH{=}CH_2)_2)CH_3$ (**4**) and **2***Z*. These complexes were separated, and **2***Z* fully characterized by X-ray diffraction. Crystals of **2***Z* are monoclinic, space group $P2_1/c$, with $Z = 4$, a 6.593(5), b 14.584(3), c 13.323(1) Å and β 95.13(4)°.

Introduction

During attempts to develop methods for the stepwise incorporation of alkynes into carbene complexes of transition metals containing a coordinated double bond [1], we prepared, as starting compounds, aminocarbene complexes of the general structure **1** [2]. It is known [3,4,5], that such complexes exist as a mixture of two

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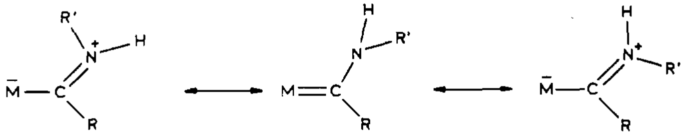
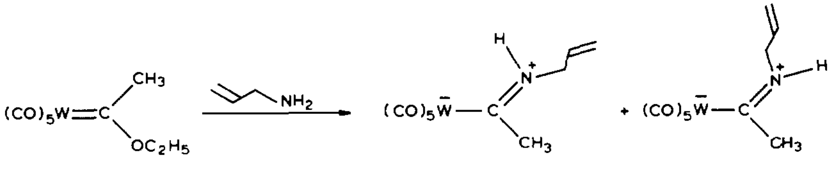
isomers differing in orientation around the C–N partial double bonds; these are readily detectable, even at room temperature, by means of NMR spectroscopy. Such isomers have not previously been separated and fully characterized. We describe here the X-ray structure of two such isomers involving tungsten.

Results and discussion

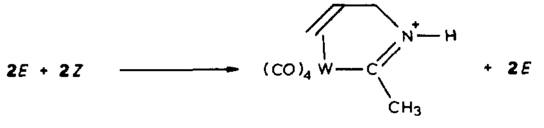
The synthesis of complexes **2***E* and **2***Z* was by the method described by Fischer and coworkers [3,4] and later used by Casey [5,6]. According to NMR spectroscopy, the mixture contains 85% of **2***E* and 15% of **2***Z*. These could not be separated by silica gel chromatography, but samples of **2***E* and **2***Z* were isolated as described below.



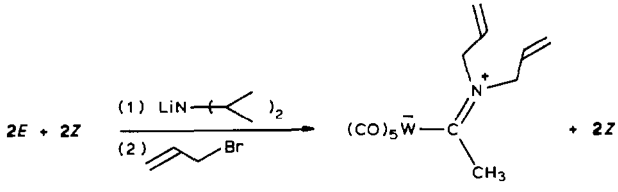
(*Z*) (**1**) (*E*)



(**2***E*) (**2***Z*)



(**3**)



(**4**)

First a solution of the mixture **2***E* and **2***Z* in benzene was refluxed to give the expected complex **3**, in which the double bond is coordinated to the metal center, along with complex **2***E*, and then separating **3** and **2***E* by column chromatography. That the double bond of complex **3** is coordinated to the metal is revealed by the ^{13}C NMR spectrum, in which the two carbon atoms of the double bond are shifted upfield, from 131 and 119.2 ppm in **2***Z*, to 73.2 and 54.7 ppm, respectively, in complex **3**.

The molecular structure of **2***E* was determined unambiguously by X-ray diffraction. As can be seen from the ORTEP view in Fig. 1, the allyl group is *trans* to the

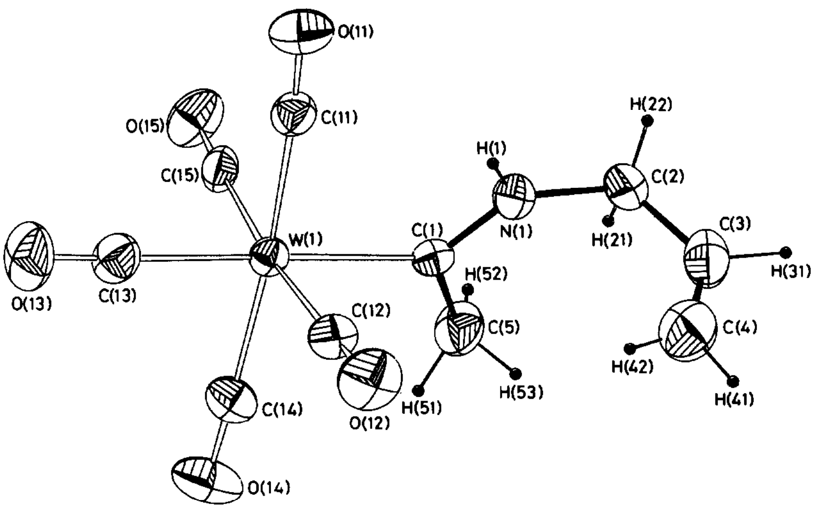


Fig. 1. ORTEP-II drawing, with atom numbering, for **2***E*, with hydrogen atoms artificially reduced, $B_H = 0.25$. Ellipsoïds represent 30% probability.

tungsten-carbon single bond, the C(1)-N(1) carbon-nitrogen bond, 1.296(8) Å, being rather like a double bond, in contrast to the C(2)-N(1) bond, 1.473(9) Å. As expected and observed [5,6], such a geometry around the C(1)-N(1) double bond does not allow coordination of the C(3)-C(4) carbon-carbon double bond to the metal.

Second, the mixture of **2***E* and **2***Z* was treated with LDA/allyl bromide. The expected complex **4** was obtained in 75% yield, and separated from the remaining

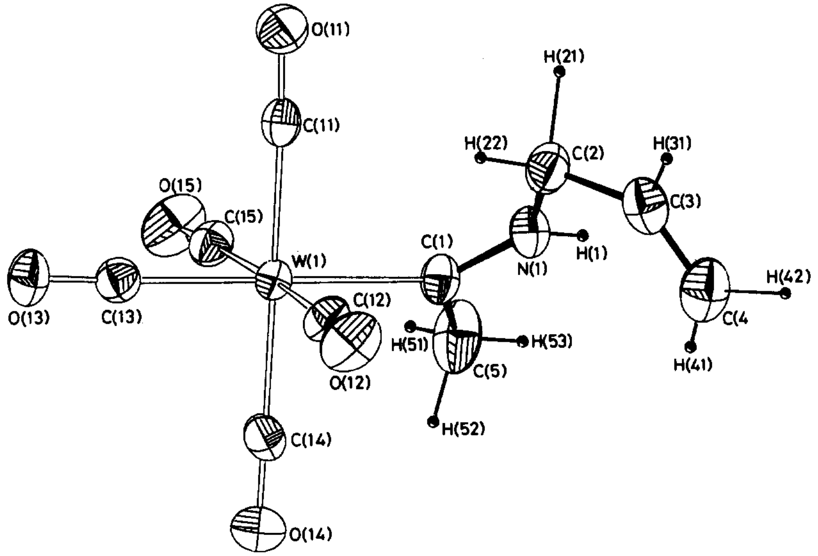


Fig. 2. ORTEP-II drawing, with atom numbering, for **2***Z* with hydrogen atoms artificially reduced, $B_H = 0.25$. Ellipsoïds represent 30% probability.

15% of the starting material by column chromatography. The recovered starting material turned out to be pure **2***Z*, as shown by its ^{1}H and ^{13}C NMR spectra.

This was confirmed by an X-ray study, the ORTEP projection of complex **2***Z* (Fig. 2) shows the expected geometry around the C=N double bond; it is clear that a rotation around the N(1)–C(2) single bond brings the C(3)=C(4) double bond in the close vicinity of the C(11)=O(11) carbonyl group. This means that with complex **2***Z*, coordination of the double bond can easily take place.

The stability of complex **2***E*, during the coordination reaction can be accounted for by assuming that under our reaction condition there is no *E*/*Z* isomerization (a reaction which does occur both photochemically and thermally, at higher temperature [4,5]). It is more difficult to explain the selective alkylation of complex **2***E*. However, the X-ray structures of the two complexes show that H(1), the proton which has to be abstracted to form the intermediate anion, is more hindered in complex **2***Z* than in complex **2***E*, especially by the C(3)=C(4) carbon–carbon double bond.

Our results show that at least at room temperature, aminocarbene complexes such as those described here can be regarded as 1,3-dipoles $\overline{\mathrm{W}}-\mathrm{C(R)}=\overset{+}{\mathrm{N}}$, which exist as stable geometrical isomers around the C=N double bond. In the particular complexes studied here, where a C=C double bond is present in an alkyl chain, the ORTEP views clearly show that only one isomer can undergo intramolecular coordination.

X-ray studies

Preliminary unit cell dimensions and symmetry informations were derived from precession photographs. All orientation and indexing operations as well as room temperature data collections were carried out on a Nonius CAD4 four-circle diffractometer. Accurate cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space ($28° < 2\theta < 32°$).

Details of crystal data and data collection parameters are given in Table 1. Intensities of two standard reflections were monitored every hour; no significant fluctuations were detected. The ψ-scans of close-to-axial reflections showed significant intensity variations; absorption corrections were then made by the empirical absorption correction procedure [7].

Computations were performed by use of the CRYSTALS system [8] adapted for a Vax 11/725. Atomic scattering factors for neutral W, C, N, O and H were taken from ref. 9. All calculations included a correction for the real and imaginary parts of the anomalous dispersion.

In both compounds, the position of W atom was determined by Harker vector analysis of three dimensional Patterson maps. All remaining non-hydrogen atoms were found from successive electron density maps. Hydrogen atoms were located on difference electron density maps; their atomic coordinates were introduced into the refinements, and they were assigned a refineable overall isotropic thermal parameter. Final refinements were by least-squares with a large block approximation to the normal matrix (with all non hydrogen atoms anisotropic). The criteria for a satisfactory completed analysis were the rms shift to standard deviations (Table 1) and no significant features in the final difference maps. The main features of the refinement are outlined in Table 1.

Table 1

Crystal data

	Compound **2***E*	Compound **2***Z*
Empirical formula	$C_{10}H_9NO_5W$	$C_{10}H_9NO_5W$
Molecular wght	407.04	407.04
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	7.188(3)	6.593(5)
b, Å	14.312(2)	14.584(3)
c, Å	12.530(2)	13.323(1)
β, °	91.06(3)	95.13(4)
V, Å^3	1289	1276
Z	4	4
Cryst. size, mm	0.41×0.11×0.06	0.32×0.14×0.10
μ(Mo-K_α), cm^{-1}	95.04	96.0
ρ_{calcd}, g/cm^3	2.10	2.12
Temperature, °C	21±1	
Radiation	Mo-K_α (λ 0.71073 Å) (graphite monochromator)	
Scan type	θ-2θ	
Scan range θ, deg.	$1.35+0.345\ \text{tg}\theta$	
2θ range, deg	3–50	
Scan speed	depending upon reflection	
Background	half of scan time, in fixed position, before and after every scan	
Reflections collected	2561 ($\bar{h}kl$, hkl)	2528 ($\bar{h}kl$, hkl)
Reflections merged	2260	2236
Merging factor	3.40	2.80
Reflections used	1637 ($F > 3\sigma(F)$)	1637 ($F > 3\sigma(F)$)
Secondary extinction	8.64	none
Weighting scheme	$w = w'\,\lvert 1-(\Delta F/6\sigma(F))^2\rvert^2$ [a]	
rms shift/esd (last cycle)	0.17	0.28
Goodness of fit	0.98	1.23
$N_{\text{ref}}/N_{\text{var.param.}}$	8.9	8.9
Scale factor	0.772	0.807
$R = \Sigma\lVert F_0\rvert - \lvert F_c\rVert/\Sigma\lvert F_0\rvert$	0.0222	0.0214
$R_w = (\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma w F_0^2)^{1/2}$	0.0262	0.0243

[a] $w' = 1/\Sigma_{r=1}^{n} \text{ArTr}(X)$ with three coefficients Ar (3.566, −1.959, 2.522 for compound **2***E*, and 3.263, −1.748, 2.407 for compound **2***Z*) for the Chebyshev series Tr(X), where $X = F_c/F_c(\text{max})$ [3].

Atomic coordinates are given in Table 2, and bond lengths and angles in Table 3. Tables of least-squares planes, torsion angles, interatomic distances and angles involving H atoms, coordinates of H atoms and anisotropic thermal parameters for heavy atoms and lists of observed and calculated structure factors can be obtained from the authors.

Experimental

All reactions were carried out in oven-dried glassware under argon. Benzene, diethyl ether and tetrahydrofuran (THF) were distilled from $LiAlH_4$. For prepara-

Table 2

Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters U_{eq} ($U_{eq} = [U_{11}U_{22}U_{33}]^{1/3}$)

Atom	x/a	y/b	z/c	U_{eq}
Compound **2** *E*				
W(1)	0.38019(3)	0.20279(1)	0.15691(1)	0.0386
C(1)	0.2792(8)	0.0652(4)	0.2068(4)	0.0467
N(1)	0.2034(8)	0.0418(3)	0.2905(4)	0.0529
C(2)	0.157(1)	0.0994(5)	0.3737(5)	0.0613
C(3)	−0.053(1)	0.0867(5)	0.4029(5)	0.0647
C(4)	−0.047(1)	0.0041(8)	−0.2902(9)	0.0971
C(5)	0.301(1)	−0.0167(5)	0.1421(6)	0.0731
C(11)	0.5175(9)	0.2341(4)	0.2955(4)	0.0439
O(11)	0.5969(8)	0.2555(3)	0.3721(3)	0.0650
C(12)	0.1239(9)	0.2709(4)	0.1886(5)	0.0520
O(12)	−0.0160(7)	0.3124(4)	0.2042(4)	0.0736
C(13)	0.4946(9)	0.3190(4)	0.1051(4)	0.0495
O(13)	0.5669(7)	0.3842(3)	0.0759(4)	0.0643
C(14)	0.242(1)	0.1729(5)	0.0185(5)	0.0567
O(14)	0.1665(9)	0.1571(5)	−0.0600(4)	0.0844
C(15)	0.6416(9)	0.1411(4)	0.1192(4)	0.0506
O(15)	0.7867(7)	0.1096(4)	0.0955(4)	0.0736
Compound **2** *Z*				
W(1)	0.19715(3)	0.21818(2)	0.01803(2)	0.0394
C(1)	0.2173(8)	0.1744(4)	−0.1502(5)	0.0421
N(1)	0.2635(8)	0.0913(4)	−0.1808(4)	0.0548
C(2)	0.286(1)	0.0533(6)	−0.2890(6)	0.0633
C(3)	0.113(1)	0.0067(1)	−0.3314(6)	0.0724
C(4)	−0.195(1)	0.0371(5)	0.3582(7)	0.0791
C(5)	0.186(1)	0.2424(6)	−0.2416(6)	0.0677
C(11)	0.3388(9)	0.1063(5)	0.0748(5)	0.0525
O(11)	0.4197(8)	0.0456(4)	0.1122(5)	0.0763
C(12)	−0.0414(9)	0.1445(5)	0.0281(6)	0.0535
O(12)	−0.1733(8)	0.1008(5)	0.0341(6)	0.0806
C(13)	0.180(1)	0.2637(6)	0.1694(5)	0.0616
O(13)	0.174(1)	0.2879(5)	0.2570(4)	0.0841
C(14)	0.0548(9)	0.3347(5)	−0.0267(6)	0.0535
O(14)	−0.0240(8)	0.4018(4)	−0.0497(6)	0.0784
C(15)	0.4468(9)	0.2835(5)	−0.0041(5)	0.0478
O(15)	0.5866(7)	0.3165(4)	−0.0168(4)	0.0688

tive column chromatography 70–230 mesh Merck silica gel was used. For preparative (PLC) and analytical thin layer chromatography (TLC) Merck G60 silica gel was used.

NMR spectra were recorded on a JEOL FX-90 or a Bruker WM 200 or WM 250 spectrometer. Tetramethylsilane was used as reference for all spectra, IR spectra were recorded on a Beckman 4240 spectrophotometer. Mass spectra were obtained with a Kratos MS 3P apparatus. Melting points were determined with a Reichert Kofler block, and are uncorrected.

Table 3

Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

Compound **2***E*		Compound **2***Z*	
W(1)-C(1)	2.206(6)	W(1)-C(1)	2.234(5)
W(1)-C(11)	2.020(7)	W(1)-C(11)	2.034(6)
W(1)-C(12)	2.019(6)	W(1)-C(12)	2.037(6)
W(1)-C(13)	2.011(7)	W(1)-C(13)	2.003(6)
W(1)-C(14)	2.030(7)	W(1)-C(14)	2.030(6)
W(1)-C(15)	2.047(6)	W(1)-C(15)	2.047(6)
C(1)-N(1)	1.296(8)	C(1)-N(1)	1.307(8)
C(1)-C(5)	1.52(1)	C(1)-C(5)	1.488(9)
N(1)-C(2)	1.473(9)	N(1)-C(2)	1.445(8)
C(2)-C(3)	1.50(1)	C(2)-C(3)	1.481(9)
C(3)-C(4)	1.27(1)	C(3)-C(4)	1.29(1)
C(15)-O(15)	1.124(8)	C(11)-O(11)	1.148(7)
C(11)-O(11)	1.141(8)	C(12)-O(12)	1.137(7)
C(12)-O(12)	1.139(8)	C(13)-O(13)	1.147(7)
C(13)-O(13)	1.152(9)	C(14)-O(14)	1.140(7)
C(14)-O(14)	1.149(8)	C(15)-O(15)	1.131(7)
C(11)-W(1)-C(1)	94.0(2)	C(11)-W(1)-C(1)	92.9(2)
C(12)-W(1)-C(1)	89.0(2)	C(12)-W(1)-C(1)	95.8(2)
C(12)-W(1)-C(11)	89.3(3)	C(12)-W(1)-C(11)	90.7(2)
C(13)-W(1)-C(1)	177.6(3)	C(13)-W(1)-C(1)	173.8(2)
C(13)-W(1)-C(11)	87.9(3)	C(13)-W(1)-C(11)	88.4(2)
C(13)-W(1)-C(12)	92.6(3)	C(13)-W(1)-C(12)	90.2(2)
C(14)-W(1)-C(1)	90.6(3)	C(14)-W(1)-C(1)	87.5(2)
C(14)-W(1)-C(11)	175.3(3)	C(14)-W(1)-C(11)	179.4(2)
C(14)-W(1)-C(12)	91.3(3)	C(14)-W(1)-C(12)	88.9(3)
C(14)-W(1)-C(13)	87.4(3)	C(14)-W(1)-C(13)	91.2(2)
C(15)-W(1)-C(1)	85.8(2)	C(15)-W(1)-C(1)	87.6(2)
C(15)-W(1)-C(11)	88.4(3)	C(15)-W(1)-C(11)	90.3(2)
C(15)-W(1)-C(12)	174.1(3)	C(15)-W(1)-C(12)	176.4(2)
C(15)-W(1)-C(13)	92.8(3)	C(15)-W(1)-C(13)	86.3(2)
C(15)-W(1)-C(14)	91.5(3)	C(15)-W(1)-C(14)	90.1(3)
N(1)-C(1)-W(1)	124.4(4)	N(1)-C(1)-W(1)	129.5(4)
C(5)-C(1)-W(1)	121.9(5)	C(5)-C(1)-W(1)	120.0(4)
C(5)-C(1)-N(1)	113.6(6)	C(5)-C(1)-N(1)	110.5(5)
C(2)-N(1)-C(1)	130.2(6)	C(2)-N(1)-C(1)	128.7(5)
C(3)-C(2)-N(1)	112.6(7)	C(3)-C(2)-N(1)	113.4(5)
C(4)-C(3)-C(2)	128.4(8)	C(4)-C(3)-C(2)	127.2(7)
O(11)-C(11)-W(1)	176.1(6)	O(11)-C(11)-W(1)	177.0(5)
O(12)-C(12)-W(1)	178.2(7)	O(12)-C(12)-W(1)	176.9(6)
O(13)-C(13)-W(1)	178.1(8)	O(13)-C(13)-W(1)	177.6(5)
O(14)-C(14)-W(1)	178.3(7)	O(14)-C(14)-W(1)	178.9(6)
O(15)-C(15)-W(1)	177.7(6)	O(15)-C(15)-W(1)	177.3(6)

*Pentacarbonyl ((3-butenylamino)(methyl)carbene)tungsten(0) (**2Z** and **2E**)*

Allylamine (17 ml, 23 mmol) was added, at room temperature to complex **1** (9 g, 23 mmol) in Et_2O (100 ml). After 3 h the solvent was evaporated, and the residue filtered through silica gel to give a yellow oil (8.7 g, 95%), which crystallized at low temperature.

cis-Tetracarbonyl ((Z)-(η^2-allylamino)(methyl)carbene)tungsten(0) (3 and 2E)

A solution of the mixture of **2***Z* and **2***E* (4 g) in benzene (50 ml) was refluxed for 48 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with light petroleum (PE) ethyl acetate (AcOEt) (95/5) gave complex **2***E* (3 g).

2*E*: m.p. 36 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): 8.7 (1H, N–H), 5.87 (1H, m, C*H*=CH_2), 5.35 (2H, m, C*H*$_2$=CH), 4.03 (2H, m, NC*H*$_2$), 2.68 (3H, CH_3). ^{13}C NMR ($CDCl_3$, 200-MHz): 260.2 (C(1)), 203.5, 199.3 (CO), 130.2 (*C*H=CH_2), 119.2 (*C*H$_2$=C), 50.1 (N*C*H$_2$), 37.1 (*C*H$_3$). Analysis. Found: C, 29.68; H, 2.28; H, 3.41. $C_{19}H_9O_5NW$ calcd.: C, 29.48; H, 2.21; N, 3.44%. Mass spectrum: *m/z* 407 (M^+).

Elution with PE/AcOEt (80/20) gave complex **3** (0.4 g, 11%), m.p. 68–69 °C. ^{1}H NMR ($CDCl_3$, 200-MHz): 8.8 (1H, N*H*), 4.59 (1H, m, C*H*=CH_2), 4.25 (1H, NC*H*), 3.87 (1H, NC*H*), 3.22 (1H, *H*CH=CH), 3.16 (1H, HC*H*=CH), 2.47 (3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 200 MHz): 265 (C(1)), 213, 209, 203 (CO), 73.2 (*C*H=CH_2), 58.0 (N*C*H$_2$), 54.7 (*C*H$_2$=CH), 39.8 (*C*H$_3$).

Pentacarbonyl ((3-dibutenylamino)(methyl)carbene)tungsten(0) (4 and 2Z)

A solution of LDA, prepared from diisopropylamine (1.5 ml) and BuLi (1 equiv.) in THF (50 ml), was added at −60 °C to a solution of the mixture of **2***E* and **2***Z* (2.5 g) in THF (20 ml). The temperature was raised to 20 °C then lowered to −70 °C, and allyl bromide was then added (1.5 ml). After 2 h at room temperature the usual work up gave a product which was chromatographed on silica gel. Elution with PE/AcOEt (95/5) gave complex **4** m.p. 31–32 °C.

^{1}H NMR ($CDCl_3$, 200 MHz): 5.8 (1H, m, C*H*=CH_2), 5.67 (1H, m, C*H*=CH_2), 5.30 (3H, m, C*H*$_2$=CH, HCH=CH), 5.10 (1H, d, HC*H*=CH), 4.7 (2H, d, N–C*H*$_2$), 4.28 (2H, d, N–C*H*$_2$E), 2.85 (3H, s, CH_2). ^{13}C NMR ($CDCl_3$, 200 MHz): 257.7 (C(1)), 203, 198.7 (CO), 131.9, 129.5, 120.5, 118.2 (2*C*H$_2$=C), 68.2 (N*C*H$_2$), 52.7 (N*C*H$_2$), 41.9 (CH_3). Mass spectrum: *m/z*: 447 (M^+).

Elution with PE/AcOEt (80/20) gave complex **2***Z* as yellow crystals (0.35 g, 15%), m.p. 63 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): 5.91 (1H, m, *C*H=CH_2), 5.37 (2H, m, C*H*$_2$=CH), 4.45 (2H, t, 5Hz, NC*H*$_2$), 2.84 (3H, s, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 200 MHz): 260.2 (C(1)), 203.5 and 198.7 (CO), 131.0 (*C*H=CH_2), 120.1 (*C*H$_2$=CH), 58.5 (NCH_2), 46.9 (*C*H$_3$), *m/z*: 407 (M^+).

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