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1-Metalla-1,3,5,7-octatetraenes by 4-Addition of (1,3-Dien-2-yl)amines to (1-Alkynyl)carbene Complexes (M = Cr, W)[1]

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Dedicated to Prof. C. G. Kreiter on the occasion of his 60th birthday

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Abstract: Addition of (1-phenyl)ethenyl-amines $H_2C=C(NR_2)Ph$ **2a,b** to (1-alkynyl)carbene complexes $(CO)_5M=C(OEt)C\equiv CPh$ **1a,b** (M= W, Cr) affords 1-metalla-1,3,5-hexatrienes **4a-c** in 90 - 95%. Addition of *N*-[1-(cyclohex-1-enyl)]ethenyl-amines $H_2C=C(NR_2)$-(~)C= $CH(CH_2)_4$~ **2c,d** to compounds **1a,b** yields novel 1-metalla-1,3,5,7 -octatetraenes $(CO)_5M=C(OEt)$-CH=C(Ph)-CH=$C(NR_2)$-(~)C=CH $(CH_2)_4$~ **4d-f** as major products together with a [4+2] cycloadduct **5d** as minor product. Compounds **4** and **5** have been fully characterized spectroscopically, compound **4d** also by X-ray analysis.

(1-Alkynyl)carbene complexes $(CO)_5M=C(OEt)C\equiv CPh$ **1a,b** (M = W, Cr) have been recently applied as building-blocks in a manifold of reactions, e.g. for the generation of carbo- and heterocyclic systems.[2] It was shown only recently that secondary enaminones[3a,b] as well as tertiary cyclic enamines ~CH=$C(NR_2)$~,[3c,d] undergo addition to the C≡C bond of (1-alkynyl)carbene complexes **1a,b** under exceedingly mild conditions to afford conjugated (*3Z*)-6-amino-1-metalla-1,3,5-hexatrienes in high yields. Compounds of the latter type could be easily transformed into cyclopentadienes,[3,d,4,5] 2,3-homopyrroles[3b] or pyran-2-ylidene complexes,[3a,6] depending on the substitution pattern and the stereochemistry of the 1-metalla-1,3,5-triene unit.

We now wish to report that a supposedly broad array of various functional groups can be introduced into 1-metalla-1,3,5-trienes, if these compounds are generated in pentane, from which solvent they usually precipitate rapidly, and thus are withdrawn from further chemical transformations. For example, 6-amino-2-ethoxy-1-metalla-1,3,5-hexatrienes **4a-c** are obtained from pentane in 90 - 95% yield, if vinylamines $H_2C=C(NR_2)Ph$ **2a,b** are added to (1-alkynyl)carbene complexes **1a,b** (a: M=W, b: M=Cr). The reaction leading to 1-metalla-1,3,5-trienes could be extended also to formation of 1-metalla-1,3,5,7-octatetraenes **4d-f** in 77 - 90 % yield, if *N*-[1-(cyclohex-1-enyl)]ethenyl-amines $H_2C=C(NR_2)$-(~)C= $CH(CH_2)_4$~ **2c,d** are reacted with compounds **1a,b** in pentane. The latter reaction mode is quite unexpected, in so far as addition of an (electron-rich) 2-amino-1,3-butadiene system **2c,d** to an (electron-poor) C≡C bond of compounds **1a,b** is expected to result in formation of either a [2+2]- or a [4+2] cycloadduct. Furthermore, [4+2] cycloadducts of open-chain 2-amino buta-1,3-dienes to (1-alkynyl)carbene complexes indeed could be generated as

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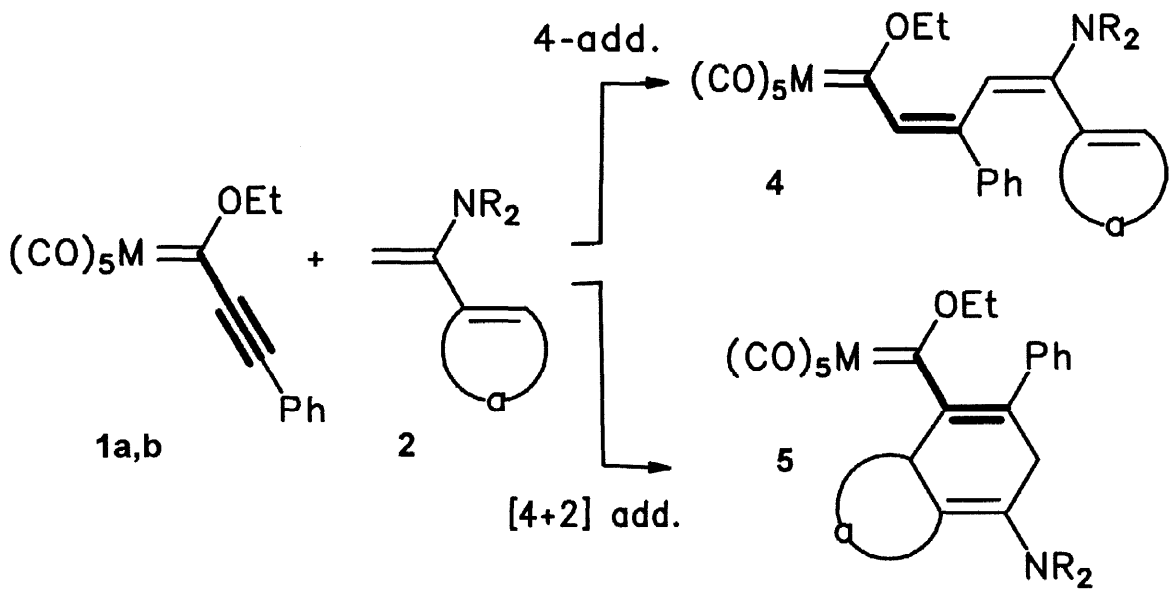
intermediates, from which dihydrofluorene derivatives are spontaneously produced in high yields by extrusion of the metal unit at 20 °C.[7] There seems to be a delicate balance, depending on the fine-tuning of the C3-C4 double bond of a 2-amino buta-1,3-diene by electronic and steric interactions, which leads to production of either a 1-metalla-1,3,5,7-tetraene or a [4+2] cycloadduct. Eventhough [4+2] cycloadducts were found to be major products in earlier studies,[7] in our investigation such compounds were not produced, except for compound **5d**, which was obtained as by-product in 5 % yield of the reaction leading to the 1-metalla-1,3,5,7-octatetraene **4d**.[8] The configuration of the novel compounds (*3Z,5E*)-**4d,e** could be unambiguously determined by ^{1}H NMR-NOEDIFF experiments at - 40 °C (**4d**), and 30 °C (**4e**), respectively, compound **4d** has been also characterized by a X-ray structure analysis. It was shown by NMR studies that compounds **4a** and **4b** undergo rapid equilibration with each other at 30 °C.

Scheme 1: 4-Addition vs. [4+2] cycloaddition of vinyl enamines $H_2C{=}C(NR_2)$-(~C=CH-a~) **2a-d** to (1-alkynyl)carbene complexes **1** [M = W (**a**), Cr (**b**)]



2	NR_2	-a-
a	morpholino	-CH=CH-CH=CH-
b	NEt_2	-CH=CH-CH=CH-
c	morpholino	$-CH_2-CH_2-CH_2-CH_2-$
d	NEt_2	$-CH_2-CH_2-CH_2-CH_2-$

4, 5	M	-a-	NR_2	[**4**]/[**5**] %
a	W	-CH=CH-CH=CH-	morpholino	92/-
b	W	-CH=CH-CH=CH-	NEt_2	95/-
c	Cr	-CH=CH-CH=CH-	NEt_2	90/-
d	W	$-CH_2-CH_2-CH_2-CH_2-$	morpholino	77/5
e	W	$-CH_2-CH_2-CH_2-CH_2-$	NEt_2	90/-
f	Cr	$-CH_2-CH_2-CH_2-CH_2-$	morpholino	87/-

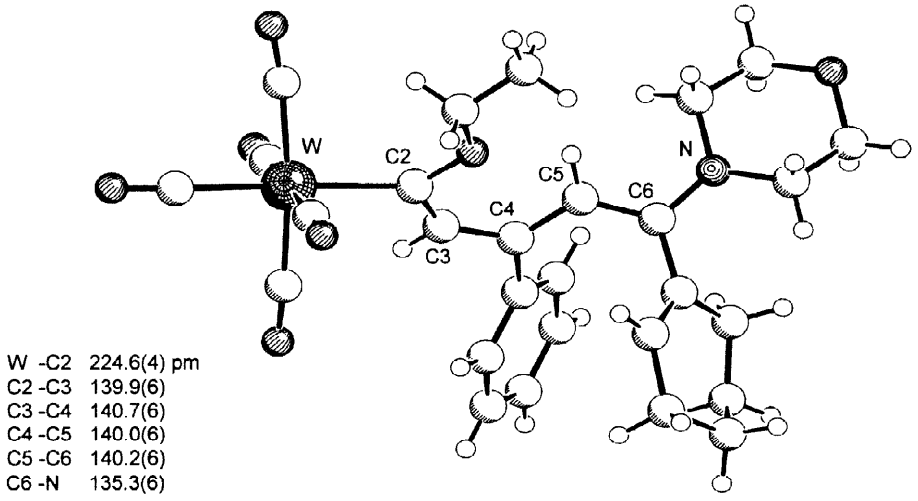


Figure 1: Molecular structure of compound (*3Z*)-**4d** in the crystal[9]

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7 (a) The first example of a [4+2]-cycloaddition of a 2-amino-1,3-butadiene to a (1-alkynyl)carbene complex has been reported by: Barluenga, J.; Aznar, F.; Barluenga, S. J. *J. Chem. Soc., Chem. Commun.*, **1995**, 1973-1974. (b) For a [4+2]-cycloaddition of 2-trimethylsiloxy-1,3-butadiene see:

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[8] All new compounds **4** and **5** have been fully characterized spectroscopically and by elemental analyses. **Typical Procedure**: *(3Z,5E)-1,1,1,1,1-Pentacarbonyl-6-(cyclohex-1-enyl)-2-ethoxy-6-morpholino-4-phenyl-1-tungsta-1,3,5-hexatriene (**4d**) and Pentacarbonyl{(2-phenyl-4-morpholino-bicyclo[4.4.0]-1,4-decadienyl)-ethoxy-methylidene}tungsten(0) (**5d**).* To (1-alkynyl)carbene complex **1a** (482 mg, 1.00 mmol) in an 5-mL screw-top vessel is added compound **2d** (193 mg, 1.00 mmol) in 4 mL of pentane. A red precipitate is collected after 30 min at 20 °C by centrifugation, washed with pentane (3 x 3 mL) and recrystallized from diethyl ether/ pentane 1:3 at - 20 °C to give compound **4d** (577 mg, 77 %, R_f = 0.8 in diethyl ether/ pentane 1:1, dark-red crystals from diethyl ether/ pentane 1:3, mp 117 °C, dec.). 35 mg (5%) of compound **5d** were obtained by crystallization from the mother liquor at - 40°C after having separated compound **4d** by crystallization at -20°C. **4d:** ^{1}H NMR (600 MHz, $CDCl_3$, -40 °C): δ 7.30 (3 H, m, *p*- and *m*-H Ph), 7.24 (2 H, m, *o*-H Ph), 7.03 (1 H, s, 3-H), 6.49 (1 H, s, 5-H), 5.68 (1 H, s broad, C=C*H* cyclohexenyl), 4.82 and 4.73(1 H each, m each, diastereotopic OCH_2CH_3), 3.5 - 4.1 (4 H, m broad, OCH_2CH_2N), 3.5 - 2.8 (4 H, m broad, OCH_2CH_2N); 1.83, 1.65, 1.49, 1.20, 0.75 (1:1:2:2:2 H, 4 CH_2 cyclohexenyl), 1.67 (3 H, OCH_2CH_3). ^{13}C NMR (600 MHz, $CDCl_3$, -40 °C): δ 286.2 (Cq, W=C), 204.8 and 198.9 [Cq each, 1:4, *trans*- and *cis*- CO, $W(CO)_5$], 168.4 (Cq, =C-N), 152.2 (Cq, cyclohexenyl), 145.3 (Cq, =C-Ph), 139.6 (CH, C3), 138.2 (CH, cyclohexenyl), 133.8 (Cq, *i*-C Ph); 127.8, 127.9 and 128.6 (CH each, Ph), 108.6 (CH, C5), 78.0 (OCH_2CH_3), 66.9 - 66.0 (OCH_2CH_2N, broad), 49.7 - 48.3 (OCH_2CH_2N broad); 27.8, 25.2, 21.3 and 20.7 (CH_2 each, cyclohexenyl), 15.6 (OCH_2CH_3). **5d:** ^{1}H NMR (600 MHz, $CDCl_3$, -40°C): δ 7.28 (2 H, m, *m*-H Ph), 7.20 (1 H, m, *p*-H Ph), 7.10 (2 H, m, *o*-H Ph), 4.56 and 4.30 (1 H each, m each, diastereotopic OCH_2CH_3), 3.9 - 3.65 (4 H, broad, OCH_2CH_2N), 3.63 (1 H, m, 7-H), 3.20 (1 H, "d", 11a-H), 3.07 (1 H, "ddd" , 4a-H), 2.94 (1 H, "dd" 4b-H), 2.88 - 2.35 (4 H, m broad, OCH_2CH_2N), 1.77 (1 H, m, 10a-H), 1.71 (1 H, m, 9a-H), 1.63 (1 H, m, 11b-H), 1.46 (1 H, m, 9b-H), 1.42 (1 H, m, 8a-H), 1.25 (3 H, t, ^3J = 7.2 Hz, OCH_2CH_3), 1.16 (1 H, m, 10b-H), 1.07 (1 H, m, 8b-H). ^{13}C NMR (600 MHz, $CDCl_3$, -40°C): δ 330.3 (Cq, C1), 203.4 and 196.7 (Cq each, 1:4, *trans* and *cis* CO , $W(CO)_5$), 152.2 (Cq, C3), 140.7 (Cq, *i*-C Ph), 134.3 (Cq, C5), 128.0 and 128.1 (CH, *o*-, *m*-Ph), 127.0 (CH, *p*-Ph), 126.1 (Cq, C2), 124.0 (Cq, C6), 79.8 (OCH_2CH_3), 67.2 (OCH_2CH_2N), 50.5 (dynamically broadened, OCH_2CH_2N), (42.5 (CH, C7), 34.5 (CH_2, C8), 30.0 (CH_2, C4), 27.4 (CH_2, C11), 27.1 (CH_2, C10), 25.7 (CH_2, C9), 14.4 (CH_3, OCH_2CH_3).

[9] Further details of the crystal structure of compound **4d** can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation.