

Organic syntheses via transition metal complexes, XCl^1 . Dihydropyridinyl carbene complexes by [4 + 2] annulation of alkenyl- or aryl imines to (1-alkynyl) carbene complexes of chromium and tungsten

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Abstract

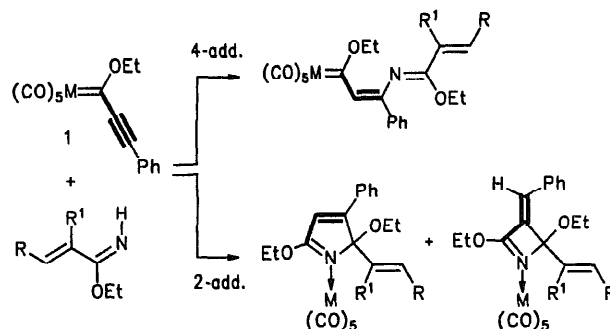
Reaction of (1-alkynyl)carbene complexes $(CO)_5M=C(OEt)C\equiv CPh$ **1a,b** ($M = W, Cr$) with alkenyl imine $PhCH=CH-CH=N(i-Pr)$ **2** affords dihydropyridinyl carbene complexes **3** (by an overall 4 + 2 cycloaddition) and zwitterionic 1-azonia-5H-cycloheptatrien-3-yl carbonylmetalates **4** (by an overall 4 + 3 cycloaddition). The product ratio 3:4 is strongly influenced by steric demand of the metal unit as well as of the substrate. Thus, compounds **3** (generated by 4-addition of the imino function to the $C\equiv C$ bond of **1a**) are major products in case of $M = W$, whilst compounds **4** (generated by 2-addition of the imino function to **1b**) are major products in case of $M = Cr$. Reaction of sterically congested imines, e.g. phenanthrene-9-carboximine **5**, affords [4 + 2] cycloadducts, e.g. **6a,b** as the only detectable products. Compounds **6** undergo hydrolysis on chromatography on silica gel and give a carbaldehyde **7**. Crystal structures are reported of compounds **3a** and **6a**. © 1997 Elsevier Science S.A.

Keywords: Dihydropyridine; Carbene complexes; Chromium and tungsten complexes; Iminium carbonylmetalates; (1-Alkynyl)carbene complexes

1. Introduction

(1-Alkynyl)carbene complexes, e.g. $(CO)_5M=C(OEt)C\equiv CPh$ **1a,b** ($M = Cr, W$) find more and more application to the synthesis of organic compounds.³ It was shown only recently that secondary enaminones [3,4], as well as tertiary cyclic enamines $\sim CH=C(NR_2) \sim$ [5,6] undergo addition to the $C\equiv C$ bond of **1a,b** under exceedingly mild conditions to afford conjugated 6-amino-1-metalla-1,3,5-hexatrienes, which are readily transformed into cyclopentadienes⁴ [5–9] 2,3-homopyrroles [4] or pyran-2-ylidene complexes [3,10,11]. Studies on reactions of 1-metalla-1,3,5-hexatrienes have been extended to nitrogen analogous 5-aza-1-metalla-1,3,5-hexatrienes and also to 5-aza-1-metalla-1,3,5,7-octatetraenes $(CO)_5M=C(OEt)-$

$CR=CR-N=C(OEt)-CR^1=CHR^2$ ($M = Cr, W$; $R =$ alkyl, aryl), which are generated together with 2,5-diethoxy 2H-pyrrole complexes (by 3 + 2 cycloaddition) as well as 2,4-diethoxy 2H-dihydroazete complexes (by 2 + 2 cycloaddition), by addition of alkenyl imidates $R^2CH=CR^1-C(OEt)=NH$ ($R^1, R^2 = Ph, Me, H$) to compounds **1** (Scheme 1) [12]. The product ratio in which these compounds are obtained is strongly influenced by the nature of the metal. Thus, formation of



Scheme 1. 5-Aza-1-metalla-1,3,5,7-octatetraenes, 2H-pyrrole- and dihydroazete complexes from (1-alkynyl)carbene complexes ($M = Cr, W$) and alkenyl *NH*-imidates.

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² X-ray analysis.

³ For recent reviews see Refs. [1,2].

⁴ For part 90 see Ref. [7].

Table 1

Atomic coordinates ($\times 10^{-3}$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for complex **3a**

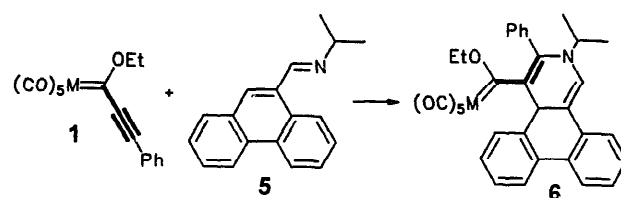
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
W	2387(1)	1324(1)	4533(1)	29(1)
C(11)	764(7)	526(4)	4090(3)	39(1)
O(11)	−129(6)	36(4)	3855(3)	62(2)
C(12)	2801(7)	63(5)	5038(3)	45(2)
O(12)	3036(7)	−668(5)	5307(3)	81(2)
C(13)	4033(7)	1996(5)	5035(3)	41(1)
O(13)	4981(6)	2326(5)	5346(2)	65(2)
C(14)	3758(7)	837(5)	3905(3)	41(1)
O(14)	4541(6)	569(4)	3560(3)	65(2)
C(15)	1070(7)	1815(5)	5183(3)	34(1)
O(15)	325(6)	2079(4)	5552(2)	53(1)
C(2)	1761(6)	2571(4)	3876(2)	25(1)
O(21)	2567(4)	3292(3)	3661(2)	30(1)
C(22)	4104(6)	3382(6)	3848(3)	45(2)
C(23)	4711(8)	4223(6)	3501(4)	56(2)
C(3)	340(5)	2618(4)	3542(2)	26(1)
C(4)	181(6)	2696(4)	2915(3)	29(1)
C(41)	1431(7)	2773(7)	2518(3)	51(2)
C(42)	1795(9)	3688(9)	2272(4)	82(4)
C(43)	2926(16)	3732(18)	1873(6)	179(12)
C(44)	3640(15)	2875(31)	1737(8)	227(18)
C(45)	3297(13)	1991(22)	1990(7)	179(12)
C(46)	2157(9)	1915(11)	2386(4)	97(4)
N(5)	−1146(5)	2577(4)	2593(2)	35(1)
C(5)	−1370(7)	2625(6)	1912(3)	48(2)
C(51)	−1821(14)	1631(9)	1622(4)	94(4)
C(52)	−2442(10)	3473(8)	1737(5)	86(3)
C(6)	−2302(6)	2243(5)	2916(3)	37(1)
C(7)	−2251(6)	2175(5)	3516(3)	34(1)
C(8)	−979(5)	2547(4)	3920(2)	25(1)
C(81)	−1364(6)	3559(4)	4214(3)	31(1)
C(82)	−2228(8)	3561(5)	4710(3)	42(2)
C(83)	−2662(9)	4459(6)	4962(3)	58(2)
C(84)	−2203(10)	5363(6)	4738(4)	67(2)
C(85)	−1351(9)	5376(5)	4251(4)	61(2)
C(86)	−917(8)	4471(5)	3986(3)	46(2)

^a *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 2

Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for complex **3a**

W–C(2)	2.225(5)	C(3)–C(2)–W	122.2(4)
C(2)–O(21)	1.318(6)	C(4)–C(3)–C(2)	121.8(5)
C(2)–C(3)	1.461(7)	C(4)–C(3)–C(8)	120.5(5)
C(3)–C(4)	1.357(7)	C(2)–C(3)–C(8)	117.7(4)
C(3)–C(8)	1.526(7)	C(3)–C(4)–N(5)	121.6(5)
C(4)–N(5)	1.381(7)	C(3)–C(4)–C(41)	123.1(5)
C(4)–C(41)	1.499(8)	N(5)–C(4)–C(41)	114.8(5)
N(5)–C(6)	1.395(7)	C(4)–N(5)–C(6)	118.4(5)
N(5)–C(5)	1.477(8)	C(4)–N(5)–C(5)	123.7(5)
C(5)–C(51)	1.502(12)	C(6)–N(5)–C(5)	117.2(5)
C(5)–C(52)	1.529(11)	N(5)–C(5)–C(51)	113.2(7)
C(6)–C(7)	1.299(8)	N(5)–C(5)–C(52)	108.7(7)
C(7)–C(8)	1.501(8)	C(7)–C(6)–N(5)	123.3(5)
C(8)–C(81)	1.533(7)	C(6)–C(7)–C(8)	122.0(5)
		C(7)–C(8)–C(3)	109.7(4)
O(21)–C(2)–C(3)	108.1(4)	C(7)–C(8)–C(81)	109.2(4)
O(21)–C(2)–W	129.2(4)	C(3)–C(8)–C(81)	112.9(4)

Scheme 4. [4 + 2] Adducts **6** from (1-alkynyl)carbene complex **1a,b** (M = W, Cr) and aryl imine **5**.

W=C2 2.255 (5) $\text{\AA}$, C2–C3 1.461 (7), C3–C4 1.357 (7) (Table 2) indicates that there is little or no conjugation within the π -system. Since the 'enamine unit' is essentially planar, C3–C4–N5–C6 -8.4 (9°), delocalization of the lone pair on the nitrogen atom into the adjacent C=C bond is possible. Two different rotamers with respect to the C2–C3 bond could be present, but the isomer shown in Fig. 1, in which the W(CO)₅ unit is arranged *syn* to 8-H is preferred for steric reasons.

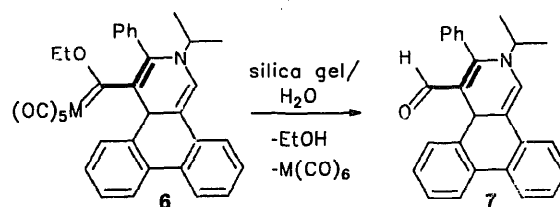
4. Dihydro-2-aza-triphenylene complexes **6**

The competing reaction paths outlined in Scheme 4 seem to be strongly influenced by steric congestion. Accordingly, reaction of the sterically crowded imine **5** with the chromium complex **1b** does not lead to production of a [4 + 3] cycloadduct, as has been observed with imine **2**, but to preferential formation a [4 + 2] adduct **6b** (75% yield). The corresponding tungsten complex **6a** is obtained in 93% yield.

Chromatography of compounds **6** on silica gel leads to hydrolysis of the M=C bond, by which carbaldehydes **7** are formed (Scheme 5).

5. Crystal structure analysis of compound **6a**

The 1-tungsta-1,3-diene unit of complex **6a** is strongly twisted, W–C2–C3–C4 -117.3 (8°) (Fig. 2, Table 3) and exhibits an alternating pattern of bond distances, W=C1 2.233 (10) $\text{\AA}$, C1–C5 1.470 (12), C5–C6 1.369 (11) (Table 4) with apparently little conjugation within the π -system. Conjugation within the enamine unit should be possible based on the planar arrangement of the unit C5–C6–N7–C8 -0.4 (13°). In

Scheme 5. Carbaldehyde **7** by hydrolysis of dihydropyridinyl carbene complexes **6a,b** on silica gel (M = Cr, W).

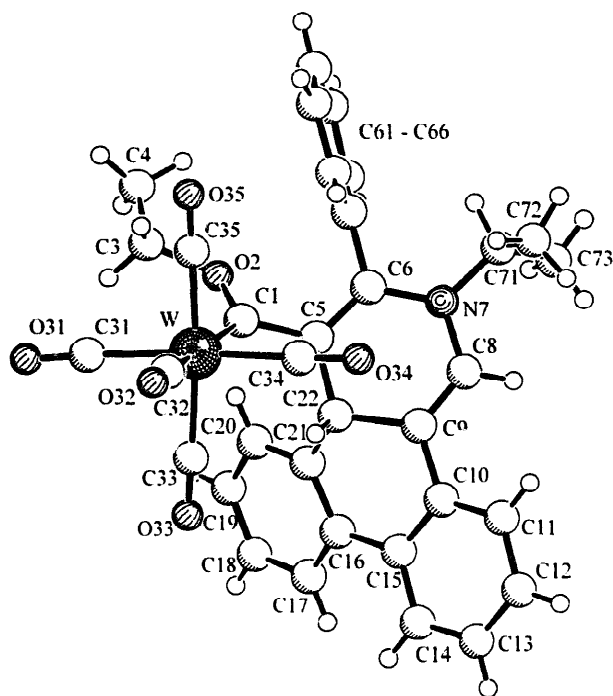


Fig. 2. Molecular structure of dihydro-aza-triphenylene carbene complex **6a**.

principle, two rotamers with respect to the C1–C5 bond may be formed, but the isomer shown in Fig. 2, in which the $W(CO)_3$ unit is arranged *syn* to 22-H is strongly preferred for steric reasons. The dihydro-2-aza-triphenylene ligand is somewhat puckered and the 'biphenyl unit' is slightly twisted, C14–C15–C16–C17 = 19.7 (14)°.

6. Experimental

All operations were performed under argon. Dried solvents were used in all experiments. Melting points are not corrected. Instrumentation: 1H NMR and ^{13}C NMR spectra were obtained with Bruker WM 300, WP 360 and Varian U600 spectrometers (Multiplicities were determined by DEPT. Chemical shifts refer to $\delta_{TMS} = 0.00$ ppm.). Low-temperature NMR measurements were carried out on Bruker AM 360 instrument. Other analyses: IR Digilab FTS 45; MS Finnigan MAT 312; elemental analysis, Perkin-Elmer 240 elemental analyzer; TLC, Merck DC-Alufolien Kieselgel 60 F₂₅₄. R_f values refer to TLC tests. Column chromatographic purifications were made on Merck Kieselgel 100.

6.1. Isopropyl-(3-phenyl-allylidene)-amine (**2**)

Cinnamaldehyde (10.2 g, 77 mmol), isopropylamine (12.3 g, 208 mmol) and molecular sieves ACROS 4 Å

(20 g) in 60 ml of benzene are reacted at 20°C for 12 h to give the imine **2** (13.2 g, 99%). 1H NMR (C_6D_6): δ 7.80 and 6.98 (2H, CH each, AB-system, $^3J = 8$ Hz, PhCH=CH), 6.63 (1H, d, $^3J = 6$ Hz, CH=N), 3.27 (1H, m, CHMe₂), 1.23 [6H, d, CH(CH₃)₂]. ^{13}C NMR (CDCl₃): δ 159.8 (CH=N), 140.9 and 127.0 (CH, AB-system, CH=CHPh), 135.7 (C_q, *i*-C Ph); 128.8, 128.6, 128.4 and 128.2 (1:1:2:1, CH each, Ph), 61.1 (NCHMe₂), 24.0 [CH(CH₃)₂].

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **6a**

	x	y	z	U(eq)
W	2491(1)	534(1)	1302(1)	49(1)
C(31)	2743(10)	−382(6)	1128(8)	72(3)
O(31)	2778(9)	−888(4)	992(8)	113(4)
C(32)	1260(14)	526(5)	273(8)	79(4)
O(32)	551(12)	542(5)	−321(7)	132(5)
C(33)	1078(10)	267(5)	2156(7)	60(2)
O(33)	298(9)	113(4)	2613(6)	96(3)
C(34)	2069(10)	1432(6)	1428(6)	59(3)
O(34)	1830(9)	1944(4)	1465(5)	82(2)
C(35)	3851(12)	735(5)	396(7)	69(3)
O(35)	4571(10)	849(4)	−131(6)	108(3)
C(1)	3976(9)	690(4)	2367(6)	49(2)
O(2)	5131(6)	456(3)	2467(5)	59(2)
C(3)	5584(11)	−32(6)	1887(9)	91(4)
C(4)	6943(13)	−131(7)	2014(12)	127(7)
C(5)	3849(8)	1208(4)	2978(5)	44(2)
C(6)	4752(8)	1664(4)	3014(5)	41(2)
C(61)	5993(8)	1627(4)	2529(5)	44(2)
C(62)	7148(9)	1505(4)	2983(7)	56(2)
C(63)	8295(11)	1481(5)	2534(8)	73(3)
C(64)	8323(11)	1560(6)	1628(8)	84(4)
C(65)	7191(10)	1665(7)	1188(7)	82(4)
C(66)	6039(9)	1721(5)	1616(6)	60(3)
N(7)	4507(7)	2217(3)	3424(5)	52(2)
C(71)	5351(10)	2752(4)	3339(7)	64(3)
C(72)	4801(15)	3213(6)	2725(10)	111(5)
C(73)	5690(12)	3022(6)	4245(9)	96(4)
C(8)	3294(9)	2312(4)	3808(6)	56(2)
C(9)	2383(8)	1885(4)	3852(5)	46(2)
C(10)	1121(9)	1968(5)	4288(6)	52(2)
C(11)	446(10)	2517(5)	4244(8)	71(3)
C(12)	−764(10)	2558(6)	4661(8)	75(3)
C(13)	−1267(12)	2069(7)	5080(8)	83(4)
C(14)	−603(10)	1532(6)	5118(6)	68(3)
C(15)	623(9)	1472(5)	4738(6)	54(2)
C(16)	1400(9)	906(5)	4848(6)	52(2)
C(17)	1186(13)	480(6)	5522(7)	76(3)
C(18)	1959(14)	−23(6)	5616(8)	84(4)
C(19)	2964(13)	−109(5)	5062(8)	77(3)
C(20)	3197(10)	301(5)	4370(7)	65(3)
C(21)	2424(9)	802(4)	4246(5)	48(2)
C(22)	2584(5)	1246(2)	3463(4)	45(2)
Cl(1)	3542(5)	1751(2)	7288(4)	296(5)
Cl(2)	5532(5)	1417(2)	6188(4)	427(10)
C(40)	3904(5)	1690(2)	6241(4)	199(11)

Table 4

Selected bond lengths [Å] and angles [°] for complex **6a**

W–C(1)	2.233(10)	O(2)–C(1)–W	129.8(6)
C(1)–C(5)	1.470(12)	C(5)–C(1)–W	120.3(6)
C(5)–C(6)	1.369(11)	C(6)–C(5)–C(1)	121.7(8)
C(5)–C(22)	1.505(9)	C(6)–C(5)–C(22)	122.2(7)
C(6)–N(7)	1.389(11)	C(1)–C(5)–C(22)	115.5(7)
C(6)–C(61)	1.484(11)	C(5)–C(6)–N(7)	122.1(7)
N(7)–C(8)	1.400(11)	C(5)–C(6)–C(61)	122.1(8)
N(7)–C(71)	1.469(12)	N(7)–C(6)–C(61)	115.4(7)
C(8)–C(9)	1.330(12)	C(6)–N(7)–C(8)	118.8(7)
C(9)–C(10)	1.476(11)	C(6)–N(7)–C(71)	123.5(7)
C(9)–C(22)	1.537(10)	C(8)–N(7)–C(71)	116.7(8)
C(10)–C(15)	1.387(13)	C(72)–C(71)–C(73)	112.0(10)
C(10)–C(11)	1.393(13)	C(9)–C(8)–N(7)	123.5(8)
C(11)–C(12)	1.407(14)	C(8)–C(9)–C(10)	124.2(8)
C(12)–C(13)	1.35(2)	C(8)–C(9)–C(22)	121.8(7)
C(13)–C(14)	1.37(2)	C(10)–C(9)–C(22)	114.0(7)
C(14)–C(15)	1.401(13)	C(15)–C(10)–C(9)	116.9(8)
C(15)–C(16)	1.487(14)	C(11)–C(10)–C(9)	121.9(9)
C(16)–C(17)	1.401(14)	C(10)–C(15)–C(16)	120.7(8)
C(16)–C(21)	1.419(12)	C(14)–C(15)–C(16)	121.4(10)
C(17)–C(18)	1.37(2)	C(17)–C(16)–C(21)	118.7(10)
C(18)–C(19)	1.35(2)	C(17)–C(16)–C(15)	123.4(9)
C(19)–C(20)	1.400(14)	C(21)–C(16)–C(15)	117.9(8)
C(20)–C(21)	1.372(13)	C(20)–C(21)–C(22)	123.1(8)
C(21)–C(22)	1.542(11)	C(16)–C(21)–C(22)	118.3(8)
Cl(1)–C(40)	1.63	C(5)–C(22)–C(9)	111.0(6)
Cl(2)–C(40)	1.79	C(5)–C(22)–C(21)	115.8(6)
		C(9)–C(22)–C(21)	105.7(6)
O(2)–C(1)–C(5)	108.7(8)	Cl(1)–C(40)–Cl(2)	107.2

6.2. Isopropyl-phenanthren-9-yl-methylene-amine (5)

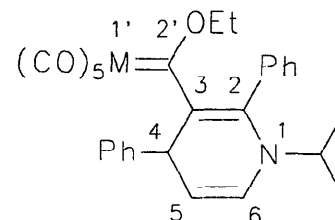
Phenanthrene-9-carboxaldehyde (1.7 g, 8.0 mmol), isopropylamine (1.9 g, 32 mmol) and molecular sieves (10 g) are reacted in 15 ml of pentane at 20°C to give imine (**5**) (1.94 g, 98%, mp 47°C). ¹H NMR (C₆D₆): δ 9.60 and 9.58 (1H, d each, ³J = 8.3 Hz, ⁵J = 1.2 Hz, 8-H), 8.61 (1H, s, HC=N), 8.49 and 8.46 (1H, t each, ³J = 8.3 Hz, ⁵J = 0.7, 5-H), 8.39 and 8.36 (1H, t each, ³J = 8.3 Hz, ⁵J = 0.7 Hz, 4-H), 7.94 (1H, s, 10-H), 7.66 (1H, m), 7.63 (1H, d), 7.55 (1H, d), 7.53 (1H, t), 7.50 (1H, d), 7.46 (1H, d), 7.44 (1H, t), 7.41 (1H, d), 7.40 (1H, d), 7.37 (1H, m), 7.34 (1H, q), 7.31 (1H, m), 7.29 (2H, d) (2H, m), 3.41 (1H, sept, NCH), 1.34 [6H, d, CH(CH₃)₂]. ¹³C NMR (C₆D₆): δ 159.0 (CH=N), 132.7 (CH, C10); 132.0, 131.9, 131.6, 131.3 and 130.8 (Cq each); 129.8, 128.6, 128.2, 127.6, 127.2, 127.1, 123.5 and 123.3 (CH each).

6.3. 3-(2-Ethoxy-1,1,1,1-pentacarbonyl-1-tungsta-2-ethenyl)-1-isopropyl-2,4-diphenyl-1,4-dihydro-pyridine (3a) and pentacarbonyl[2-ethoxy-1-isopropyl-4,5-diphenyl-1-azonia-5H-cycloheptatriene-3-yl]tungstate (4a)

Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg 1.00 mmol) and iso-

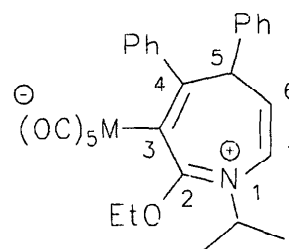
propyl-(3-phenyl-allylidene)-amine (**2**) (173 mg, 1.00 mmol) is reacted as described under 6.4 to give an orange solid of a mixture of **3a**:**4a** = 6:1 (540 mg, 82%). Chromatography with pentane/diethyl ether (10:1) on silica gel affords compound **3a** (512 mg, 78%, *R*_f = 0.6 pentane/dichloromethane (5:1), orange crystals from diethyl ether/pentane 1:4 at –5°C, mp 120°C) and compound **4a** (85 mg, 13%).

3a. ¹H NMR (C₆D₆): δ 7.39, 7.36, 7.20 and 7.05 (2:2:3:3H, m each, 2 Ph), 5.87 (1H, d, ³J = 7.6 Hz, 4-H), 5.59 (1H, d, ³J = 6.0 Hz, 6-H), 5.23 (1H,



ddd, ³J = 7.6 and 6.0 Hz, ⁵J = 0.5 Hz, 5-H), 4.10 and 3.80 (1:1H, m each, diastereotopic OCH₂), 3.21 (1H, sept, NCHMe₂), 0.64 [6H, d broad, NCH(CH₃)₂], 0.53 (3H, t, OCH₂CH₃). ¹³C NMR (CDCl₃): δ 310.8 (C_q, W=C), 202.3 and 197.9 [1:4, C_q each, *trans*- and *cis*-CO W(CO)₅], 147.0 (C_q, C2), 136.8 and 136.3 (C_q, *i*-C each, 2 Ph), 130.0 (C_q, C3); 131.0, 128.6, 128.4, 128.1, 128.0, 127.9, 127.1 and 126.2 (1:1:2:1:1:1:2:1, CH each, 2 Ph), 122.8 (CH, C6), 108.1 (CH, C5), 78.2 (OCH₂), 48.9 (CH, C4), 45.3 (CHMe₂), 21.7 and 21.0 [N(CH₃)₂], 14.0 (OCH₂CH₃). IR (diethyl ether), cm^{–1} (%): 2059.3 (55), 1923.4 (100) [ν(C≡O)]. MS (70 eV), ¹⁸⁴W, *m/e* (%): 655 (20) [M⁺], 627 (10) [M–CO], 599 (15) [M–2 CO], 573 (70), 513 (75), 486 (70), 442 (65), 413 (55), 331 (50) [ligand], 302 (70), 285 (70), 258 (70), 241 (80), 215 (50), 167 (35), 149 (80), 83 (60), 71 (80), 55 (100). Anal. Calcd. for C₂₈H₂₅NO₆W (655.4): C, 51.32; H, 3.84; N, 2.14. Found: C, 51.16; H, 3.77; N, 2.14.

4a. ¹H NMR (C₆D₆, 600 MHz): δ 7.39, 7.24 and 7.00 (2:2:6H, m each, 2 Ph), 6.13 (1H, t, ³J = 7.9 and 7.6 Hz, 6-H), 5.78 (1H, dd, ³J = 7.6 Hz,



⁴J = 1.7, 7-H), 4.55 and 4.50 (2H, m each, diastereotopic OCH₂), 4.29 (1H, m, NCHMe₂), 3.42 (1H,

d, $^3J = 7.9$ Hz, 5-H), 1.07 and 0.78 [3H each, d each, $\text{NCH}(\text{CH}_3)_2$], 1.02 (3H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6 , 600 MHz): δ 202.6 and 200.3 [1:4, C_q each, *trans*- and *cis*-CO $\text{W}(\text{CO})_5$], 200.0 (C_q , W–C), 181.9 (C_q , $\text{C}=\text{N}^+$), 160.5 (C_q , C4), 142.5 (C_q , C7), 139.2 and 138.2 (C_q , *i*-C each, 2 Ph); 131.5, 130.0, 129.7, 129.6, 129.4, 128.8, 128.3 and 126.6 (CH each, 2 Ph), 110.6 (CH, C6), 67.2 (OCH_2), 53.5 (NCHMe_2), 50.7 (CH, C5), 21.6 and 19.3 [$\text{NCH}(\text{CH}_3)_2$], 14.4 (OCH_2CH_3). Anal. Calcd. for $\text{C}_{28}\text{H}_{25}\text{NO}_6\text{W}$ (655.4): C, 51.32; H, 3.84; N, 2.14. Found: C, 51.67; H, 3.90; N, 2.23.

X-ray crystal structure analysis of **3a**: formula $\text{C}_{28}\text{H}_{25}\text{NO}_6\text{W}$, $M = 655.34$, $0.75 \times 0.40 \times 0.30$ mm, $a = 9.299(1)$, $b = 13.208(1)$, $c = 21.640(2)$ Å, $\beta = 94.15(1)^\circ$, $V = 2650.9(4)$ Å³, $\rho_{\text{calc}} = 1.642$ g cm^{−3}, $\mu = 43.99$ cm^{−1}, empirical absorption correction via φ scan data ($0.718 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 5722 reflections collected ($+h$, $-k$, $\pm l$), $[(\sin \theta)/\lambda] = 0.62$ Å^{−1}, 5383 independent and 4443 observed reflections [$I \geq 2\sigma(I)$], 325 refined parameters, $R = 0.040$, $wR^2 = 0.110$, max. residual electron density 1.46 (−2.21) e Å^{−3}, hydrogens calculated and refined as riding atoms. All data sets were collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92. Further information about the X-ray crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD 407268, the names of the authors, and the journal citation.

6.4. 3-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-chroma-2-ethenyl)-1-isopropyl-2,4-diphenyl-1,4-dihydro-pyridine (3b) and pentacarbonyl[2-ethoxy-1-isopropyl-4,5-diphenyl-1-azonia-5H-cycloheptatriene-3-yl]chromate (4b)

To pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**1b**) (350 mg, 1.00 mmol) and 2 ml of pentane in a 5-ml screwtop vessel is added with stirring isopropyl-(3-phenyl-allylidene)-amine (**2**) (173 mg, 1.00 mmol) in 2 ml of pentane. After 20 min at 20°C the mixture is shaken until it is homogeneous and then kept at 20°C in a dark place without stirring. After ca. 6 d compound **1b** is consumed completely (according to TLC analysis) and a brown solid precipitate is formed, which is isolated by centrifugation and washed with pentane (3 × 1 ml), (418 mg, 80%, mixture of **3b**:**4b** = 1:12 according to ^1H NMR integration). Fractional crystallization from diethyl ether/pentane affords yellow compound **4b** (387 mg, 74%, mp 80°C) and

compound **3b** (31 mg, 6%) which is accumulated in the mother liquor.

4b. ^1H NMR (CDCl_3): δ 7.46, 6.72 and 7.00 (2:2:6H, m each, 2 Ph), 6.06 (1H, dd, $^3J = 7.5$ and 7.6 Hz, 6-H), 5.82 (1H, d, $^3J = 7.5$ Hz, 7-H), 4.52 (2H, m, OCH_2), 4.27 (1H, m, NCHMe_2), 3.46 (1H, d, $^3J = 7.6$ Hz, 5-H), 1.13 and 0.82 [3H each, d each, diastereotopic $\text{CH}(\text{CH}_3)_2$], 1.02 (3H, t, OCH_2CH_3). ^{13}C NMR (CDCl_3): δ 224.2 and 218.8 [1:4, C_q each, *trans*- and *cis*-CO $\text{Cr}(\text{CO})_5$], 217.5 (C_q , Cr–C), 180.8 (C_q , $\text{C}=\text{N}^+$), 158.5 (C_q , C4), 145.1 (C7), 141.9 and 138.2 (C_q , *i*-C each, 2 Ph); 128.3, 128.2, 127.7, 127.3, 126.6 and 123.9 (CH each, 2 Ph), 120.5 (CH, C6), 66.6 (OCH_2), 54.8 (NCHMe_2), 50.6 (CH, C5), 21.7 and 19.4 [$\text{NCH}(\text{CH}_3)_2$], 14.4 (OCH_2CH_3). IR (diethyl ether), cm^{−1} (%): 2045.5 (100), 1964.9 (75), 1927.5 (90), 1882.0 (95), 1867.9 (80) [$\nu(\text{C}\equiv\text{O})$]. MS (70 eV), m/e (%): 523 (5) [M^+], 467 (5) [$\text{M}-2\text{CO}$], 411 (10) [$\text{M}-4\text{CO}$], 383 (40) [$\text{M}-5\text{CO}$], 331 (40), 303 (75), 274 (65), 261 (55), 232 (56), 202 (30), 149 (45), 111 (30), 97 (39), 83 (64), 69 (76), 57 (100). Anal. Calcd. for $\text{C}_{28}\text{H}_{25}\text{CrNO}_6$ (523.1): C, 64.23; H, 4.82; N, 2.68. Found: C, 64.24; H, 5.04; N, 2.80.

3b. ^1H NMR (C_6D_6): δ 7.52–7.34, 7.23–6.97 (4:6H, m each, 2 Ph), 5.92 (1H, d, $^3J = 7.6$ Hz, 6-H), 5.53 (1H, d, $^3J = 5.5$ Hz, 4-H), 5.16 (1H, m, 5-H), 4.12 and 3.90 (1H each, diastereotopic OCH_2), 3.16 (1H, m, NCHMe_2), 0.69 (3H, t, OCH_2CH_3), 0.58 [6H, broad, diastereotopic $\text{NCH}(\text{CH}_3)_2$].

6.5. 4-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-tungsta-2-ethenyl)-2-isopropyl-3-phenyl-2,5-dihydro-2-aza-triphenylene (6a) and 2-isopropyl-3-phenyl-2,5-dihydro-2-aza-triphenylene-4-carbaldehyde (7)

To pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg 1.00 mmol) and isopropyl-(phenanthren-9-yl-methylene)-amine (**5**) (247 mg, 1.00 mmol) in a 5-ml screwtop vessel is added 3.5 ml of pentane and the mixture is stirred at 20°C for ca. 40 h. An orange solid precipitate is formed, which is removed by centrifugation, washed with pentane (3 × 1 ml) and dried in vacuo to give an analytically clean sample of compound **6a** (675 mg, 93%, $R_f = 0.4$ pentane/dichloromethane 5:1, red crystals from dichloromethane/pentane 1:4 at −5°C, mp 120°C). Chromatography of **6a** on silica leads to partial decomposition. Thus, after elution of red compound **6a**, elution with pentane/diethyl ether 1:1 affords aldehyde **7** (86 mg, 23%, $R_f = 0.7$ in diethyl ether, colorless crystals from dichloromethane at −5°C, mp 97°C).

6a. ^1H NMR (CDCl_3): δ 7.87 and 7.74 (1H each, dd each, 7-H and 14-H); 7.42, 7.34, 7.32 and 7.19 (1H each, td each; 8-H, 9-H, 12-H and 13-H); 7.34 (3H, m broad, *m*- and *p*-H Ph), 7.25 and 7.12 (1H each, 'd'

broad, *o*-H Ph), 7.23 and 6.85 (1H each, ddd each, 10-H and 11-H), 6.27 (1H, d, $^5J = 1.7$ Hz, 1-H), 5.91 (1H, s broad, 5-H), 4.70 and 3.80 (1:1H, m each, diastereotopic OCH_2), 3.44 (1H, m, NCHMe_2), 1.09 (3H, t, OCH_2CH_3), 1.08 and 1.06 [3:3H, d each, $^3J = 6.7$ Hz, $^5J = 1.7$, $\text{NCH}(\text{CH}_3)_2$]. ^{13}C NMR (CDCl_3): δ 310.2 (C_q , $\text{W}=\text{C}$), 202.2 and 197.5 [1:4, C_q each, *trans*- and *cis*-CO $\text{W}(\text{CO})_5$], 142.0 (C_q , C3), 137.6 (C_q , C4), 136.7 (C_q , C6a), 135.5 (C_q , *i*-C Ph), 133.9 (C_q , C10a), 133.1 (C_q , C10aa), 131.7 (C_q , C14a); 130.6, 128.8, 128.1, 128.0, 127.9, 127.7, 127.3, 126.8, 126.5, 124.4, 124.3, 123.8, 123.2 and 117.8 (CH each), 116.7 (C_q , C6), 77.9 (OCH_2), 49.1 (NCHMe_2), 45.2 (CH, C5), 21.5 and 21.0 [$\text{NCH}(\text{CH}_3)_2$], 14.2 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 2058.9 (80), 1973.6 (20), 1921.8 (100), 1911.1 (99) [$\nu(\text{C}\equiv\text{O})$]. MS (70 eV), ^{184}W , m/e (%): 729 (1) [M^+], 645 (1), 589 (1) [$\text{M}-5$ CO], 515 (1), 405 (50) [ligand], 376 (25) [ligand-Et], 360 (30), 332 (30), 317(60), 149 (25), 111 (30), 83 (45), 57 (100). Anal. Calcd. for $\text{C}_{34}\text{H}_{27}\text{NO}_6\text{W}$ (729.4): C, 55.98; H, 3.73; N, 1.92. Found: C, 55.81; H, 3.65; N, 1.82.

7. ^1H NMR (CDCl_3): δ 9.08 (1H, d, $^6J = 0.7$ Hz, $\text{O}=\text{CH}$), 7.87 and 7.84 (1H each, 'd' each, 7-H and 14-H), 7.52 and 7.24 (2H each, m each; 8-H, 9-H, 12-H and 13-H), 7.40 (5H, m broad, Ph), 7.30 and 7.05 (1H each, 'd' each; 10-H and 11-H), 6.23 (1H, d, $^4J = 1.5$ Hz, 1-H), 4.87 (1H, d, $^4J = 1.5$ Hz, 5-H), 3.63 (1H, sept, NCHMe_2), 1.25 and 1.01 [3:3H, d each, $\text{NCH}(\text{CH}_3)_2$]. ^{13}C NMR (CDCl_3): δ 191.0 ($\text{O}=\text{CH}$), 158.8 (C_q , C3), 138.7 (C_q , C4), 135.5 (C_q , C18), 134.3 (C_q , C17), 133.1 (C_q , *i*-C Ph), 132.6 (C_q , C16), 121.2 (C_q , C15), 111.8 (C_q , C6), 130.2 (CH, C1); 129.6, 128.9, 128.8, 128.7, 128.3, 127.5, 127.0, 126.3, 124.6, 124.0, 123.8, 123.0, 117.1 (CH each), 49.9 (NCHMe_2), 35.7 (CH, C5), 21.7 and 21.3 [$\text{NCH}(\text{CH}_3)_2$]. MS (70 eV), m/e (%): 377 (100) [M^+], 348 (15) [$\text{M}-\text{CHO}$], 334 (75) [$\text{M}-\text{CHMe}_2$], 306 (20), 260 (10), 111 (20), 85 (50), 97 (30), 71 (45), 57 (60). Anal. Calcd. for $\text{C}_{27}\text{H}_{23}\text{NO}$ (377.5): C, 85.91; H, 6.14; N, 3.71. Found: C, 86.15; H, 6.07; N, 3.87.

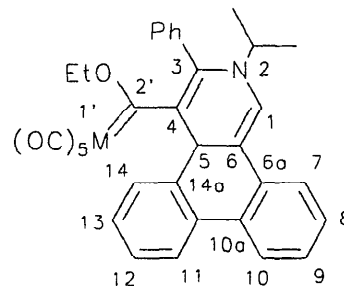
X-ray crystal structure analysis of **6a**, formula $\text{C}_{34}\text{H}_{27}\text{NO}_6\text{W} + \text{CH}_2\text{Cl}_2$, $M = 814.34$, $0.30 \times 0.20 \times 0.10$ mm, $a = 10.317(2)$, $b = 21.981(4)$, $c = 15.065(3)$ Å, $\beta = 90.64(1)^\circ$, $V = 3416.2(11)$ Å³, $\rho_{\text{calc}} = 1.583$ g cm^{-3} , $\mu = 35.82$ cm^{-1} , empirical absorption correction via φ scan data ($0.878 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 293$ K, $\omega/2\theta$ scans, 7194 reflections collected ($\pm h, -k, -l$), $[(\sin\theta)/\lambda] = 0.62$ Å⁻¹, 6931 independent and 4156 observed reflections [$I \geq 2\sigma(I)$], 400 refined parameters, $R = 0.057$, $wR^2 = 0.148$, max. residual electron density 1.66 (−1.73) e Å⁻³, hydrogens calculated and refined as riding atoms. All data sets were collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN,

structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

6.6. 4-(2-Ethoxy-1,1,1,1-pentacarbonyl-1-chroma-2-ethenyl)-2-isopropyl-3-phenyl-2,5-dihydro-2-aza-triphenylene (**6b**) and 2-isopropyl-3-phenyl-2,5-dihydro-2-aza-triphenylene-4-carbaldehyde (**7**)

Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**1b**) (350 mg 1.0 mmol) and isopropyl-(phenanthren-9-yl-methylene)-amine (**5**) (247 mg, 1.00 mmol) is reacted as described above and affords compound **6b** analytically almost pure (445 mg, 75%, orange solid). Chromatography on silica gel with pentane/dichloromethane (5:1) yields red complex **6b** (316 mg, 53%, $R_f = 0.6$ in pentane/dichloromethane 3:1, red crystals from dichloromethane/pentane 1:4 at -5°C , mp $> 83^\circ\text{C}$, dec.) and aldehyde **7**.

6b. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$ 4:1): δ 7.84 and 7.68 (1H each, 'd' each, 7-H



and 14-H), 7.40, 7.36, 7.30 and 7.24 (1H each, 't' each; 8-H, 9-H, 12-H and 13-H); 7.30 (3H, m broad, *m*- and *p*-H Ph), 7.27 and 7.10 (1H each, 'd' broad, *o*-H Ph), 7.15 and 6.78 (1H each, 'd' each, 10-H and 11-H), 6.25 (1H, d, $^5J = 1.7$ Hz, 1-H), 5.92 (1H, s, 5-H), 4.87 and 3.88 (1:1H, m each, diastereotopic OCH_2), 3.38 (1H, sept, NCHMe_2), 1.15 (3H, OCH_2CH_3), 1.07 [6H, d broad, $\text{NCH}(\text{CH}_3)_2$]. ^{13}C NMR (CDCl_3): δ 336.5 (C_q , $\text{Cr}=\text{C}$), 223.2 and 216.9 [1:4, C_q each, *trans*- and *cis*-CO $\text{Cr}(\text{CO})_5$], 142.2 (C_q , C3), 136.6 (C_q , C4), 135.7 (C_q , C6a), 135.6 (C_q , C10a), 134.2 (C_q , C10aa), 134.0 (C_q , *i*-C Ph), 133.1 (C_q , C14a); 130.6, 128.9, 128.8, 128.1, 127.9, 127.7, 127.6, 126.8, 126.5, 124.4, 124.2, 123.8, 123.3 and 117.8 (CH each), 116.2 (C_q , C6), 75.5 (OCH_2), 49.0 (NCHMe_2), 43.8 (CH, C5), 21.6 and 21.1 [$\text{NCH}(\text{CH}_3)_2$], 14.4 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 2051.0 (90), 1976.0 (55), 1940.2 (97), 1910.8 (100) [$\nu(\text{C}\equiv\text{O})$]. MS (70 eV), m/e (%): 541 (10) [$\text{M}-2$ CO], 457 (25) [$\text{M}-5$ CO], 411 (65) [$\text{M}-5$ CO-EtOH], 360 (95), 317 (100), 289 (25), 153 (10), 125 (15), 109 (20), 97 (30), 83 (50), 71 (45), 58 (80). Anal. Calcd. for $\text{C}_{34}\text{H}_{27}\text{CrNO}_6$ (597.6): C, 68.34; H, 4.55; N, 2.34. Found: C, 68.38; H, 4.77; N, 2.56.

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