Organic Syntheses via Transition Metal Complexes, XCVII[◇]

Mesoionic Pyrrolium Complexes and Dihydropyrroles by Cycloaddition of (Non-enolizable) Imines to an [(1-Alkynyl)carbene]tungsten Complex☆

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Reaction of the [(1-alkynyl)carbene]tungsten complex $(CO)_5W{=}C(OEt)C{\equiv}CPh$ (**1a**) with non-enolizable imines, e.g. 9-fluorenone imines **2** [NR = N(*i*Pr), N(*c*-C_6H_{11})], affords novel mesoionic pyrrolium carbonyltungstates **3** (by [3+2] cycloaddition) together with dihydropyrroles **4** (by dichotomy of the C=N bond and subsequent insertion of the carbene carbon atom into an NC–H bond). Cross-conjugated azametallatrienes **6** and pentacarbonyltungsten complexes **7** of the dihydropyrroles **4** have been identified to be precursors to compound **4**. Compounds **3b**, **4a**, and **6a** have been characterized by X-ray crystal structure analyses.

Reactions of imines with group-VI heteroatom-stabilized carbene complexes of the Fischer-type are varied and have provided some useful synthetic applications. Depending on the type of carbene complex and the imine, nucleophilic substitution at the carbene carbon atom,[2] condensation at the α-carbon atom (under thermal conditions) or formation of β-lactams[3] (under the influence of sun light) is achieved. The latter type of reaction has been extensively studied by Hegedus et al., and many *N*-substituted imines have been converted into β-lactams. Reactions of imines with α,β-unsaturated carbene complexes are channeled by competing 4-addition of the nitrogen atom to a C=C (or C≡C) bond, and by 2-addition to the M=C, respectively. For example, reactions of *NH*-ketimines $R_2C{=}NH$ (R = alkyl, aryl) with the [(1-alkynyl)carbene]chromium complex $(CO)_5Cr{=}C(OEt)C{\equiv}CPh$ (**1b**) were shown to afford mainly 5-aza-1-chroma-1,3,5-hexatrienes $(CO)_5Cr{=}C(OEt)CH{=}C(Ph)N{=}CR_2$ by 4-addition.[4] Alkenyl *NH*-imidates $R^2CH{=}CR^1{-}C(OEt){=}NH$ (R^1, R^2 = Ph, Me, H) and (1-alkynyl)carbene complexes **1a**, **b** (M = W, Cr) were found to produce 5-aza-1-metalla-1,3,5,7-octatetraenes $(CO)_5M{=}C(OEt){-}CR{=}CR{-}N{=}C(OEt){-}CR^1{=}CHR^2$ (R = alkyl, aryl) by 4-addition, but also 2,5-diethoxy-2*H*-pyrrole and 2,4-diethoxy-2*H*-dihydroazete complexes, both of which by 2-addition (in an overall [3+2] and [2+2] cycloaddition, respectively).[5] Furthermore, reactions of both alkenyl *N(alkyl)*-imines, and -imidates, respectively, involve participation of the alkenyl unit, but lead to different types of products with (1-alkynyl)carbene complexes **1a**, **b**. Whilst the alkenyl *N(alkyl)*-imines, e.g. $PhCH{=}CH{-}CH{=}N(iPr)$ yield (dihydropyridinyl)carbene complexes (in an overall [4+2] cycloaddition initiated by 4-addition) and mesoionic 1-azonia-5*H*-cycloheptatrien-3-yl carbonylmetalates (in an overall [4+3] cycloaddition initiated by 2-addition),[6][7] alkenyl *N(alkyl)*-imidates, e.g. $RCH{=}CH{-}C(OEt)NR^1$ (R, R^1 = aryl, alkyl) were found to afford binuclear compounds as the only products, resulting from a domino [4+2] and [2+2] cycloaddition of two equivalents of compound **1**.[8] Thus, with respect to the addition of α,β-unsaturated imines to (1-alkynyl)carbene complexes **1**, it should be noted that open-chain adducts as well as four- and five-membered *N*-heterocyclic rings are obtained from *N*-unsubstituted alkenyl imidates, whilst bicyclic systems are generated from *N*-substituted alkenyl imidates, and six- and seven-membered rings are generated from *N*-substituted alkenylimines (but supposedly not from *N*-unsubstituted alkenylimines).

Reaction of (1-Alkynyl)carbene Complex 1a with Non-enolizable Imines 2

The investigation of fundamental reaction paths of imines and imidates with (1-alkynyl)carbene complexes **1** was extended to aliphatic compounds. It was found that enolizable imidates, e.g., *O*-alkyl lactims $\sim(CH_2)_n{-}N{=}C(OR)\sim$ (n = 3−6) and (1-alkynyl)carbene complexes **1a**, **b** gave 1-azacycloalkene derivatives as the main products, involving the transfer of an α-hydrogen atom.[1] Focusing more strongly on the reactivity of the C=N bonds in aliphatic systems, it was envisaged that non-enolizable imines might yield pyrrolium (= azoniacyclopentadiene) complexes by [3+2] cycloaddition of a C_3 unit of compounds **1** to the C=N bond (Scheme 1). This reaction mode was anticipated as an extension of the recently described access to cyclopen-

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[++] X-ray structure analyses.

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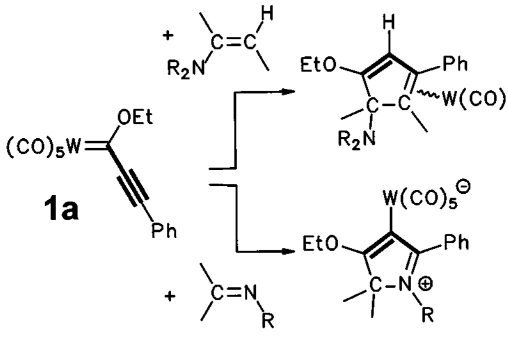
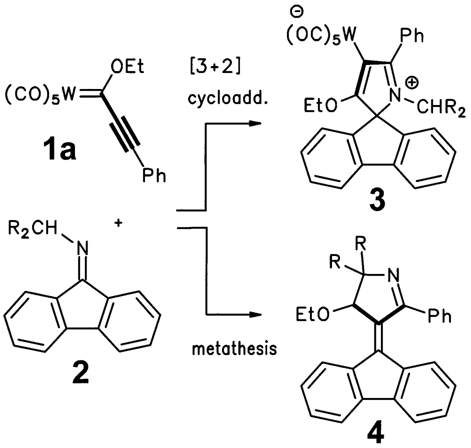
tadienes by [3+2] cycloaddition of (1-alkynyl)carbene complexes to HC=C(N) bonds.[9]

Scheme 1. [3+2] Cycloaddition of [(1-alkynyl)carbene]tungsten complex **1a** to olefines and imines, respectively



Reaction of the (1-alkynyl)carbene complex **1a** with non-enolizable imines, like fluorenone imines **2a**, **b** at 90°C, 2 h, molar ratio 1:1, affords two types of compounds in a clean reaction: (a) novel pyrrolium complexes **3a**, **b** as minor and (b) dihydropyrroles **4a**, **b** as major products (Scheme 2). Compounds **3** and **4** were isolated by chromatography on silica gel and characterized spectroscopically as well as by X-ray crystal structure analyses. Whilst it is quite obvious that compounds **3** are generated in an overall [3+2] cycloaddition as outlined above (Scheme 1), formation of compounds **4** seems to involve a more complicated reaction sequence (v.s.).

Scheme 2. Two different routes to pyrrole derivatives from non-enolizable imines 2 and (1-alkynyl)carbene complex **1a**

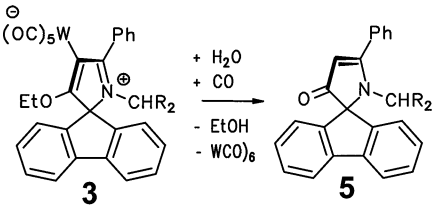


2−4	R,R	[**3**] + [**4**]	[**3**]/[**4**]
a	Me,Me	93%	1:8
b	$-[CH_2]_4-$	89%	2:7

Spectroscopy and Structure Determinations

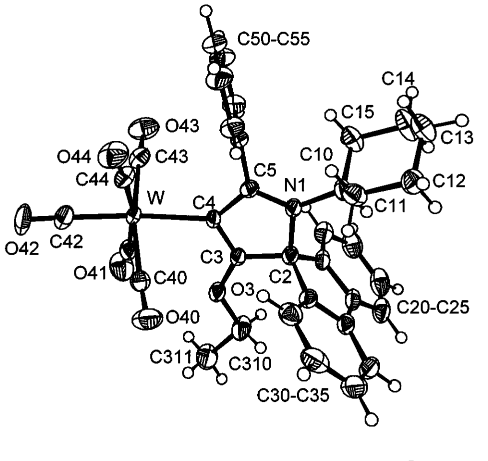
The mesoionic character of the novel pyrrolium compounds **3** is indicated in its ^{13}C-NMR spectrum by a characteristic upfield shift of the signal W−*C*(ring) (**3a**: δ = 187.9; **3b**: δ = 187.3), which now is observed in a range similar to that found for iminium carbonylmetalates[10] derived from vinylogous seven-membered *N*-heterocyclic ligands[7] (W−*C*: δ = 181.9).[6c] Furthermore, the signal of *C*=N^+ is appreciably shifted downfield (**3a**: δ = 198.2; **3b**: δ = 197.3) if compared to a normal C=N bond. Compounds **3** are first representatives of a (supposedly) large group of mesoionic pyrrolium complexes, which, like sydnones and related species,[11] can not be satisfactorily described by Lewis formulas excluding charge separation. In line with expectation, compounds **3** were found to undergo hydrolysis of the enol ether unit with formation of a spiro compound **5** as the only detectable product, in addition to $W(CO)_6$ (Scheme 3).

Scheme 3. Hydrolysis of zwitterionic pyrrolium complexes **3**



Structural details of spiro compounds **3** are based on a crystal structure analysis of compound **3b** (Figure 1, Table 1). The distance W−C4 [2.276(4)] Å is longer than in non-heteroatom (carbene)tungsten complexes, such as $(CO)_5W{=}CPh_2$ [2.15(1)][12] and even longer than in pyrylium pentacarbonyltungstates, e.g. 2.193(5).[13] In line with the mesoionic character of compound **3b** is the pattern of alternating bond lengths found in the *N*-heterocyclic ring [N−C2 1.474(5), C2−C3 1.517(5), C3−C4 1.357(5), C4−C5 1.434(6), C5−N 1.324(5) Å] and an essentially planar arrangement of the bonds to the nitrogen atom (sum of valence angles is 360.0°). The plane defined by the five-membered heterocycle bisects the angle between two neighboring carbonyltungsten groups, C3−C4−W−C41 −37.5 (4)°, and is arranged almost perpendicular to the phenyl group, C4−C5−C50−C51 97.6 (5)°.

Figure 1. Molecular structure of the mesoionic pyrrolium complex **3b**



The structure of the dihydropyrroles **4a**, **b** is based on the ^1J-, ^2J-, and $^3J(^{13}C,^1H)$ coupling constants in the NMR

Table 1. Selected bond lengths [Å] and angles [°] for pyrrolium compound **3b**

N(1)–C(5)	1.324(5)	N(1)–C(2)–C(3)	100.5(3)
N(1)–C(2)	1.474(5)	N(1)–C(2)–C(20)	112.8(3)
N(1)–C(10)	1.485(5)	C(3)–C(2)–C(20)	117.0(3)
C(2)–C(3)	1.517(5)	N(1)–C(2)–C(30)	112.7(3)
C(2)–C(20)	1.521(6)	C(3)–C(2)–C(30)	112.4(3)
C(2)–C(30)	1.535(6)	C(20)–C(2)–C(30)	102.0(3)
C(3)–O(3)	1.331(5)	O(3)–C(3)–C(4)	121.9(4)
C(3)–C(4)	1.357(5)	O(3)–C(3)–C(2)	125.1(3)
C(4)–C(5)	1.434(6)	C(4)–C(3)–C(2)	112.8(3)
C(4)–W	2.276(4)	C(3)–C(4)–C(5)	103.3(3)
C(5)–C(50)	1.488(5)	C(3)–C(4)–W	123.7(3)
O(3)–C(310)	1.434(5)	C(5)–C(4)–W	132.1(3)
C(310)–C(311)	1.496(7)	N(1)–C(5)–C(4)	114.6(3)
		N(1)–C(5)–C(50)	122.6(4)
C(5)–N(1)–C(2)	108.7(3)	C(4)–C(5)–C(50)	122.7(4)
C(5)–N(1)–C(10)	132.5(3)	C(3)–O(3)–C(310)	123.7(4)
C(2)–N(1)–C(10)	118.8(3)	O(3)–C(310)–C(311)	107.0(4)
N(1)–C(2)–C(3)	100.5(3)		

spectra, as well as on a crystal structure analysis of compound **4a** (Figure 2, Table 2). The *N*-heterocyclic ring exhibits the expected pattern of bond lengths [C1–C2 1.514(3), C2–C3 1.554(4), C3–N4 1.489(3), N4–C5 1.291(3), C1–C5 1.481(3) Å] and is slightly twisted against the fluorenylidene unit, C5–C1–C6–C7 18.0 (4)°.

Figure 2. Molecular structure of the dihydropyrrol **4a**

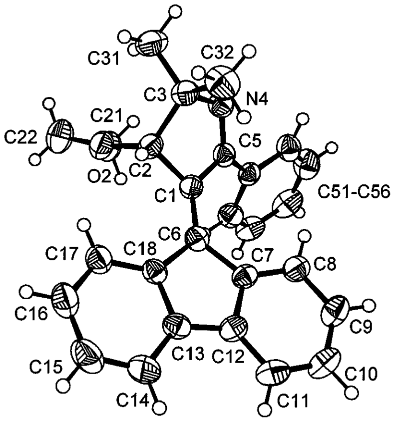


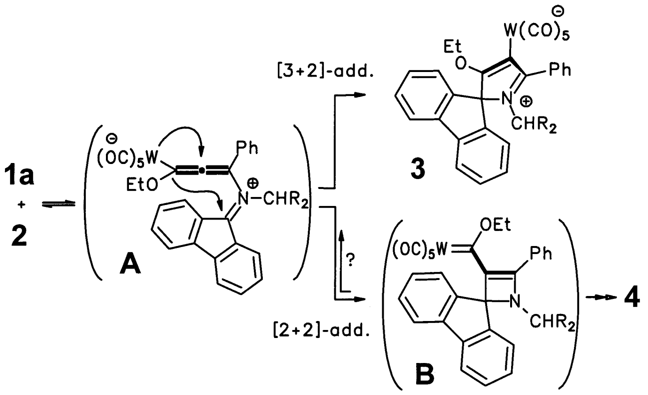
Table 2. Selected bond lengths [Å] and angles [°] for dihydropyrrole **4a**

C(1)–C(6)	1.352(3)	O(2)–C(2)–C(1)	115.5(2)
C(1)–C(5)	1.481(3)	O(2)–C(2)–C(3)	114.6(2)
C(1)–C(2)	1.514(3)	C(1)–C(2)–C(3)	100.4(2)
C(2)–O(2)	1.428(3)	C(21)–O(2)–C(2)	115.5(2)
C(2)–C(3)	1.554(4)	O(2)–C(21)–C(22)	109.4(2)
O(2)–C(21)	1.428(3)	N(4)–C(3)–C(31)	110.7(2)
C(21)–C(22)	1.503(4)	N(4)–C(3)–C(32)	108.3(2)
C(3)–N(4)	1.489(3)	C(31)–C(3)–C(32)	110.0(2)
C(3)–C(31)	1.522(4)	N(4)–C(3)–C(2)	104.0(2)
C(3)–C(32)	1.528(4)	C(31)–C(3)–C(2)	113.9(2)
N(4)–C(5)	1.291(3)	C(32)–C(3)–C(2)	109.8(2)
C(5)–C(51)	1.477(3)	C(5)–N(4)–C(3)	108.9(2)
		N(4)–C(5)–C(51)	119.9(2)
C(6)–C(1)–C(5)	131.0(2)	N(4)–C(5)–C(1)	113.2(2)
C(6)–C(1)–C(2)	124.8(2)	C(51)–C(5)–C(1)	126.0(2)
C(5)–C(1)–C(2)	103.5(2)		

Reaction Course

Since there is ample precedence for reactions of (1-alkynyl)carbene complex $(CO)_5W{=}C(OEt)C{\equiv}CPh$ (**1a**) with nitrogen bases N (and also phosphanes) to form zwitterionic adducts $^{-}(OC)_5W{-}C(OEt){=}C{=}C(Ph)N^{+}$ as initial products,[14] it is suggested for the present case that an intermediate **A** might be generated from addition of an imine **2** to the (1-alkynyl)carbene complex **1a**. A zwitterionic species **A** might act as precursor to both a five-membered cycloadduct **3** and a four-membered dihydroazete derivative **B** (Scheme 4).

Scheme 4. Competing [3+2] and [2+2] cycloadditions of (1-alkynyl)carbene complex **1a** to the C=N bond of non-enolizable imines **2**

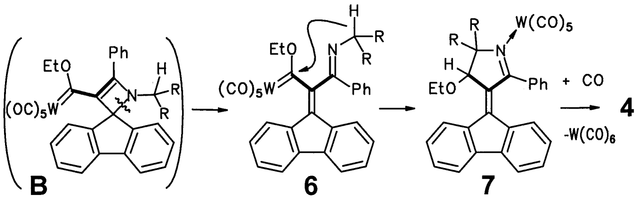


It is suggested that dihydroazetes **B** would be key intermediates en route to dihydropyrroles **4**. This assumption is supported by the fact that organometallic intermediates **6** and **7** could be isolated and characterized.

Organometallic Reaction Intermediates

Reaction of (1-alkynyl)carbene complex **1a** with fluorenone imines **2** at 20°C (instead of 90°C, as it has been applied for the reaction given in Scheme 2), affords two colored compounds **6** and **7**, which were isolated by column chromatography on silica gel (Scheme 5). It could be easily demonstrated that the azametallatriene unit of compounds **6** in solution undergoes a thermally induced ring closure to give dihydropyrroles **7**, from which finally pyrroles **4** and $W(CO)_6$ are obtained as the only products.

Scheme 5. Organometallic intermediates en route to dihydropyrroles **4**



	yield [%]		yield [%]
3a	11	**3b**	20
4a	48	**4b**	35
6a	30	**6b**	13
7a	–	**7b**	4

Cross-Conjugated Azametallatrienes 6

Since the signal of the W=C group in the ^{13}C-NMR spectra of compounds **6** (**6a**: δ = 321.8; **6b**: δ = 321.2) is observed in a range typical of non-conjugated (carbene)-tungsten complexes, e.g. $(CO)_5W{=}\mathit{C}(OEt)Me$ (δ = 319.6), little or no π-conjugation is expected within the W=C−C=C moiety. Furthermore, π-conjugation is not expected to be effective within the C=C−C=N group, since the *C*=N signal (**6a**: δ = 157.9; **6b**: δ = 157.8) appears in the normal range. Strong distortion from planarity of the W=C−C=C as well as of the C=C−C=N unit [W−C1−C2−C3 −109.0(3), N28−C21−C2−C3 −94.0(4)°] is confirmed by an X-ray structure analysis of compound **6a** (Figure 3, Table 3). It should be noted that the structural features of the M=C−C(=C)−C=N backbone in compound **6a** are unique and different from that of other cross-conjugated azametallatrienes, e.g. $(CO)_5W{=}C(OEt){-}C({=}CHNC_4H_8){-}C(Ph){=}NPh$,[15] in which partial planarisation of the $(CO)_5W{=}C{-}C{=}C(N)$ portion of the ligand is achieved by π-electron delocalization. Rapid equilibration of diastereomers by rotation about the C1−C2 bond of **6a** is indicated by dynamic line-broadening of the ^{1}H-NMR signals of the diastereotopic OCH_2 group at 20°C.

Figure 3. Molecular structure of the cross-conjugated azametallatriene **6a**

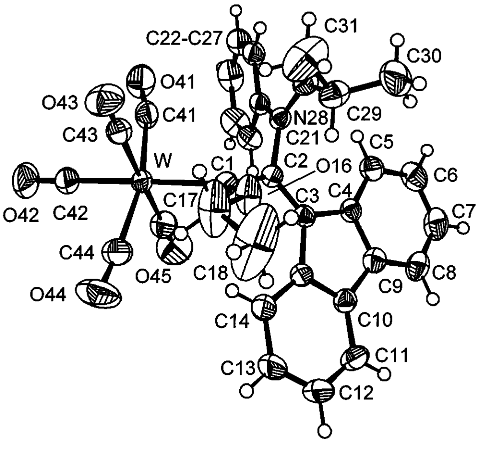


Table 3. Selected bond lengths [Å] and angles [°] for cross-conjugated azametallatriene **6a**

W−C(1)	2.180(3)	O(16)−C(1)−W	130.0(2)
C(1)−O(16)	1.309(4)	C(2)−C(1)−W	125.3(2)
C(1)−C(2)	1.504(4)	C(3)−C(2)−C(1)	123.2(2)
C(2)−C(3)	1.351(4)	C(3)−C(2)−C(21)	123.0(2)
C(2)−C(21)	1.520(4)	C(1)−C(2)−C(21)	113.7(2)
C(21)−N(28)	1.270(4)	N(28)−C(21)−C(22)	117.7(2)
C(21)−C(22)	1.493(4)	N(28)−C(21)−C(2)	124.0(2)
N(28)−C(29)	1.474(4)	C(22)−C(21)−C(2)	118.3(2)
C(29)−C(31)	1.519(6)	C(21)−N(28)−C(29)	122.5(3)
C(29)−C(30)	1.521(5)	N(28)−C(29)−C(31)	108.3(3)
O(16)−C(17)	1.459(4)	N(28)−C(29)−C(30)	107.1(3)
C(17)−C(18B)	1.43(2)	C(31)−C(29)−C(30)	112.6(4)
C(17)−C(18A)	1.45(2)	C(1)−O(16)−C(17)	123.3(3)
		C(18B)−C(17)−O(16)	111.4(12)
O(16)−C(1)−C(2)	104.7(2)	C(18A)−C(17)−O(16)	106.5(11)

Structural characterization of compound **7b** is based on NMR spectra. The sets of ^{13}C- and ^{1}H-NMR signals of dihydropyrrole **4b** and its pentacarbonyltungsten derivative **7b** are quite similar. Characteristic downfield shifts are observed for the signals *C*=N (**4b**: δ = 170.2; **7b**: δ = 179.2) and *C*−N (**4b**: δ = 77.1; **7b**: δ = 83.3).

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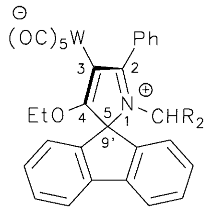
Experimental Section

All operations were performed under argon. Dried solvents were used in all experiments. − Melting points are not corrected. − Instrumentation: ^{1}H- and ^{13}C-NMR spectra were obtained with Bruker WM 300, WP 360 and Varian U 600 spectrometers (multiplicities were determined by DEPT. Chemical shifts refer to δ_{TMS} = 0.00. ^{13}C shifts were assigned on the basis of ^{1}J(CH) and $^{2,3}J$(CH) correlation experiments). Low-temperature NMR measurements were carried out with Bruker AM 360 instrument. − Other analyses: IR Diglab FTS 45; MS Finnigan MAT 312; elemental analysis, Perkin-Elmer 240 elemental analyzer; TLC, Merck DC-Alufolien Kieselgel 60 F_{254}. R_f values refer to TLC tests. − Column-chromatographic purifications were made on Merck Kieselgel 100.

(Fluoren-9-ylidene)alkylamine (**2**) was obtained in high yields by condensation of 9-fluorenone (1.80 g, 10 mmol) with the corresponding amine (10 mmol) in 30 ml of pentane and 15 g of molecular sieves (Acros, 4 Å) at 20°C, 24 h, and were purified by distillation prior to use.

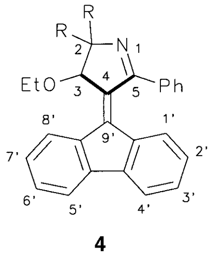
Pentacarbonyl[5-(2,2′-biphenylene)-4-ethoxy-1-isopropyl-2-phenyl-1-azoniacyclopenta-1,3-dien-3-yl]tungstate (**3a**), *3-Ethoxy-4-(fluoren-9-ylidene)-2,2-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrole* (**4a**), *Pentacarbonyl[1-ethoxy-2-(fluoren-9-ylidene)-3-(isopropylimino)-3-phenylprop-1-ylidene]tungsten* (**6a**): To pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg 1.00 mmol) in a 3-ml screw-top vessel is added (fluoren-9-ylidene)isopropylamine (**2a**) (221 mg, 1.00 mmol) in 3 ml of toluene. The mixture is shaken until homogeneity (ca. 3 min). After ca. 5 min at 20°C, a dark oil begins to precipitate which consists of compound **3a** and $W(CO)_6$. After compound **1a** is consumed completely (ca. 2 d at 20°C according to TLC), the supernatant is decanted and the solid washed with *n*-pentane (3 × 1 ml). The solution is separated by chromatography on silica gel. Elution with pentane/dichloromethane (2:1) affords a brown fraction with compound **6a** (R_f = 0.4 in pentane/dichloromethane, 2:1, 215 mg, 30%, brown crystals from pentane at −40°C, mp 102°C). Elution with diethyl ether affords a yellow fraction of compound **4a** (180 mg, 48%, R_f = 0.8 in diethyl ether, yellow crystals from cyclohexane/dichloromethane (4:1) at −78°C, mp 106°C). The solid residue of the reaction mixture (ca. 240 mg) is dissolved in dichloromethane (ca. 3 ml). $W(CO)_6$ is removed by crystalization at −15°C and compound **3a** is obtained from the mother liquor at 20°C after addition of pentane (2 ml) (ca. 78 mg, 11%, amber-colored crystals). If **1a** (52 mg, 0.11 mmol) and **2a** (22 mg, 0.10 mmol) in 1 ml of C_6D_6 are heated to 90°C for 2 h the ^{1}H-NMR spectrum of the solution shows signals of compounds **4a** and **3a** in a molar ratio of 8:1 as the only products. Removal of the solvent gives a residue of 39 mg, which corresponds to 82% of compound **4a** and 11% of compound **3a**.

3a: ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.33, 7.26 and 7.18 (2:2:1 H; "d", "t", "t"; Ph), 7.30 (2 H, d, 4′-H and 5′-H), 7.10 (2 H, t, 3′-H and 6′-H), 7.05 (2 H, d, 1′-H and 8′-H), 6.95 (2 H, t, 2′-H and 7′-H), 3.29 and 0.70 (2:3 H; q and t, OCH_2CH_3), 2.73 (1 H, quint, NCH), 0.18 [6 H, d, $CH(CH_3)_2$]. − ^{13}C NMR (C_6D_6): δ = 204.8 and 201.8 [1:4, C_q each, *cis*- and *trans*-CO $W(CO)_5$], 198.2 (C_q, C2), 187.9 (C_q, C3), 142.8 (2 C_q, C8a′ and C9a′), 137.3 (2 C_q, C4a′ and C4aa′), 136.0 (C_q, *i*-C Ph), 135.8 (C_q, C4), 130.9 (2 CH, C2′ and C7′), 130.3 (*p*-CH Ph), 129.8 (2 CH, C3′ and C6′), 128.1 (2 *m*-CH Ph), 127.8 (2 *o*-CH Ph), 124.5 (2 CH, C1′ and C8′), 121.6 (2 CH, C4′ and C5′), 84.2 (C_q, C5 ≡ C9′), 65.9 (OCH_2), 50.8 (NCH), 22.4 [$C(CH_3)_2$], 14.8 (OCH_2CH_3). − IR (diffuse reflection): ṽ [cm^{-1} (%)] = 2048.5 (30), 1975.0 (10), 1950.4 (20), 1895.2 (100), 1858.5 (80) [ν(C≡O)]. − $C_{32}H_{25}NO_6W$ (703.4): calcd. C 54.64, H 3.58, N 1.99; found C 54.61, H 3.69, N 2.05.



3

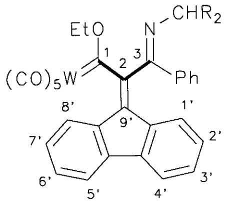
4a: ^1H NMR (C_6D_6, 600 MHz): δ = 8.49 (1 H, d, ^3J = 7.7 Hz, 8′-H), 7.85 and 7.04 (2:3 H, broad each, Ph), 7.45 (1 H, d, ^3J = 7.4 Hz, 1′-H), 7.35 (1 H, d, ^3J = 7.5 Hz, 5′-H), 6.87 (1 H, d, ^3J = 7.9 Hz, 4′-H); 7.24, 7.18, 7.08, and 6.90 (1 H each, t each, 2′-H, 3′-H, 6′-H and 7′-H), 5.07 (1 H, s, 3-H), 3.52 and 3.34 (1:1 H, m each, OCH_2), 1.68 and 1.12 [3:3 H, s each, $C(CH_3)_2$], 1.02 (3 H, t, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 170.2 (C_q, C=N, C5), 141.9 and 141.8 (C_q each, C4 and C9′), 140.4 (C_q, C8a′), 140.1 (C_q, C9a′), 138.4 (C_q, C4aa′), 136.6 (C_q, C4a′), 136.3 (C_q, *i*-C Ph); 130.1 (2 C), 129.7, 129.2, 128.9, 128.8 (2 C, broad), 128.1 (2 C), 126.64, 126.63, 119.9 and 119.6 (CH each, fluorene and Ph), 90.6 (CH, C3), 74.4 (C_q, C2), 62.3 (OCH_2), 27.8 and 22.9 [$C(CH_3)_2$], 15.8 (OCH_2CH_3). − MS (70 eV); *m/z* (%): 379 (100) [M^+], 350 (30) [M^+ − Et], 332 (5), 322 (5), 265 (70) [M^+ − $NCMe_2$ − HCOEt], 215 (5), 165 (10) [fluorenyl], 146 (10), 104 (50), 58 (15). − $C_{27}H_{25}NO$ (379.5): calcd. C 85.45, H 6.64, N 3.69; found C 85.53, H 6.55, N 3.85.



4

X-ray Crystal Structure Analysis of **4a**:[16] Formula $C_{27}H_{25}NO$, M = 379.48, 0.30 × 0.20 × 0.20 mm, a = 14.371(4), b = 8.989(1), c = 16.259(4) Å, β = 92.12(2)°, V = 2098.9(8) Å^3, $\rho_{calcd.}$ = 1.201 g cm^{-3}, μ = 0.72 cm^{-1}, empirical absorption correction with φ-scan data (0.975 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 293 K, ω/2θ scans, 4422 reflections collected (+h, −k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4248 independent and 1858 observed reflections [$I \geq 2\,\sigma(I)$], 265 refined parameters, R = 0.048, wR^2 = 0.093, max. residual electron density 0.19 (−0.23) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[17]

6a: ^1H NMR (C_6D_6): δ = 8.40 (2 H, s broad, *o*-H Ph); 7.71, 7.56, 7.39 and 7.29 (1 H each, "d" each; 1′-H, 4′-H, 5′-H and 8′-H); 7.16, 7.10, 6.89 and 6.59 (1 H each, "t" each; 2′-H, 3′-H, 6′-H and 7′-H), 7.00 (3 H, m broad, *m*- and *p*-H Ph), 4.81 (1 H, sept, NCH), 4.78 and 4.26 (1 H each, m broad each, OCH_2), 1.19 and 1.17 [6 H, d, $C(CH_3)_2$], 1.03 (3 H, t, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 321.8 (C_q, W=C), 203.4 and 196.8 [1:4, C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 157.9 (C_q, C=N, C3), 152.2 (C_q, C9′); 144.6, 142.3, 141.8, 137.7, 137.0, and 134.7 (C_q each, C2, C4a′, C4aa′, C8a′, C9a′, and *i*-C Ph); 130.8, 129.9 (2 C), 129.7, 129.5, 128.7 (2 C), 127.8, 127.3, 127.0, 126.9, 120.5, and 120.1 (CH each, fluorene and Ph), 81.2 (OCH_2), 53.8 (NCH), 25.5 and 24.1 [$C(CH_3)_2$], 13.6 (OCH_2CH_3). − IR (hexane): ṽ [cm^{-1} (%)] = 2072.0 (35), 1994.7 (10), 1964.8 (60), 1945.0 (100) [ν(C≡O)]. − MS (70 eV); *m/z* ^{184}W (%): 703 (1) [M^+], 647 (1) [M^+ − 2 CO], 619 (3) [M^+ − 3 CO], 563 (2) [M^+ − 5 CO], 504 (2), 463 (2), 379 (100) [M^+ − $W(CO)_5$], 350 (35), 322 (6), 265 (65), 180 (10), 165 (25), 111 (15), 104 (75), 83 (35), 71 (55), 57 (80). − $C_{32}H_{25}NO_6W$ (703.4): calcd. C 54.64, H 3.58, N 1.99; found C 54.63, H 3.70, N 2.00.



6

X-ray Crystal Structure Analysis of **6a**:[16] Formula $C_{32}H_{25}NO_6W$, M = 703.38, 0.30 × 0.30 × 0.10 mm, a = 9.962(2), b = 12.281(2), c = 12.929(2) Å, α = 88.20(1), β = 85.64(2), γ = 66.31(1)°, V = 1444.3(4) Å^3, $\rho_{calcd.}$ = 1.617 g cm^{-3}, μ = 40.43 cm^{-1}, empirical absorption correction with φ-scan data (0.788 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 293 K, ω/2θ scans, 6134 reflections collected (±h, ±k, +l), [(sinθ)/λ] = 0.62 Å^{-1}, 5861 independent and 5338 observed reflections [$I \geq 2\,\sigma(I)$], 375 refined parameters, R = 0.020, wR^2 = 0.052, max. residual electron density 1.02 (−0.90) e Å^{-3}, C18 refined as splitted atom, hydrogen atoms calculated and refined as riding atoms.[17]

Pentacarbonyl[5-(2,2′-biphenylene)-1-cyclohexyl-4-ethoxy-2-phenyl-1-azoniacyclopenta-1,3-dien-3-yl]tungstate (**3b**), *3-Ethoxy-4-(fluoren-9-ylidene)-2-pentamethylene-5-phenyl-3,4-dihydro-2H-pyrrole* (**4b**), *Pentacarbonyl[1-ethoxy-3-cyclohexylimino-2-(fluoren-9-ylidene)-3-phenylprop-1-ylidene]tungsten* (**6b**), *Pentacarbonyl[3-ethoxy-4-(fluoren-9-ylidene)-2-pentamethylene-5-phenyl-3,4-dihydro-2H-pyrrole]tungsten* (**7b**): To pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) in a 3-ml screw-top vessel is added fluoren-9-ylidenecyclohexylamine (**2b**) (260 mg, 1.00 mmol) in 2.5 ml of pentane. The mixture is shaken until it becomes homogeneous. After ca. 1−2 h at 20°C, a dark precipitate begins to form consisting of compound **3b** and $W(CO)_6$. After ca. 2−3 d at 20°C (TLC), the reaction is almost complete. The supernatant is decanted and the solid residue washed with toluene (3 × 1 ml). Pentane and toluene extracts are combined, brought to dryness (20°C, 10 Torr) and separated by chromatography on silica gel with pentane/dichloromethane (2:1) to give successively a small amount of red compound **7b** (R_f = 0.6 in pentane/dichloromethane, 2:1, 30 mg, 4%), the brown compound **6b** (R_f = 0.4 in pentane/dichloromethane 2:1, 100 mg, 13%, brown crystals from pentane at −40°C). Elution with diethyl ether affords yellow product **4b** (131 mg, 35%, R_f = 0.3 in pentane/diethyl ether (10:1), yellow crystals from toluene/pentane 1:1 at −15°C, mp 172°C). The solid residue of the reaction mixture (ca. 260 mg) is dissolved in dichloromethane (ca. 3 ml). $W(CO)_6$ is removed by crystalization at −15°C and compound **3b** is obtained from the mother liquor at 20°C after addition of pentane (2 ml) (ca. 150 mg, 20%, amber-colored crystals). If **1a** (52 mg, 0.11 mmol) and **2b** (26 mg, 0.10 mmol) in 1 ml of C_6D_6 are heated to 90°C for 2 h the ^{1}H-NMR spectrum of the solution shows signals of compounds **4b** and **3b** in a molar ratio of ca. 3.5:1 as the only detectable products. Removal of the solvent and of $W(CO)_6$ leaves a residue of 44 mg, which corresponds to 69% of the pyrrol derivative **4b** and 20% of compound **3b**.

3b: ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.38, 7.30, and 7.22 (2:2:1 H; d, t, t; Ph), 7.36 (2 H, d, 4′-H and 5′-H), 6.99 (2 H, t, 3′-H and 6′-H), 7.15 (2 H, t, 2′-H and 7′-H), 7.10 (2 H, d, 1′-H and 8′-H), 3.30 and 0.70 (2:3 H; q and t, OCH_2CH_3), 2.50 (1 H, m, NCH); 0.98, 0.90, 0.80, 0.75, and 0.11 (2 H each, CH_2 cyclohexyl). − ^{13}C NMR (C_6D_6): δ = 204.8 and 201.0 [1:4, C_q each, *cis*- and *trans*-CO $W(CO)_5$], 197.3 (C_q, C2), 187.1 (C_q, C3), 142.1 (2 C_q, C8a′ and C9a′), 136.5 (2 C_q, C4a′ and C4aa′), 135.6 (C_q, *i*-C Ph), 134.3 (C_q, C4), 130.5 (2 CH, C2′ and C7′), 129.7 (*p*-CH Ph), 129.0 (2 CH, C3′ and C6′), 127.9 (2 *m*-CH Ph), 127.2 (2 *o*-CH Ph), 124.0 (2 CH, C1′ and C8′), 121.1 (2 CH, C4′ and C5′), 83.6 (C_q, C5 ≡ C9′), 65.2 (OCH_2), 59.6 (NCH); 32.9, 25.7, 24.2 (2:2:1, CH_2 each, cyclohexyl), 14.3 (OCH_2CH_3). − IR (diffuse reflection): $\tilde{\nu}$ [cm^{-1} (%)] = 2048.3 (30), 1975.1 (10), 1950.7 (20), 1895.3 (100), 1858.9 (80) [ν(C≡O)]. − MS (70 eV); *m/z* ^{184}W (%): 743 (1) [M^+], 687 (1) [M^+ − 2 CO], 659 (3) [M^+ − 3 CO], 603 (2) [M^+ − 5 CO], 391 (60), 308 (100). − $C_{35}H_{29}NO_6W$ (743.5): calcd. C 56.54, H 3.93, N 1.88; found C 56.33, H 3.71, N 1.97.

4b: ^{1}H NMR (C_6D_6, 600 MHz): δ = 8.56 (1 H, d, ^3J = 7.4 Hz, 8′-H), 7.90 and 7.10 (2:3 H, broad each, Ph), 7.45 (1 H, d, 1′-H), 7.35 (1 H, d, 5′-H); 7.25, 7.16, 7.04, and 6.90 (1 H each, t each, 2′-H, 3′-H, 6′-H, and 7′-H), 6.63 (1 H, d, ^3J = 7.9 Hz, 4′-H), 5.29 (1 H, s, 3-H), 3.52 and 3.38 (1:1 H, m each, OCH_2); 2.15, 1.72, 1.50, 1.31 (2:2:2:2, CH_2 each, cyclohexyl), 1.03 (3 H, t, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 170.2 (C_q, C=N, C5), 141.9 and 141.8 (C_q each, C4 and C9′), 140.7 (C_q, C8a′), 140.3 (C_q, C9a′), 138.3 (C_q, C4aa′), 136.8 (C_q, C4a′), 136.2 (C_q, *i*-C Ph); 130.0, 129.7, 129.2, 128.9 (2 C), 128.8 (2 C, broad), 128.1 (2 C), 126.6, 126.5, 119.9, and 119.6 (CH each, fluorene and Ph), 88.9 (CH, C3), 77.1 (C_q, C2), 62.1 (OCH_2); 37.4, 32.2, 26.3, 24.4, 23.4 (CH_2 each, cyclohexyl), 15.9 (OCH_2CH_3). − MS (70 eV); *m/z* (%): 419 (100) [M^+], 390 (30) [M^+ − Et], 265 (70), 165 (10) [fluorenyl], 146 (10), 104 (30). − $C_{30}H_{29}NO$ (419.6): calcd. C 85.88, H 6.97, N 3.34; found C 85.59, H 6.85, N 3.45.

6b: ^{1}H NMR (C_6D_6): δ = 8.40 (2 H, s broad, *o*-H Ph); 7.70, 7.52, 7.40, and 7.26 (1 H each, "d" each; 1′-H, 4′-H, 5′-H, and 8′-H); 7.13, 7.10, 6.80, and 6.54 (1 H each, "t" each; 2′-H, 3′-H, 6′-H, and 7′-H), 7.05 (3 H, m broad, *m*- and *p*-H Ph), 4.82 (1 H, "t", NCH), 4.78 and 3.95 (1 H each, m broad each, OCH_2), 1.80 and 1.20 (5 H each, m each broad, cyclohexyl), 0.87 (3 H, t, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 321.2 (C_q, W=C), 202.2 and 196.9 [1:4, C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 157.8 (C_q, C=N, C3), 152.5 (C_q, C9′); 141.9, 141.5, 137.7, 137.1, 136.3, and 132.4 (C_q each, C2, C4a′, C4aa′, C8a′, C9a′, and *i*-C Ph); 130.8, 129.9 (2 C), 129.7, 129.5, 128.7 (2 C), 127.8, 127.3, 127.0, 126.9, 120.5, and 120.1 (CH each, fluorene and Ph), 80.6 (OCH_2), 61.9 (NCH); 33.9, 26.1, 24.5, 24.3, and 22.7 (CH_2 each, cyclohexyl), 13.9 (OCH_2CH_3). − IR (hexane): $\tilde{\nu}$ [cm^{-1} (%)] = 2071.9 (30), 1994.4 (10), 1964.7 (60), 1945.3 (100) [ν(C≡O)]. − MS (70 eV); *m/z* ^{184}W (%): 743 (1) [M^+], 715 (1) [M^+ − CO], 659 (1) [M^+ − 3 CO], 603 (1) [M^+ − 5 CO], 419 (100) [M^+ − $W(CO)_5$], 390 (60), 265 (60).

7b: ^{1}H NMR (C_6D_6, 600 MHz): δ = 8.70 (1 H, d, ^3J = 7.4 Hz, 8′-H), 7.98 and 7.15 (2:3 H, broad each, Ph), 7.22 (1 H, d, 5′-H), 7.12 (1 H, d, 1′-H), 7.08 (1 H, dd, 6′-H), 7.05 (1 H, dd, 7′-H), 6.84 (1 H, dd, 2′-H), 6.46 (1 H, dd, 3′-H), 6.16 (1 H, d, 4′-H), 5.46 (1 H, s, 3-H), 3.46 and 3.37 (1:1 H, m each, OCH_2); 2.78, 2.47, 1.84, 1.80, 1.56, 1.44, 1.42, 1.24, 1.15, 1.10, and 1.02 (1 H each, m each, cyclohexyl), 1.03 (3 H, t, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 201.8 and 198.8 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 179.2 (C_q, C=N, C5), 147.3 and 142.3 (C_q each, C4 and C9′), 142,2 (C_q, C9a′), 140.0 (C_q, C8a′), 108.7 (C_q, C4aa′), 137.6 (C_q, C4a′), 136.0 (C_q, *i*-C Ph); 131.5, 131.0, 130.1, 128.2, 128.5, 128.3, 127.7, 126.8, 120.0 (CH each, fluorene); 129.8, 129.0 and 128.3 (CH each broad, Ph), 83.2 (C_q, C2), 82.7 (CH, C3), 61.1 (OCH_2); 36.6, 35.4, 25.3, 24.4, 24.2 (CH_2 each, cyclohexyl), 15.5 (OCH_2CH_3). − IR (hexane): $\tilde{\nu}$ [cm^{-1} (%)] = 2063.7 (30), 1982.6 (10), 1928.2 (100), 1914.2 (60) [ν(C≡O)]. − MS (70 eV); *m/z* ^{184}W (%): 743 (10) [M^+], 715 (40) [M^+ − CO], 659 (50) [M^+ − 3 CO], 603 (40) [M^+ − 5 CO], 543 (100), 419 (80) [M^+ − $W(CO)_5$], 390 (60), 265 (60).

X-ray Crystal Structure Analysis of **3b**:[16] Formula $C_{35}H_{29}NO_6W$, M = 743.47, 0.50 × 0.30 × 0.10 mm, a = 9.626(2), b = 16.259(3), c = 19.291(3) Å, β = 91.51(1)°, V = 3018.2(10) Å^3, $\rho_{calcd.}$ = 1.636 g cm^{-3}, μ = 38.75 cm^{-1}, empirical absorption correction via φ-scan data (0.684 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 6296 reflections collected (±h, −k, −l), [(sinθ)/λ] = 0.62 Å^{-1}, 6110 independent and 5305 observed reflections [$I \geq 2\,\sigma(I)$], 389 refined parameters, R = 0.031, wR^2 = 0.083, max. residual electron density 1.54 (−2.24) e Å^{-3} close to tungsten, hydrogen atoms calculated and refined as riding atoms.[17]

3-(2,2′-Biphenylene)-1-isopropyl-5-phenyl-1,2-dihydropyrrol-3-one (**5a**): Pentacarbonyl[1-isopropyl-4-ethoxy-2-phenyl-1-azoniacyclopenta-1,3-dien-3-yl]tungstate (**3a**) (70 mg, 0.10 mmol) in $CHCl_3$ (1 ml) is treated with water (1.8 mg, 0.01 mmol) for 6 h at 20°C. Evaporation of the solvent leaves compound **5a** together with $W(CO)_6$. − ^{1}H NMR (C_6D_6): δ = 7.46 (2 H, d, 4′-H and 5′-H), 7.35 (2 H, d, 1′-H and 8′-H), 7.26 (2 H, "t", *m*-H Ph), 7.17 and 7.08 (2 H each, dd each; 2′-H, 3′-H, 6′-H, and 7′-H), 7.09 (3 H, *o*- and *p*-H Ph), 5.40 (1 H, s, 4-H), 3.41 (1 H, m, NCH), 0.50 [6 H, d, $CH(CH_3)_2$]. − ^{13}C NMR (C_6D_6): δ = 195.5 (C_q, C=O), 179.3 (C_q, C5), 143.9 (2 C_q, C8a′ and C9a′), 142.5 (2 C_q, C4a′ and C4aa′), 133.6 (C_q, *i*-C Ph); 129.6, 128.9, and 128.6 (CH each, 1:2:2, Ph), 124.2 (2 CH, C2′ and C7′), 120.8 (2 CH, C3′ and C6′), 101.1 (CH, C4), 82.3 (C_q, C2 ≡ C9′), 49.7 (NCH), 23.1 [$C(CH_3)_2$]. − IR (diffuse reflection): $\tilde{\nu}$ [cm^{-1} (%)] = 1675.5 (100) [ν(C=O)].

3-(2,2′-Biphenylene)-1-cyclohexyl-5-phenyl-1,2-dihydropyrrol-3-one (**5b**): Pentacarbonyl[1-cyclohexyl-4-ethoxy-2-phenyl-1-azoniacyclopenta-1,3-dien-3-yl]tungstate (**3b**) (74 mg, 0.10 mmol) in $CHCl_3$ (1 ml) is treated with water (1.8 mg, 0.10 mmol) for 6 h at 20°C. Evaporation of the solvent leaves compound **5b** together with $W(CO)_6$. − ^{1}H NMR (C_6D_6): δ = 7.52 (2 H, d, 4′-H and 5′-H), 7.40 (2 H, d, 1′-H and 8′-H), 7.31 (2 H, "d", *o*-H Ph), 7.19 and 7.09 (2 H each, dd each; 2′-H, 3′-H, 6′-H and 7′-H), 7.15 and 7.12 (2:1 H, *m*- and *p*-H Ph), 5.41 (1 H, s, 4-H), 3.29 (1 H, m, NCH); 1.40, 1.00, 0.85, 0.42, and 0.21 (3:3:2:1:1, CH_2 cyclohexyl). − ^{13}C NMR (C_6D_6): δ = 195.5 (C_q, C=O), 179.4 (C_q, C5), 144.1 (2 C_q, C8a′ and C9a′), 142.4 (2 C_q, C4a′ and C4aa′), 133.6 (C_q, *i*-C Ph); 129.6, 128.9, and 128.6 (CH each, 1:2:2, Ph), 124.4 (2 CH, C2′ and C7′), 120.9 (2 CH, C3′ and C6′), 100.6 (CH, C4), 82.2 (C_q, C2 ≡ C9′), 58.9 (NCH); 34.2, 26.2, and 25.0 (CH_2 each, 2:2:1, cyclohexyl). − IR (diffuse reflection): $\tilde{\nu}$ [cm^{-1} (%)] = 1676.1 (100) [ν(C=O)].

☆ Dedicated to Professor *E. O. Fischer* on the occasion of his 80th birthday

[1] Part XCVI: R. Aumann, Z. Yu, R. Fröhlich, *Organometallics* **1998**, *117*, 2897.

[2] E. O. Fischer, H. Hollfelder, F.R. Kreissl, W. Uedelhoven, *J. Organomet. Chem.* **1976**, *113*, C31.

[3] L. S. Hegedus, M. A.. McGuire, L. M. Schultze, Y. Chen, O. P. Anderson, *J. Am. Chem. Soc.* **1984**, *106*, 2680.

[4] F. Funke, M. Duetsch, F. Stein, M. Noltemeyer, A. de Meijere, *Chem. Ber.* **1994**, *127*, 911.

[5] R. Aumann, R. Fröhlich, F. Zippel, *Organometallics* **1997**, *16*, 2571.

[6] [6a] J. Barluenga, M. Tomás, J. A. López-Pelegrín, E. Rubio, *Tetrahedron Lett.* **1997**, *38*, 3981. − [6b] R. Aumann, Z. Yu, see ref. [142] in ref.[14]. − [6c] R. Aumann, Z. Yu, R. Fröhlich, *J. Organomet. Chem.* **1997**, *549*, 311.

[7] J. Barluenga, M. Tomás, E. Rubio, J.A. López-Pelegrín, S. García-Granda, P. Pertierra, *J. Am. Chem. Soc.* **1996**, *118*, 695.

[8] R. Aumann, B. Hildmann, R. Fröhlich, *Organometallics* **1998**, *17*, 1197.

[9] [9a] R. Aumann, K. Roths, M. Grehl, *Synlett* **1993**, 669. − [9b] R. Aumann, M. Kößmeier, K. Roths, R. Fröhlich, *Synlett* **1994**, 1041. − [9c] R. Aumann, K. Roths, M. Läge, B. Krebs, *Synlett* **1993**, 667. − [9d] A. G. Meyer, R. Aumann, *Synlett* **1995**, 1011. − [9e] R. Aumann, A. G. Meyer, R. Fröhlich, *Organometallics* **1996**, *15*, 5018. − [9f] R. Aumann, M. Kößmeier, F. Zippel, *Synlett* **1997**, 621.

[10] R. Aumann, K. Roths, R. Fröhlich, *Organometallics* **1997**, *16*, 5893.

[11] For a review see, e.g.: [11a] Y. Noël, *Bull. Soc. Chim. Fr.* **1964**, *5*, 173. − [11b] F. H. Stewart, *Chem. Rev.* **1964**, *64*, 129.

[12] C. P. Casey, T. J. Burkhardt, C. A. Bunnell, J. C. Calabrese, *J. Am. Chem. Soc.* **1977**, *99*, 2127.

[13] R. Aumann, K. Roths, B. Jasper, R. Fröhlich, *Organometallics* **1996**, *15*, 1257.

[14] See, e.g., review: R. Aumann, H. Nienaber, *Adv. Organomet. Chem.* **1997**, *41*, 163.

[15] R. Aumann, B. Jasper, R. Fröhlich, *Organometallics* **1995**, *14*, 3167.

[16] Data sets were collected with an Enraf Nonius CAD4 diffractometer using an FR591 rotating anode generator. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics DIAMOND.

[17] Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge by quoting the depository numbers CCDC-102622, -102623 and -102624, the names of the authors, and the journal citation on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int code + 44-12238 336-033, e-mail: deposit@ccdc.cam.ac.uk].

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