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Addition of *N*-aryl imines to alkyne(pentacarbonyl)chromium and tungsten — a novel route to alkenyl(amino)carbene complexes

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Dedicated to Professor Dirk Walther on the occasion of his 60th birthday.

Abstract

Photolysis of $[M(CO)_6]$ in CH_2Cl_2 gives $[(CO)_5M(CH_2Cl_2)]$ (M = Cr, W). Replacement of CH_2Cl_2 by arylacetylene, $HC{\equiv}CC_6H_4R$-*p* (R = Me, H, Br), produces the thermolabile arylacetylene complexes $[(CO)_5M(HC{\equiv}CC_6H_4R\text{-}p)]$. Addition of *N*-phenyl benzylideneimines, $PhN{=}C(C_6H_4R'\text{-}p)H$ (R′ = Me, H, Cl), to solutions of these alkyne complexes affords alkenyl(amino)carbene complexes, $[(CO)_5M{=}C(NPhH)C(C_6H_4R\text{-}p){=}C(C_6H_4R'\text{-}p)H]$, and 2-azetidin-1-ylidene complexes, $[(CO)_5M{=}\overline{C{-}NPh{-}C(C_6H_4R'\text{-}p)H{-}C}(C_6H_4R\text{-}p)H]$. The formation of the alkenyl(amino)carbene complexes is favored. The ratio alkenyl(amino)carbene/2-azetidin-1-ylidene complex is 2.5–3 for M = W and 6.5–8 for M = Cr. Both types of complexes are obtained as mixtures of isomers. The 2-azetidin-1-ylidene complexes are very likely formed by cycloaddition of the imines to the C=C bond of vinylidene complexes resulting from tautomerization of the alkyne complexes. The cycloaddition is highly stereoselective. Predominantly, the *syn* isomer is obtained (*syn*/*anti* ≥ 9). In contrast, the alkenyl(amino)carbene complexes are presumably derived from the alkyne complexes via cycloaddition of the imines to the coordinated alkyne and subsequent 1,2-hydrogen shift and ring opening. Preferentially, the *E* isomers (where both aryl substituents are *cis* with respect to the C=C bond) are produced. The structure of the major isomer of the alkenyl(amino)carbene complex $[(CO)_5W{=}C(NPhH)C(C_6H_4Me\text{-}p){=}C(Ph)H]$ has been established by X-ray structural analysis.

Keywords: *N*-aryl imines; Alkyne(pentacarbonyl)chromium; Alkyne(pentacarbonyl)tungsten

1. Introduction

Vinylidene complexes may be regarded as organometallic analogues of ketenes. Ketenes react with imines by cycloaddition to afford β-lactams [1]. Analogously, several vinylidene complexes have been shown to readily add imines to the C=C bond to form four-membered transition-metal-substituted *N*-heterocycles (Scheme 1). Examples include the formation of 2-azetidin-1-ylidene complexes from $[Cp(CO)(L)Fe{=}C{=}CR_2]^+$ [L = $P(OMe)_3$, PPh_3; R = H, Me] and MeN=C(H)aryl or thiazolines [2,3], from vinylidene complexes of manganese and rhenium and imines [4], and from $[(CO)_5W{=}C{=}CPh_2]$ and imines [5]. In general, oxidative decomplexation of the four-membered ring yields β-lactams in moderate to good yields. A vinylidene complex, $[(CO)_5Cr{=}C{=}CH_2]$, was also proposed as an intermediate in the reactions of pentacarbonyl[hydroxy(methyl)carbene]chromium with dicyclohexyl carbodiimide [6] and of tetramethylammonium acetyl(pentacarbonyl)chromate toluene-4-sulfonyl chloride/imines [2,7], to give 2-azetidin-1-ylidene complexes (Scheme 1).

Usually, the vinylidene complexes are generated either from carbyne complexes, from acyl complexes or from carbene complexes.

Recently, we observed that reactions of photochemically generated $[(CO)_5M(CH_2Cl_2)]$ with phenylacetylene and *N*-alkyl imines [8] also afforded 2-azetidin-1-yli-

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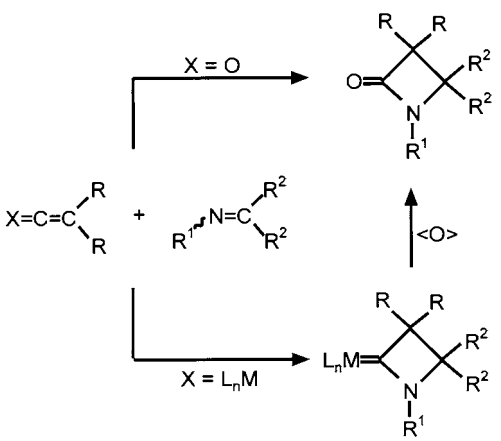
dene complexes and we proposed the following sequence: (a) substitution of phenylacetylene for coordinated CH_2Cl_2; (b) tautomerization of the resulting alkyne complexes $[(CO)_5M(HC{\equiv}CPh)]$ to give the corresponding vinylidene complexes $[(CO)_5M{=}C{=}C(Ph)H]$; which (c) are then trapped by the imine as 2-azetidin-1-ylidene complexes.

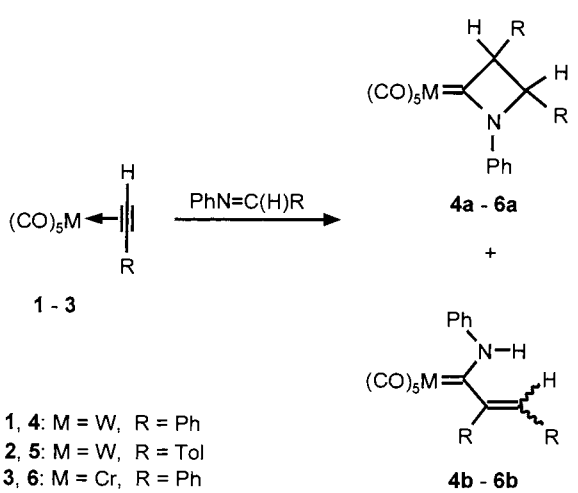
We now report that the corresponding reactions of $[(CO)_5M(CH_2Cl_2)]$ with arylacetylene and *N*-aryl imines essentially take a different course giving rise to the formation of alkenyl(amino)carbene complexes.

2. Results and discussion

Addition of arylacetylenes at −80°C to solutions of $[(CO)_5M(CH_2Cl_2)]$ freshly prepared by irradiation of the metal hexacarbonyls $[M(CO)_6]$ in dichloromethane at −85°C afforded the arylacetylene(pentacarbonyl) complexes **1**–**3** via replacement of the coordinated dichloromethane by alkynes (Scheme 2). Subsequent reaction of **1**–**3** with two equivalents of *N*-phenyl benzylideneimine and *N*-phenyl *p*-methylbenzylideneimine, respectively, yielded isomeric mixtures of the (expected) 2-azetidin-1-ylidene complexes **4a**–**6a** and the (rather unexpected) alkenyl(amino)carbene complexes **4b**–**6b** (Scheme 2). Independent of the substituent and the metal, predominantly the alkenyl(amino)carbene complexes were formed. Within error limits, the yield ratios **4b**/**4a** and **5b**/**5a** were the same (about 2.5). However, substitution of chromium for tungsten more strongly favored the formation of the alkenyl(amino)carbene complex (**6b**/**6a** = 6.5).



Scheme 1.



Scheme 2.

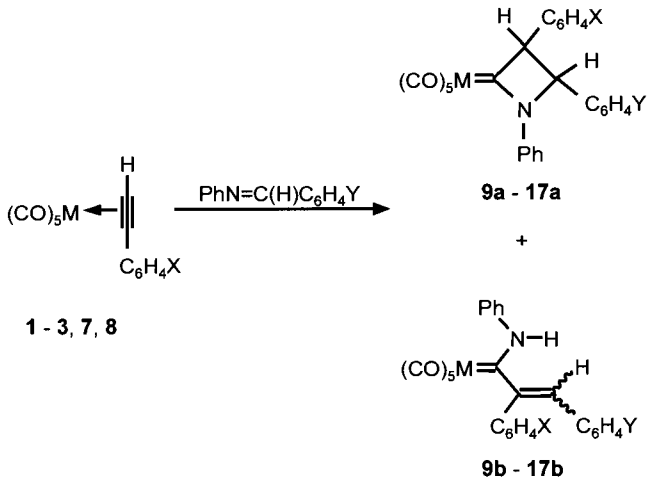
The ^{1}H-NMR data indicated that after chromatographic work-up the 2-azetidin-1-ylidene complexes **4a**–**6a** were obtained as mixtures of two stereoisomers (*syn* and *anti*), which could not be separated by column chromatography. The resonances of the protons bonded to the ring C(aryl) atoms of the major isomer appeared as doublets at $\delta = 6.51$–6.64 and 4.53–4.67 ppm ($^3J_{H,H} = 4.6$–4.7 Hz, each), suggesting a *syn* arrangement of these protons. The coupling constant for the corresponding signals of the minor isomer at $\delta =$ 5.74–5.83 and 3.94–4.10 ppm was $^3J_{H,H} = 1.7$ Hz, establishing that these protons were *anti* to each other. Therefore, the thermodynamically less stable *syn* isomers dominated in each case.

The *syn*/*anti* ratio increased only slightly both with the substituent R (M = W: *syn*/*anti* = 84:16 [R = Ph], 90:10 [*p*-Tol] and the metal (R = Ph: *syn*/*anti* = 84:16 [W], 80:20 [Cr]).

The alkenyl(amino)carbene complexes were similarly obtained as mixtures of two isomers. Presumably, the isomers differed by the arrangement of the substituents at the C=C bond. The ratio of isomers was about 9:1. Predominantly, the *E* isomers (both aryl substituents are mutually *cis*) were formed as deduced from the ^{1}H-NMR chemical shifts for =CH based on the anisotropy of the vicinal aryl substituent and the X-ray structural analysis of **11b**.

When alkynes and benzylideneimines with different *para* substituents at the aryl groups were employed, the formation of only one regioisomer of the 2-azetidin-1-ylidene complexes and the alkenyl(amino)carbene complexes was observed. In all cases, the aryl substituent of the alkyne ended up at the C4 position of the 2-azetidin-1-ylidene complex and at the C_α position (adjacent to the carbene carbon) of the C=C bond in the alkenyl(amino)carbene complexes (Scheme 3).

The yields of **9a**–**14a** and **9b**–**14b** were similar to those of the tungsten complexes **4a**–**5a** and **4b**–**5b**. The same applied to the chromium complexes **15a**–**17a** and **15b**–**17b**. The ratios of alkenyl(amino)carbene complex/2-azetidin-1-ylidene complex were about 3 (M = W) and 8 (M = Cr). Usually, two isomeric alkenyl(amino)carbene complexes were formed. The isomeric ratio varied between 7:3 and 9:1.



	1/9	1/10	2/11	3/12	7/13	7/14	3/15	8/16	8/17
M	W	W	W	W	W	W	Cr	Cr	Cr
X	H	H	Me	Me	Br	Br	H	Me	Me
Y	Me	Cl	H	Cl	H	Me	Me	H	Cl

Scheme 3.

Table 1
Selected bond lengths (Å) and bond angles (°) for **11b**

Bond lengths			
W(1)–C(1)	2.044(6)	W(1)–C(2)	2.040(6)
W(1)–C(3)	2.041(6)	W(1)–C(4)	2.027(6)
W(1)–C(5)	2.024(7)	W(1)–C(6)	2.239(6)
C(6)–C(7)	1.503(7)	C(6)–N(1)	1.324(6)
C(7)–C(8)	1.362(8)	C(7)–C(21)	1.479(7)
C(8)–C(31)	1.476(8)	N(1)–C(11)	1.439(6)
C(11)–C(12)	1.379(9)		
Bond angles			
C(1)–W(1)–C(5)	87.7(3)	C(2)–W(1)–C(5)	89.4(3)
C(3)–W(1)–C(5)	84.5(3)	C(4)–W(1)–C(5)	89.2(2)
C(1)–W(1)–C(6)	91.4(2)	C(2)–W(1)–C(6)	86.4(2)
C(3)–W(1)–C(6)	96.6(2)	C(4)–W(1)–C(6)	95.1(2)
C(5)–W(1)–C(6)	175.7(2)	W(1)–C(6)–C(7)	121.6(3)
W(1)–C(6)–N(1)	128.7(4)	C(7)–C(6)–N(1)	109.2(5)
C(6)–C(7)–C(8)	118.6(5)	C(6)–C(7)–C(21)	116.7(5)
C(8)–C(7)–C(21)	124.6(5)	C(7)–C(8)–C(31)	129.9(5)
C(6)–N(1)–C(11)	128.9(5)	N(1)–C(11)–C(12)	117.9(5)
N(1)–C(11)–C(16)	120.5(5)	C(7)–C(21)–C(22)	121.9(5)
C(7)–C(21)–C(26)	120.2(4)	C(8)–C(31)–C(32)	117.4(5)
C(8)–C(31)–C(36)	124.9(5)		

The structure of the major isomer of the alkenyl(amino)carbene complex **11b** obtained from $[(CO)_5W(HC{\equiv}CTol\text{-}p)]$ and PhN=C(H)Ph was established by an X-ray structural analysis (Table 1 and Fig. 1).

The most important features of the structure of **11b** are

1. the mutual *cis* orientation of both aryl groups at the $C_\alpha = C_\beta$ bond;
2. the attachment of the *p*-tolyl group to the C_α atom;
3. the strong deviation of the carbene and the olefinic plane from coplanarity (torsion angle W(1)–C(6)–C(7)–C(8) 120.6(4)°; for a projection of the molecule along the C(6)–C(7) axis see Fig. 2) and;
4. the *Z* orientation of the phenyl group at the partial C(6)–N(1) double bond (1.324(6) Å).

The carbene carbon is planar coordinated (sum of angles: 359.5°). However, the formation of an extended W(1)–C(6)–C(7)–C(8) π system is prevented by the tilt of the olefin against the carbene plane, which is probably due to reduction in steric congestion. As a consequence, the C(6)–C(7) bond is rather long (1.503(7) Å). The distance compares well with that in carbene complexes with an orthogonal or almost orthogonal arrangement of the carbene and the alkene plane (e.g. 1.511(12) Å in $[(CO)_5W{=}C(NEt_2)–C(CH{=}CH_2){=}C(H)C_6H_4Me\text{-}p]$ (torsion angle −84.5(11)°) [9] and 1.488(8) Å in $[(CO)_5Cr{=}C(OMe)–C(Me){=}C(H)Me]$ [10]). In contrast, the bond length of the central C–C single bond in complexes with a coplanar or an almost coplanar arrangement of the carbene and the alkene plane is usually in the range 1.40–1.47 Å (e.g. 1.427(4) Å in $[(CO)_5Cr{=}C(NH_2)–CH{=}C(NMe_2)Ph]$ {torsion angle

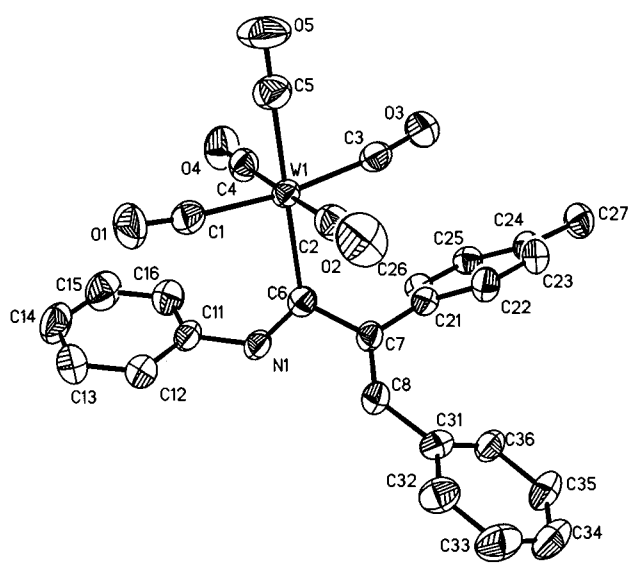


Fig. 1. Structure of the major isomer of complex **11b** (hydrogen atoms omitted for clarity).

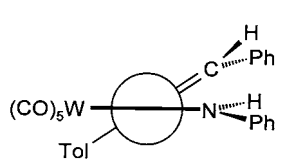
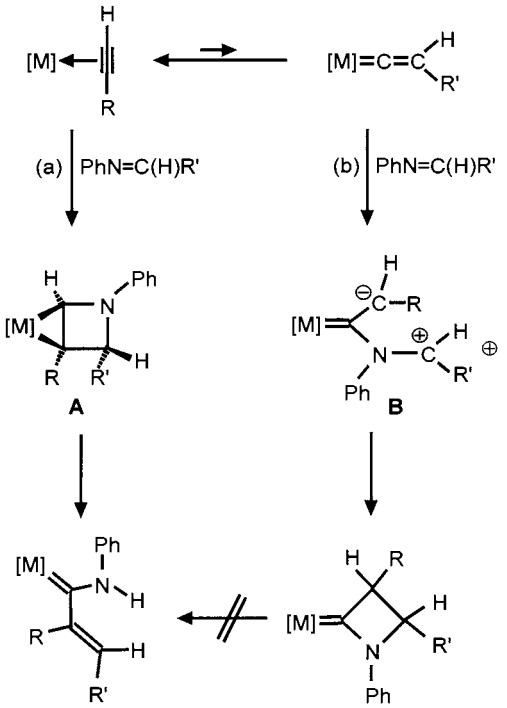


Fig. 2. Projection of complex **11b** along the C(6)–C(7) axis.



Scheme 4.

169.4°} [11], 1.418(5) Å in $[(CO)_5Cr{=}C\{N{=}C(OMe)Ph\}\text{-}CH{=}C(H)NMe_2]$ (torsion angle 175.7°) [12] and 1.407(5) Å in $[(CO)_5Cr{=}C(OEt)\text{–}CH{=}C(Ph)\{N(CH_2)_4\}]$ (torsion angle 173.0°) [13]). To reduce unfavorable steric interaction the planes at N(1) and C_α are strongly tilted against the carbene plane (torsion angles: C(6)–C(7)–C(21)–C(22) 123.6(6)°, C(6)–N(1)–C(11)–C(12) −110.7(7)°). As is usually observed with $(CO)_5M$–carbene complexes, the carbene plane bisects the adjacent OC–W–CO angle (torsion angle C(3)–W(1)–C(6)–C(7) 40.6(4)°).

The 2-azetidin-1-ylidene complexes are presumably formed by tautomerization of the alkyne complexes to vinylidene complexes, addition of the *N*-aryl benzylideneimine to the metal-bound vinylidene carbon atom and subsequent ring-closure (Scheme 4, route (b)). A similar mechanism has already been proposed for the formation of 2-azetidin-1-ylidene complexes from $[(CO)_5W(alkyne)]$ complexes and *N*-alkyl imines [8]. Although it was not possible to detect the vinylidene complexes by IR or NMR spectroscopy, the presence of the vinylidene complex tautomers in solution is plausible on the basis of trapping experiments with alcohols, ynamines and alkoxyalkynes to give alkoxycarbene [14] and cyclobutenylidene complexes [15], respectively. The cycloaddition is regiospecific. The formation of the regioisomeric 3-azetidin-1-ylidene complexes has not been observed.

It is reasonable to assume that the alkenyl(amino)carbene complexes are derived from the 2-azetidin-1-ylidene complexes either by: (a) deprotonation at C4, followed by subsequent ring opening and reprotonation at nitrogen; or (b) by 1,3-migration of the proton at C4 and ring opening. However, both mechanisms disagree with the experimental facts. The transformation of 2-azetidin-1-ylidene complexes into alkenyl(amino)carbene complexes can be induced neither thermally nor by the presence in excess of imines, aniline or NaOMe. When trifluoroacetic acid was added to solutions of **5a**, only decomposition of **5a** was observed. The formation of the alkenyl(amino)carbene complex **5b** could not be detected. These observations indicate that **5b** is not derived from **5a** but rather that in the reaction of $[(CO)_5M(alkyne)]$ complexes with *N*-aryl imines, 2-azetidin-1-ylidene and alkenyl(amino)carbene complexes are formed simultaneously.

A mechanism consistent with all observations is shown in Scheme 4, path (a). Cycloaddition of the imine (very likely in a stepwise fashion) to the carbon–carbon bond of the coordinated alkyne presumably gives the dehydroazetidine π-complex **A**. A subsequent 1,2-hydrogen shift and ring opening by an electrocyclic process could finally produce the alkenyl(amino)carbene complexes. The formation of the *Z* isomer (with respect to the partial C(carbene)–N bond) is very likely determined in the 1,2-hydrogen shift step, that of the *cis* isomer (with respect to the C=C bond) presumably in the cycloaddition step to form the four-membered ring in A.

In summary, the reactions of imines with terminal alkynes coordinated to $(CO)_5M$-fragments strongly depend on the substituent at nitrogen of the imine. *N*-Alkyl imines exclusively give 2-azetidin-1-ylidene complexes. Other coupling products have so far not been observed. In contrast, in the reactions with the less nucleophilic *N*-aryl imines predominantly alkenyl(amino)carbene complexes are formed and the corresponding 2-azetidin-1-ylidene complexes are obtained in rather small amounts. It is very likely that the type of product is already determined in the initial reaction step and depends on whether the imine adds to the alkyne or the vinylidene tautomer.

Alkenylcarbene complexes are usually prepared either by the classical Fischer route via addition of alkenyl lithium to a metal carbonyl and subsequent alkylation of the resulting metallate [16], by addition of protic nucleophiles to the C≡C bond of alkynylcarbene complexes [17,18], by insertion of π-donor substituted alkynes into the M=C bond of carbene complexes [16,19] or by cycloaddition of olefins to alkynylcarbene complexes [18]. The synthesis of alkenylcarbene complexes from alkyne complexes and imines constitutes a new approach to this type of carbene complexes.

3. Experimental

3.1. General

All operations were performed under an inert atmosphere (nitrogen or argon) by using standard Schlenk techniques. Solvents were dried by refluxing over CaH_2 (CH_2Cl_2, pentane) or sodium–benzophenone ketyl (Et_2O) and were freshly distilled prior to use. The silica gel used for chromatography (Baker, silica gel for flash chromatography) was nitrogen saturated. The yields refer to analytically pure compounds and were not optimized. Instrumentation: ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC 250 or a Bruker WM 250 spectrometer. ^{1}H-NMR resonances of solutions in $CDCl_3$ are reported relative to TMS, those of solutions in acetone-d_6 and the ^{13}C-NMR-resonances relative to the residual solvent peaks of acetone-d_6 and $CDCl_3$. If not specifically mentioned, IR and NMR spectra are taken at room temperature (r.t.). IR: Biorad FTS 60 spectrophotometer; MS: Finnigan MAT 312 (EI, 70 eV or FAB, NBOH [3-nitrobenzyl alcohol]). The peaks of the tungsten complexes are listed with respect to ^{184}W. Elemental analyses: Heraeus CHN-O-RAPID. Photolysis reactions were carried out in a duran glass apparatus by using a mercury high pressure lamp (TQ 150, Fa. Heraeus). The imines [20] and *p*-bromophenylacetylene [21] were prepared according to literature procedures.

3.2. Generation of (η^2-alkyne)metal complexes **1**–**3**, **7**, **8**

The (η^2-alkyne)metal complexes **1** and **3** were generated as described in Ref. [8]; the complexes **2**, **7**, and **8** were analogously generated. These (η^2-acetylene)-pentacarbonyl complexes were unstable and quickly decomposed at temperatures above -20 (M = Cr) or 0°C (M = W). Therefore, the highly concentrated solutions containing the (η^2-alkyne)pentacarbonyl complexes obtained by these procedures were used immediately for the reactions with imines.

3.2.1. Pentacarbonyl(η^2-*p*-tolylacetylene)tungsten (**2**)

IR (CH_2Cl_2, 243 K) ν(CO) (cm^{-1}): 2085 m, 1956 vs, 1933 sh. ^{1}H-NMR ($CDCl_3$, 238 K): δ 7.36 (d, J = 8.7 Hz, 2H, aryl), 7.26 (d, J = 8.7 Hz, 2H, aryl), 6.03 (s, 1H, ≡CH), 2.42 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$, 238 K): δ 203.7 (*trans*-CO), 196.1 (*cis*-CO), 139.7, 130.2, 129.6, 122.3 (aryl), 80.4 (≡C–Tol), 63.8 (≡CH), 21.6 (Me).

3.2.2. (η^2-*p*-Bromophenylacetylene)-pentacarbonyltungsten (**7**)

IR (CH_2Cl_2, 243 K) ν(CO) (cm^{-1}): 2085 m, 1958 vs, 1937 sh. ^{1}H-NMR ($CDCl_3$, 238 K): δ 7.62–7.29 (m, 4H, aryl), 6.39 (s, 1H, ≡CH). ^{13}C-NMR ($CDCl_3$, 238 K): δ 203.6 (*trans*-CO), 196.0 (*cis*-CO), 132.0, 131.3, 127.7, 125.5 (aryl), 67.6 (≡C–C_6H_4), 58.4 (≡C–H).

3.2.3. Pentacarbonyl(η^2-*p*-tolylacetylene)chromium (**8**)

IR (CH_2Cl_2, 243 K) ν(CO) (cm^{-1}): 2074 m, 1953 vs, 1887 sh. ^{1}H-NMR ($CDCl_3$, 238 K): δ 7.45–7.08 (m, 4H, aryl), 4.81 (s, 1H, ≡CH), 2.32 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$, 238 K): δ 224.0 (*trans*-CO), 214.8 (*cis*-CO), 140.2, 130.9, 129.6, 119.7 (C_6H_4), 67.8 (*C*–Tol), 57.3 (C–H), 21.5 (Me).

3.3. Reaction of (η^2-alkyne)pentacarbonylmetal complexes with *N*-phenyl imines

At -30°C, a solution of *N*-phenyl *p*-methylbenzylideneimine, *N*-phenyl benzylideneimine, and *N*-phenyl *p*-chlorbenzylideneimine {(Ph)N=C(H)R, R = *p*-Tol, Ph, *p*-chlorphenyl; two equivalents each relative to [M(CO)$_6$]}, respectively, in 3–4 ml of CH_2Cl_2 was added to a freshly prepared and highly concentrated solution of the acetylene complexes **1**–**3**, **7** and **8**, respectively. The solution was stirred for 90 min and gradually warmed to r.t. The solvent was removed in vacuo to give a brown oil. The oil was chromatographed at -30°C on neutral Al_2O_3. First, with 5:1 pentane–dichloromethane a yellow band was eluted that contained the 2-azetidin-1-ylidene complexes (**4a**–**6a**, **9a**–**17a**) as a mixture of the *syn* and *anti* isomers. Then, with 10:13.5 pentane–dichloromethane a second yellow fraction was eluted, which afforded the amino(ethenyl)carbene complexes (**4b**–**6b**, **9b**–**17b**) after removal of the solvent in vacuo.

3.3.1. Pentacarbonyl{(2,3,4-triphenyl)-2-azetidin-1-ylidene}tungsten (**4a**) and pentacarbonyl[1,2-diphenylethenyl(phenylamino)carbene]tungsten (**4b**)

Compound **4a**. Yield: 0.30 g (18% relative to [W(CO)$_6$]). Two isomers: 84% *syn*, 16% *anti*. M.p. 113°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.73–6.85 (m, 15H, 3 aryl), 6.56 (d, J = 4.7 Hz, 1H, 3-CH), 4.60 (d, J = 4.7 Hz, 1H, 4-CH). ^{1}H-NMR ($CDCl_3$) *anti* isomer: δ 5.83 (d, J = 1.7 Hz, 1H, 3-CH), 4.01 (d, J = 1.7 Hz 1H, 4-CH). ^{13}C-NMR ($CDCl_3$): δ 271.2 (C1), 202.8 (*trans*-CO), 197.4 (*cis*-CO), 140.2, 130.1, 129.7, 129.6, 129.3, 129.2, 129.1, 128.7, 127.9, 127.5, 126.6, 122.6 (3 aryl), 78.0 (C3), 66.5 (C4). MS *m*/*z* (%): 607 (15) [M$^+$], 523 (27) [M$^+$ − 3CO], 467 (19) [M$^+$ − 5CO], 364 (100) [M$^+$ − 5CO − C − CPh(H)], 180 (23) [M$^+$ − W(CO)$_5$ − C–CPh(H)]. Anal. Found: C, 50.91; H, 3.15; N, 2.72. $C_{26}H_{17}NO_5W$ (607.3). Calc.: C, 51.38; H, 2.80; N, 2.31%.

Compound **4b**. Yield: 0.78 g (45% relative to [W(CO)$_6$]). M.p. 142°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 10.25 (s, br, 1H, NH), 7.68–6.90 (m, 15H, 3 aryl), 6.72, 6.34 (2 s,

together 1H, CH). ^{13}C-NMR ($CDCl_3$): δ 262.5 (C1), 203.5 (*trans*-CO), 197.8 (*cis*-CO), 155.6 (C2), 142.2, 136.0, 135.0, 130.0, 129.8, 129.6, 129.3, 128.9, 128.6, 128.3, 128.0, 127.4, 126.9, 125.3 (3 aryl + C3). MS *m*/*z* (%): 607 (2) [M^+], 523 (10) [$M^+ - 3CO$], 467 (19) [$M^+ - 5CO$], 282 (15) [$M^+ - W(CO)_5$], 182 (100) [$M^+ - W(CO)_5 - C{-}CPh(H)$]. Anal. Found: C, 51.03; H, 2.90; N, 2.34. $C_{26}H_{17}NO_5W$ (607.3). Calc.: C, 51.38; H, 2.80; N, 2.31%.

3.3.2. Pentacarbonyl[(2-phenyl-3,4-di-p-tolyl)-2-azetidin-1-ylidene]tungsten (**5a**) and pentacarbonyl-[1,2-p-ditolylethenyl(phenylamino)carbene]tungsten (**5b**)

Compound **5a**. Yield: 0.32 g (18% relative to [$W(CO)_6$]). Two isomers: ca. 90% *syn*, 10% *anti*. M.p.: 102°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2061 m, 1929 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.70–6.77 (m, 13H, 3 aryl), 6.51 (d, $J = 4.6$ Hz, 1H, 3-CH), 4.53 (d, $J = 4.6$ Hz, 1H, 4-CH), 2.21, 2.15 (2 s, 6H, 2 Me). ^{1}H-NMR ($CDCl_3$) *anti* isomer: δ 7.70–6.77 (m, 13H, 3 aryl), 5.74 (d, $J = 1.7$ Hz, 1H, 3-CH), 3.94 (d, $J = 1.7$ Hz, 1H, 4-CH), 2.38, 2.34 (2 s, 6H, 2 Me). ^{13}C-NMR ($CDCl_3$): δ 268.9 (C1), 202.9 (*trans*-CO), 197.5 (*cis*-CO), 143.4, 140.1, 137.1, 131.1, 129.9, 129.8, 129.6, 129.1, 129.0, 128.8, 126.7, 122.8, (3 aryl), 78.3 (C3), 66.4 (C4), 21.2, 21.1 (2 Me). MS *m*/*z* (%): 635 (8) [M^+], 551 (21) [$M^+ - 3CO$], 495 (18) [$M^+ - 5CO$], 392 (100) [$M^+ - 5CO - C -$ tolyl]. Anal. Found: C, 52.81; H, 3.59; N, 2.36. $C_{28}H_{21}NO_5W$ (635.3). Calc.: C, 52.93; H, 3.33; N, 2.20%.

Compound **5b**. Yield 0.78 g (43% relative to [$W(CO)_6$]). Two isomers: ratio ca. 9:1. M.p. 106°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2061 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 10.04, 10.22 (2 s, together 1H, NH), 7.52–6.87 (m, 13H, 3 aryl), 6.75, 6.24 (2 s, together 1H, =CH), 2.39, 2.35, 2.27, 2.24 (4 s, together 6H, 2 Me). ^{13}C-NMR ($CDCl_3$): δ 261.8 (C1), 203.6 (*trans*-CO), 197.9 ($J_{W,C} = 127.0$ Hz, *cis*-CO), 154.5 (C2), 142.3, 138.7, 138.1, 137.3, 133.1, 132.2, 130.0, 129.7, 129.4, 128.9, 128.8, 126.8, 124.1 (3 aryl + C3), 21.3, 21.2 (2 Me). MS *m*/*z* (%): 635 (5) [M^+], 551 (44) [$M^+ - 3CO$], 495 (58) [$M^+ - 5CO$], 310 (100) [$M^+ - W(CO)_5$], 194 (75) [$M^+ - W(CO)_5 - C{=}C$(tolyl)H]. Anal. Found: C, 53.17; H, 3.59; N, 2.36. $C_{28}H_{21}NO_5W$ (635.3). Calc.: C, 52.93; H, 3.33; N, 2.20%.

3.3.3. Pentacarbonyl[(2,3,4-triphenyl)-2-azetidin-1-ylidene]chromium (**6a**) and pentacarbonyl[1,2-diphenylethenyl(phenylamino)carbene]chromium (**6b**)

Compound **6a**. Yield 0.08 g (6% relative to [$Cr(CO)_6$]). Two isomers: 80% *syn*, 20% *anti*. M.p. 81°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1933 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 6.64 (d, $J = 4.7$ Hz, 1H, 3-CH), 4.67 (d, $J = 4.7$ Hz, 1H, 4-CH) *anti* isomer: δ 7.70–6.87 (m, 15H, 3 aryl), 5.78 (d, $J = 1.7$ Hz, 1H, 3-CH), 4.10 (d, $J = 1.7$ Hz, 1H, 4-CH). ^{13}C-NMR ($CDCl_3$): δ 139.5, 134.1, 132.5, 129.7, 129.6, 129.2, 128.1, 127.9, 127.7, 127.4, 126.3, 123. (3 aryl), 77.9 (C3), 65.4 (C4); *anti* isomer: δ 294.7 (C1), 222.8 (*trans*-CO), 216.7 (*cis*-CO), 139.3, 135.2, 129.5, 129.2, 128.9, 128.6, 126.7, 124.6 (3 aryl), 84.2 (C3), 68.1 (C4). MS *m*/*z* (%): 475 (7) [M^+], 419 (4) [$M^+ - 2CO$], 391 (6) [$M^+ - 3CO$], 363 (36) [$M^+ - 4CO$], 335 (100) [$M^+ - 5CO$]. Anal. Found: C, 65.83; H, 3.88; N, 3.10. $C_{26}H_{17}CrNO_5$ (475.5). Calc.: C, 65.69; H, 3.60; N, 2.95%.

Compound **6b**: Yield 0.50 g (39% relative to [$Cr(CO)_6$]). Two isomers: ratio ca. 8:2. M.p. 93°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1933 vs. ^{1}H-NMR ($CDCl_3$): δ 10.47, 10.32 (2 s, together 1H, NH), 7.59–7.09 (m, 17H, 3 aryl), 6.51, 6.32 (2 s, together 1H, CH). ^{13}C-NMR ($CDCl_3$): δ 284.7 (C1), 223.7 (*trans*-CO), 216.6 (*cis*-CO), 155.6 (C2), 141.5, 135.4, 135.1, 129.9, 129.8, 129.7, 129.1, 128.8, 128.2, 127.8, 127.1, 123.4 (3 aryl + C3). MS *m*/*z* (%): 475 (2) [M^+], 447 (0.5) [$M^+ -$ CO], 419 (1) [$M^+ - 2CO$], 391 (2) [$M^+ - 3CO$], 363 (12) [$M^+ - 4CO$], 335 (43) [$M^+ - 5CO$]. Correct elemental analysis could not be obtained due to inseparable impurities.

3.3.4. Pentacarbonyl[(2,4-diphenyl-3-p-tolyl)-2-azetidin-1-ylidene]tungsten (**9a**) and pentacarbonyl[1-phenyl-2-p-tolylethenyl(phenylamino)carbene]tungsten (**9b**)

Compound **9a**. Yield 0.14 g (8% relative to [$W(CO)_6$]). Two isomers: ca. 90% *syn*, 10% *anti*. M.p. 113°C. IR (CH_2Cl_2, 298 K) ν(CO) (cm^{-1}): 2062 m, 1929 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.72–6.78 (m, 14H, 3 aryl), 6.52 (d, $J = 4.7$ Hz, 1H, 3-CH), 4.58 (d, $J = 4.7$ Hz, 1H, 4-CH), 2.13 (s, 3H, Me) *anti* isomer: δ 7.72–6.78 (m, 14H, 3 aryl), 5.80 (d, $J = 1.6$ Hz, 1H, 3-CH), 4.00 (d, $J = 1.6$ Hz, 1H, 4-CH), 2.34 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 270.8 (C1), 202.8 (*trans*-CO), 197.4 (*cis*-CO), 140.1, 137.7, 134.3, 130.1, 129.7, 129.6, 129.0, 128.9, 128.1, 127.5, 126.6, 122.7 (3 aryl), 78.1 (C3), 66.5 (C4), 21.0 (Me). MS *m*/*z* (%): 621 (11) [M^+], 537 (23) [$M^+ - 3CO$], 481 (21) [$M^+ - 5CO$], 378 (100) [$M^+ - 5CO$-C(tolyl)2H], 194 (33) [$M^+ - W(CO)_5$-C(tolyl)$_2$H]. Anal. Found: C, 51.90; H, 3.26; N, 2.40. $C_{27}H_{19}NO_5W$ (621.30). Calc.: C, 52.20; H, 3.08; N, 2.25%.

Compound **9b**: Yield 1.09 g (62% relative to [$W(CO)_6$]). Two isomers: ratio ca. 7:3. M.p. 123°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2062 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 10.18, 10.11 (2 s, together 1H, NH), 7.55–7.00 (m, 14H, 3 aryl), 6.75, 6.33 (2 s, 1 H, CH), 2.29, 2.25 (3s, together 3 H, Me). ^{13}C-NMR ($CDCl_3$): δ 260.2 (C1), 202.7 (*trans*-CO), 196.6 (*cis*-CO), 153.4 (C2), 141.0, 137.2, 135.1, 130.7, 128.9, 128.7, 128.5, 128.2, 127.9, 127.7, 126.7, 125.9 (3 aryl + C3), 20.3 (Me). MS *m*/*z* (%): 621 (6) [M^+], 537 (53) [$M^+ - 3CO$], 481 (72) [$M^+ - 5CO$], 296 (33) [$M^+ - W(CO)_5$]. Anal. Found:

C, 52.39; H, 3.11; N, 2.16. $C_{27}H_{19}NO_5W$ (621.30). Calc.: C, 52.20; H, 3.08; N, 2.25%.

*3.3.5. Pentacarbonyl[(3-p-chlorophenyl-2,4-diphenyl)-2-azetidin-1-ylidene]tungsten (**10a**) and pentacarbonyl-[2-p-chlorophenyl-1-phenylethenyl(phenylamino)-carbene]tungsten (**10b**)*

Compound **10a**. Yield 0.31 g (17% relative to $[W(CO)_6]$). Two isomers: 80% *syn*, 20% *anti*. M.p. 108°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.90–6.73 (m, 14H, 3 arom.), 6.52 (d, $J = 4.8$ Hz, 1H, 3-CH), 4.60 (d, $J = 4.8$ Hz, 1H, 4-CH). ^{1}H-NMR ($CDCl_3$) *anti* isomer: δ 5.80 (d, $J = 1.4$ Hz, 1H, 3-CH), 3.95 (d, $J = 1.6$ Hz, 1H, 4-CH). ^{13}C-NMR ($CDCl_3$): δ 271.2 (C1), 202.8 (*trans*-CO), 197.4 (*cis*-CO), 140.1, 134.2, 132.9, 130.1, 129.7, 129.6, 129.2, 129.1, 128.3, 128.1, 122.7 (3 aryl), 78.0 (C3), 66.5 (C4). MS m/z (%): 641 (11) [M^+], 557 (17) [$M^+ - 3CO$], 501 (12) [$M^+ - 5CO$], 398 (92) [$M^+ - 5CO - 2C - 2H - Ph$], 306 (100) [$M^+ - 5CO - 2C - 2H - Ph - NPh$]. Anal. Found: C, 48.68; H, 2.67; N, 2.60. $C_{26}H_{16}ClNO_5W$ (641.0). Calc.: C, 48.66; H, 2.51; N, 2.18%.

Compound **10b**. Yield 0.97 g (53% relative to $[W(CO)_6]$; three isomers: 70, 20, 10%). M.p. 128°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): 10.19, 10.34, 10.42 (3 s, together 1H, NH), 7.58–6.89 (m, 14 H, 3 aryl), 6.67, 6.30, 6.23 (3 s, together 1H, =CH). ^{13}C-NMR ($CDCl_3$): δ 262.5 (C1), 203.4 (*trans*-CO), 197.7 (*cis*-CO), 156.1 (C2), 142.1, 135.6, 133.8, 133.5, 131.2, 129.8, 129.7, 129.4, 129.1, 128.5, 126.9, 125.9 (3 aryl + C3). MS m/z (%): 641 (7) [M^+], 557 (40) [$M^+ - 3CO$], 501 (43) [$M^+ - 5CO$], 316 (100) [$M^+ - W(CO)_5$]. Anal. Found: C, 49.11; H, 2.64; N, 2.32. $C_{26}H_{16}ClNO_5W$ (641.0). Calc.: C, 48.66; H, 2.51; N, 2.18%.

*3.3.6. Pentacarbonyl[(2,3-diphenyl-4-p-tolyl)-2-azetidin-1-ylidene]tungsten (**11a**) and pentacarbonyl[2-phenyl-1-p-tolylethenyl(phenylamino)carbene]tungsten (**11b**)*

Compound **11a**. Yield: 0.32 g (18% relative to $[W(CO)_6]$), *syn*/*anti* ratio > 97:3. M.p. 113°C. IR (CH_2Cl_2, 298 K) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 7.76–6.90 (m, 14H, 3 aryl), 6.61 (d, $J = 4.7$ Hz, 1H, 3-CH), 4.58 (d, $J = 4.7$ Hz, 1H, 4-CH), 2.13 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 270.1 (C1), 203.9 (*trans*-CO), 198.1 (*cis*-CO), 141.2, 137.5, 134.2, 132.6, 131.1, 130.5, 130.2, 129.5, 129.0, 128.6, 128.0, 124.4 (3 aryl), 80.0 (C3), 66.9 (C4), 21.1 (Me). MS m/z (%): 621 (17) [M^+], 537 (78) [$M^+ - 3CO$], 481 (100) [$M^+ - 5CO$], 296 (75) [$M^+ - W(CO)_5 - H$]. Anal. Found: C, 52.05; H, 3.19; N, 2.48. $C_{27}H_{19}NO_5W$ (621.3). Calc.: C, 52.20; H, 3.08; N, 2.25%.

Compound **11b**. Yield: 0.84 g (48% relative to $[W(CO)_6]$). Two isomers ratio ca. 7:3. M.p. 123°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 10.13 (s, br, 1H, NH), 7.47 – 6.96 (m, 14H, 3 aryl), 6.79, 6.33 (2 s, together 1H, CH), 2.37, 2.26 (2 s, together 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 262.7 (C1), 203.5 (*trans*-CO), 197.8 (*cis*-CO), 155.5 (C2), 142.3, 138.9, 135.2, 132.9, 130.0, 129.8, 129.7, 129.6, 128.2, 128.0, 126.9 (3 aryl + C3), 21.4 (Me). MS m/z (%): 621 (7) [M^+], 537 (19) [$M^+ - 3CO$], 481 (36) [$M^+ - 5CO$], 297 (68) [$M^+ - W(CO)_5$], 205 (100) [$M^+ - W(CO)_5 - NPh(H)$]. Anal. Found: C, 52.16; H, 3.17; N, 2.32. $C_{27}H_{19}O_5NW$ (621.3). Calc.: C, 52.20; H, 3.08; N, 2.25%.

*3.3.7. Pentacarbonyl[(3-p-chlorophenyl-2-phenyl-4-p-tolyl)-2-azetidin-1-ylidene]tungsten (**12a**) and pentacarbonyl[2-p-chlorophenyl-1-p-tolylethenyl-(phenylamino)carbene]tungsten (**12b**)*

Compound **12a**. Yield 0.30 g (16% relative to $[W(CO)_6]$). Two isomers: 94% *syn*, 6% *anti*. M.p. 108°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.68–6.81 (m, 13H, 3 aryl), 6.48 (d, $J = 4.6$ Hz, 1H, 3-CH), 4.56 (d, $J = 4.7$ Hz, 1H, 4-CCH), 2.21 (s, 3H, Me); *anti* isomer: δ 5.77 (d, $J = 1.6$ Hz, 1H, 3-CH), 3.92 (d, $J = 1.6$ Hz, 1H, 4-CH), 2.31 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 271.1 (C1), 201.8 (*trans*-CO), 196.3 (*cis*-CO), 138.9, 136.4, 132.8, 130.6, 129.8, 128.8, 128.7, 128.0, 127.5, 121.6 (3 aryl), 76.4 (C3), 65.2 (C4), 20.1 (Me). MS m/z (%): 655 (17) [M^+], 571 (27) [$M^+ - 3CO$], 515 (15) [$M^+ - 5CO$], 412 (100) [$M^+ - 5CO - N(Ph)C$]. Anal. Found: C, 49.43; H, 2.98; N 2.13. $C_{27}H_{18}ClNO_5W$ (655.7). Calc.: C, 49.41, H, 2.77; N, 2.14%.

Compound **12b**. Yield: 1.14 g (61% relative to $[W(CO)_6]$). Two isomers: ratio ca. 9:1. M.p.: 127°C. IR (CH_2Cl_2, 298 K) ν(CO) (cm^{-1}): 2063 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 10.19 (s, br, 1H, NH), 7.65–7.02 (m, 13H, aryl), 6.69 (s, 1H, =CH), 2.39, 2.36 (2s, together 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 260.5 (C1), 202.8 (*trans*-CO), 196.5 ($J_{W,C} = 128.3$ Hz, *cis*-CO), 154.7 (C2), 140.9, 138.0, 132.4, 131.3, 130.1, 128.9, 128.7, 128.6, 128.3, 127.3, 125.7, 123.7 (3 aryl + C3), 20.4 (Me). MS m/z (%): 655 (11) [M^+], 571 (100) [$M^+ - 3CO$], 515 (64) [$M^+ - 5CO$], 412 (63) [$M^+ - 5CO - N(Ph)C$]. Anal. Found: C, 49.43; H, 2.98; N 2.13. $C_{27}H_{18}ClNO_5W$ (655.7). Calc.: C, 49.41; H, 2.77; N, 2.14%.

*3.3.8. [(4-p-Bromophenyl-2,3-diphenyl)-2-azetidin-1-ylidene]pentacarbonyltungsten (**13a**) and [1-p-bromophenyl-2-phenylethenyl(phenylamino)carbene]-pentacarbonyltungsten (**13b**)*

Compound **13a**. Yield: 0.38 g (20% relative to $[W(CO)_6]$). Two isomers: 90% *syn*, 10% *anti*. M.p. 113°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2064 m, 1931 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.72–6.85 (m, 14 H, 3

aryl), 6.56 (d, $J = 4.7$ Hz, 1H, 3-CH), 4.56 (d, $J = 4.7$ Hz, 1H, 4-CH). ^{1}H-NMR ($CDCl_3$) *anti* isomer: δ 5.76 (d, $J = 1.6$ Hz, 1H, 3-CH), 3.97 (d, $J = 1.6$ Hz, 1H, 4-CH). ^{13}C-NMR ($CDCl_3$): δ 269.1 (C1), 203.0 (*trans*-CO), 196.3 (*cis*-CO), 138.9, 132.3, 131.6, 131.2, 130.6, 130.3, 128.7, 128.6, 128.3, 127.5, 125.4, 121.6 (3 aryl), 82.5 (C3, *syn*), 76.8 (C3, *anti*), 67.6 (C4, *anti*), 64.7 (C4, *syn*). MS m/z (%): 685 (10) [M^+], 603 (14) [$M^+ - 3CO$], 545 (10) [$M^+ - 5CO$]. Anal. Found: C, 45.57; H, 2.84; N, 1.94. $C_{26}H_{16}BrNO_5W$ (686.2). Calc.: C, 45.51; H, 2.35; N, 2.04.

Compound **13b**. Yield: 0.87 g (45% relative to [$W(CO)_6$]). Two isomers: ratio ca. 8:2. M.p. 131°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2063 m, 1930 vs. ^{1}H-NMR ($CDCl_3$): δ 10.35, 10.23 (s, br, 1H, NH), 7.59–7.07 (m, 14H, 3 aryl), 6.34, 6.70 (2s, together 1H, CH). ^{13}C-NMR ($CDCl_3$): δ 262.5 (C1), 203.3 (*trans*-CO), 197.6 ($J_{W,C} = 106$ Hz, *cis*-CO), 154.8 (C2), 142.0, 134.9, 134.6, 132.4, 132.0, 131.4, 130.0, 129.9, 129.7, 128.7, 126.8 (3 aryl + C3). MS m/z (%): 687 (0.6) [M^+], 601 (4) [$M^+ - 3CO$], 545 (4) [$M^+ - 5CO$], 360 (100) [$M^+ - W(CO)_5$]. Anal. Found: C, 45.78; H, 2.58; N, 2.33. $C_{26}H_{16}BrNO_5W$ (686.2). Calc.: C, 45.51; H, 2.35; N, 2.04%.

3.3.9. [(4-p-Bromophenyl-2-phenyl-3-p-tolyl)-2-azetidin-1-ylidene]pentacarbonyltungsten (**14a**) and [1-p-bromophenyl-2-tolylethenyl(phenylamino)carbene]-pentacarbonyltungsten (**14b**)

Compound **14a**. Yield 0.16 g (8% relative to [$W(CO)_6$]). Two isomers: 75% *syn*, 25% *anti*. M.p. 113°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2062 m, 1929 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.69–6.75 (m, 13H, 3 aryl), 6.51 (d, $J = 4.6$ Hz, 1H, 3-CH), 4.53 (d, $J = 4.7$ Hz, 1H, 4-CH), 2.17 (s, 3H, Me). ^{1}H-NMR ($CDCl_3$) *anti* isomer: δ 5.71 (d, $J = 1.6$ Hz, 1H, 3-CH), 3.95 (d, $J = 1.6$ Hz, 1H, 4-CH), 2.34 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$) *syn* isomer: δ 268.5 (C1), 202.9 (*trans*-CO), 197.2 (*cis*-CO), 139.6, 139.2, 134.6, 132.0, 130.7, 130.3, 130.0, 129.5, 129.4, 126.5, 123.3, 122.1 (3 aryl), 82.7 (C3), 68.4 (C4), 21.3 (Me); *anti* isomer: δ 5.71 (d, $J = 1.6$ Hz, 1H, 3-CH), 3.95 (d, $J = 1.6$ Hz, 1H, 4-CH), 2.34 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$) *syn* isomer: δ 269.5 (C1), 203.2 (*trans*-CO), 197.7 (*cis*-CO), 139.9, 138.4, 133.7, 132.0, 131.7, 130.1, 129.7, 129.6, 129.5, 126.8, 122.8, 122.1 (3 aryl), 77.7 (C3), 65.8 (C4), 21.2 (Me). MS m/z (%): 701 (13) [M^+], 617 (28) [$M^+ - 3CO$], 559 (22) [$M^+ - 5CO$], 456 (83) [$M^+ - 5CO - C - N(Ph)$], 272 (28) [$M^+ - W(CO)_5 - C - N(Ph)$]. Anal. Found: C, 45.95; H, 2.91; N, 2.28. $C_{27}H_{18}BrNO_5W$ (700.2). Calc.: C, 46.32; H, 2.59; N, 2.00%.

Compound **14b**. Yield 0.89 g (45% relative to [$W(CO)_6$]). Two isomers: ratio ca. 9:1. M.p. 132°C. IR (CH_2Cl_2, 298 K) ν(CO) (cm^{-1}): 2062 m, 1929 vs. ^{1}H-NMR ($CDCl_3$): δ 10.16, 10.24 (2 s, together 1H, NH), 7.58–6.97 (m, 13 H, 3 aryl), 6.67, 6.29 (2 s, 1H, CH), 2.38, 2.25 (2 s, together 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 262.3 (C1), 203.3 (*trans*-CO), 197.7 (*cis*-CO), 154.0 (C2), 142.1, 138.5, 135.2, 132.4, 132.0, 131.7, 131.5, 131.1, 129.9, 129.8, 129.2, 126.9, 123.0 (3 aryl + C3), 21.3 (Me). MS m/z (%): 701 (8) [M^+], 617 (73) [$M^+ - 3CO$], 559 (87) [$M^+ - 5CO$], 377 (100) [$M^+ - W(CO)_5$]. Anal. Found: C, 46.32; H, 2.87; N, 2.12. $C_{27}H_{18}BrNO_5W$ (700.2). Calc.: C, 46.32; H, 2.59; N, 2.00%.

3.3.10. Pentacarbonyl[(2,4-diphenyl-3-p-tolyl)-2-azetidin-1-ylidene]chromium (**15a**) and pentacarbonyl[1-phenyl-2-tolylethenyl(phenylamino)-carbene]chromium (**15b**)

Compound **15a**. Yield 0.07 g (5% relative to [$Cr(CO)_6$]). Two isomers: 90% *syn*, 10% *anti*. M.p. 80°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1933 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.67–6.76 (m, 14H, 3 aryl), 6.59 (d, $J = 4.3$ Hz, 1H, 3-CH), 4.65 (d, $J = 4.5$ Hz, 1H, 4-CH), 2.13 (s, 3H, Me). *anti* isomer: δ 5.81 (d, $J = 1.6$ Hz, 1H, 3-CH), 3.96 (d, $J = 1.6$ Hz, 1H, 4-CH). ^{13}C-NMR ($CDCl_3$): δ 294.8 (C1), 223.0 (*trans*-CO), 217.2 (*cis*-CO), 140.0, 138.0, 134.7, 130.3, 130.1, 129.8, 129.7, 129.3, 128.5, 127.9, 126.9, 123.6 (3 aryl), 78.5 (C3), 66.0 (C4), 21.6 (Me). MS m/z (%): 489 (5) [M^+], 433 (3) [$M^+ - 2CO$], 405 (4) [$M^+ - 3CO$], 377 (4) [$M^+ - 4CO$], 349 (77) [$M^+ - 5CO$]. Anal. Found: C, 66.29; H, 4.45; N, 2.89. $C_{27}H_{19}CrNO_5 \cdot 0.14$ pentane (489.5 + 10.1). Calc.: C, 66.54; H, 4.14; N, 2.80%.

Compound **15b**. Yield 0.57 g (43% relative to [$Cr(CO)_6$]). Two isomers: ratio ca. 8:2. M.p. 104°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1933 vs. ^{1}H-NMR ($CDCl_3$): δ 10.38, 10.51 (2 s, together 1H, NH), 7.68–6.92 (m, 14H, 3 aryl), 6.50, 6.25 (2 s, together 1H, CH), 2.31, 2.27 (2 s, together 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 284.3 (C1), 223.7 (*trans*-CO), 216.7 (*cis*-CO), 154.9, 160.4 (2 C2), 141.6, 137.9, 137.4, 135.7, 132.4, 132.2, 129.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 128.2, 127.9, 127.1, 124.8, 124.8, 124.3, 124.1, 120.9 (6 aryl + C3), 21.2, 21.6 (2 Me). MS m/z (%): 489 (2) [M^+], 461 (3) [$M^+ - CO$], 433 (3) [$M^+ - 2CO$], 405 (12) [$M^+ - 3CO$], 349 (100) [$M^+ - 5CO$]. Anal. Found: C, 65.61; H, 4.01; N, 2.96. $C_{27}H_{19}CrNO_5$ (489.5). Calc.: C, 66.26; H, 3.91; N, 2.86%.

3.3.11. Pentacarbonyl[(2,3-diphenyl-4-p-tolyl)-2-azetidin-1-ylidene]chromium (**16a**) and pentacarbonyl[(2-phenyl-1-tolylethenyl(phenylamino)-carbene]chromium (**16b**)

Compound **16a**. Yield 0.07 g (5% relative to [$Cr(CO)_6$]). Two isomers: 80% *syn*, 20% *anti*. M.p.

79°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1933 vs. ^{1}H-NMR ($CDCl_3$) *syn* isomer: δ 7.68–6.87 (m, 14H, 3 aryl), 6.60 (d, $J = 4.5$ Hz, 1H, 3-CH), 4.62 (d, $J = 4.5$ Hz, 1H, 4-CH), 2.17 (s, 3H, Me); *anti* isomer: δ 7.68–6.87 (m, 14H, 3 aryl), 5.71 (d, $J = 1.6$ Hz, 1H, 3-CH), 4.07 (d, $J = 1.7$ Hz, 1H, 4-CH), 2.37 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 296.0 (C1), 222.8 (*trans*-CO), 216.9 (*cis*-CO), 140.0, 137.1, 133.0, 131.1, 129.8, 129.7, 129.5, 129.2, 128.7, 128.2, 126.5, 123.4, (3 aryl), 84.7 (C3, *anti*), 78.5 (C3, *syn*), 68.1 (C4, *anti*), 65.8 (C4, *syn*), 21.2 (Me, *anti*), 21.1(Me, *syn*). MS m/z (%): 489 (6) [M^+], 405 (5) [$M^+ - 3CO$], 378 (22) [$M^+ - 4CO$]; 349 (86) [$M^+ - 5CO$], 296 (7) [$M^+ - Cr(CO)_5$-H]. Anal. Found: C, 66.09; H, 4.02; N, 3.03. $C_{27}H_{19}CrNO_5$ (489.45). Calc.: C, 66.26; H, 3.91; N, 2.86%.

Compound **16b**. Yield 0.62 g (46% relative to [$Cr(CO)_6$]). Two isomers: ratio ca. 7:3. M.p. 105°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1933 vs. ^{1}H-NMR ($CDCl_3$): δ 10.34, 10.64 (2 s, together 1H, NH), 7.55–7.03 (m, 14H, 3 aryl), 6.47, 6.18 (2 s, together 1H, CH), 2.36, 2.27 (2 s, together 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 284.6 (C1), 223.8 (*trans*-CO), 216.7 (*cis*-CO), 155.6 (C2), 141.6, 138.8, 138.0, 135.3, 132.3, 129.9, 129.7, 129.6, 129.2, 128.2, 127.1, 123.4 (3 aryl + C3), 21.3 (Me). MS m/z (%): 489 (2) [M^+], 461 (3) [$M^+ - CO$], 433 (1) [$M^+ - 2CO$], 405 (15) [$M^+ - 3CO$], 349 (100) [$M^+ - 5CO$], 296 (50) [$M^+ - Cr(CO)_5 - H$]. Anal. Found: C, 66.54; H, 4.05; N 2.92. $C_{27}H_{19}CrNO_5$ (489.5). Calc.: C, 66.26; H, 3.91; N, 2.86%.

3.3.12. Pentacarbonyl[(3-p-chlorophenyl-2-phenyl-4-p-tolyl)-2-azetidin-1-ylidene]chromium (**17a**) and pentacarbonyl[2-p-chlorophenyl-1-tolylethenyl(phenylamino)carbene]chromium (**17b**)

Compound **17a**. Yield 0.08 g (6% relative to [$Cr(CO)_6$]). Two isomers *syn*/*anti* > 9:1. M.p. 73°C. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1934 vs. ^{1}H-NMR (acetone-d_6): *syn* isomer: δ 8.00–7.02 (m, 14H, 3 aryl + 3-CH), 4.91 (d, $J = 4.5$ Hz, 1H, 4-CH), 2.18 (s, 3H, Me); *anti* isomer: δ 8.00–7.02 (m, 14H, 3 aryl + 3-CH), 5.70 (d, $J = 1.5$ Hz, 3-CH), 0 4.05 (d, $J = 1.5$ Hz, 1H, 4-CH), 2.22 (s, 3H, Me);. ^{13}C-NMR (acetone-d_6): δ 293.8 (C1), 223.9 (*trans*-CO), 217.6 (*cis*-CO), 133.7, 133.1, 132.4, 130.9, 130.6, 130.4, 130.0, 129.8, 129.6, 129.1, 125.0, 117.7 (3 aryl), 79.5 (C3), 66.4 (C4), 21.2 (Me). MS m/z (%): 523 (5) [M^+], 495 (1) [$M^+ - CO$], 467 (2) [$M^+ - 2CO$], 439 (4) [$M^+ - 3CO$], 411 (33) [$M^+ - 4CO$], 383 (100) [$M^+ - 5CO$]. Correct elemental analysis could not be obtained due to inseparable impurities.

Compound **17b**. Yield 0.56 g (39% relative to [$Cr(CO)_6$]). Two isomers *syn*/*anti* ratio ca. 7:3. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 2055 m, 1934 vs. ^{1}H-NMR ($CDCl_3$): δ 10.69, 10.56 (2 s, together 1H, NH), 7.51–6.77 (m, 13 H, 3 aryl), 6.30, 6.10 (2 s, together 1H, CH), 2.36, 2.26 (2 s, together 3H, Me). ^{13}C-NMR ($CDCl_3$): δ 287.4, 282.5 (2 C1), 223.8, 223.1 (2 *trans*-CO), 216.8, 216.4 (2 *cis*-CO), 155.6, 149.7 (2 C2), 141.3, 139.4, 138.8, 138.2, 133.9, 133.5, 132.9, 132.6, 131.5, 130.9. 130.3, 129.7, 129.6, 129.5, 129.2, 129.0, 128.2, 126.9, 123.9, 121.5, 119.9 (6 aryl + 2 C3), 21.3, 21.2 (2 Me). MS m/z (%): 523 (0.4) [M^+], 495 (2) [$M^+ - CO$], 467 (0.5) [$M^+ - 2CO$], 439 (9) [$M^+ - 3CO$], 383 (63) [$M^+ - 5CO$], 330 (41) [$M^+ - Cr(CO)_5 - H$]. Anal. Found: C, 61.98; H, 3.77; N, 3.07. $C_{27}H_{18}ClCrNO_5$ (523.9). Calc.: C, 61.90; H, 3.46; N, 2.67%.

3.4. X-ray structural analysis of **11b**

$C_{27}H_{19}NO_5W$, molecular mass (621.30), crystal size $0.2 \times 0.2 \times 0.2$ mm^3 (obtained by recrystallization from 3:1 pentane–dichloromethane at -30°C); crystal system triclinic, space group $P\bar{1}$, $a = 8.785(3)$, $b = 12.254(7)$, $c = 12.798(5)$ Å, $\alpha = 102.15(4)$, $\beta = 105.42(3)$, $\gamma = 95.97(4)$°; $V = 1279.6(10)$ Å^3, $Z = 2$, $D_{calc} = 1.723$ g cm^{-1}, λ (Mo–K_α) = 0.71073 Å, $F(000)$ 646; Wyckoff scan, 2θ range 4.0–54.0°, scan rate variable 2.0–29.3° min^{-1} in ω; 5589 independent reflections, 4680 reflections with $F > 4\sigma(F)$; 319 refined parameters; $R = 0.033$, $R_w = 0.035$. Largest difference peak and hole: +0.77 and −1.13 e Å^{-3}). The measurements were performed at −26°C, with a crystal of **11b** mounted in a glass capillary on a Siemens R3m/V diffractometer (graphite monochromator, Mo–K_α radiation, $\lambda = 0.71073$ Å). A semi-empirical absorption correction (based on ten reflections) was carried out. The structure was solved by Patterson methods using the SHELXTL-PLUS (VMS) program package. The positions of the hydrogen atoms were calculated by assuming ideal geometry ($d_{C-H} = 0.96$ Å), and their coordinates were refined together with those of the attached C atoms as 'riding models'. The positions of all other atoms were refined anisotropically by the full-matrix least-squares method.

4. Supplementary material

Crystallographic data for the structural analysis of [$(CO)_5W$=C(NPhH)C(C_6H_4Me-*p*)=C(Ph)H]·1/2CH_2Cl_2 (**11b**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 136352. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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