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Synthesis of azetidinylidene complexes from $[(CO)_5M(CH_2Cl_2)]$, phenylacetylene and imines and oxidative decomplexation to give β-lactams

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Abstract

Photolysis of $[M(CO)_6]$ in CH_2Cl_2 gives $[(CO)_5M(CH_2Cl_2)]$. Substitution of phenylacetylene for CH_2Cl_2 produces the thermolabile phenylacetylene complexes $[(CO)_5M(HC{\equiv}CPh)]$ [M = Cr (**1**), Mo (**2**), W (**3**)]. Addition of *N*-alkyl benzylideneimines, RN=C(Ph)H, to solutions of **1**–**3** affords the 2-azetidin-1-ylidene complexes $[(CO)_5M{=}\overline{C{-}NR{-}C(Ph)H{-}C}(Ph)H]$ [M = Cr, Mo, W; R = Et, *i*-Pr]. The reaction presumably proceeds 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). The reaction of **3** with dialkylcarbodimides, RN=C=NR (R = *c*-Hex, *i*-Pr), yields 3-imino-2-azetidin-1-ylidene complexes, $[(CO)_5W{=}\overline{C{-}NR{-}C(=NR){-}C}(Ph)H]$. By oxidative cleavage of the Cr=C bond in $[(CO)_5Cr{=}\overline{C{-}NR{-}C(Ph)H{-}C}(Ph)H]$ the corresponding β-lactams are obtained in high yields. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Azetidinylidene complexes; Oxidative decomplexation; β-lactams

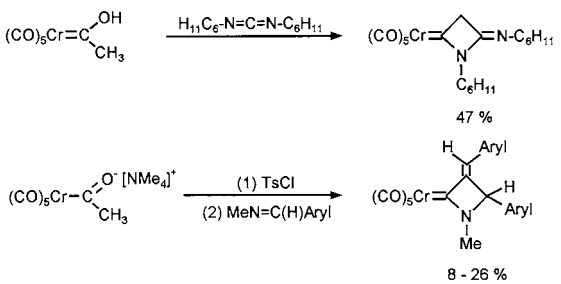
1. Introduction

Vinylidene complexes may be regarded as organometallic analogues of ketenes. Ketenes react with imines by cycloaddition to afford β-lactams [1]. The reaction is generally carried out with ketenes of the form $R_2C{=}C{=}O$. It has not been successfully applied to $R(H)C{=}C{=}O$, except when these are generated in situ by decomposition of a diazo ketone [1a].

Ketene complexes have been proposed as key intermediates in the synthesis of β-lactams by photolysis of carbene complexes in the presence of imines [2]. It has been suggested that these ketene complexes arise from photoinduced coupling of a carbonyl and the carbene ligand in $[(CO)_5M{=}C(R^1)R^2]$ complexes.

The vinylidene complex $[(CO)_5Cr{=}C{=}CH_2]$ was proposed as an intermediate in the reactions of pentacarbonyl[hydroxy(methyl)carbene]chromium with dicyclohexyl carbodiimide [3] and of tetramethylammonium acetyl(pentacarbonyl)chromate toluene-4-sulfonyl chloride/imines [4,5], to give azetidinylidene complexes (Scheme 1).

The formation of azetidinylidene complexes by cycloaddition of imines to the C=C bond of isolable or at least spectroscopically detectable vinylidene complexes has also been observed. $[Cp(CO)(L)Fe{=}C{=}CR_2]^+$ [L =



Scheme 1.

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$P(OMe)_3$, PPh_3; R = H, Me] adds MeN=C(H)Aryl and thiazolines to give azetidinylidene complexes [5,6]. Analogously, azetidinylidene complexes of manganese and rhenium have been prepared by cycloaddition of imines to vinylidene complexes [7]. Usually, oxidative decoordination of the four-membered ring yields β-lactams in moderate to good yields. In addition to chromium, manganese and rhenium vinylidene complexes, the tungsten complex $[(CO)_5W{=}C{=}CPh_2]$ has also been shown to add imines and to afford azetidinylidene complexes [8]. All organometallic routes are either restricted with respect to the imine and the vinylidene substituents (as in the case of the chromium complex) or require multi-step procedures for the synthesis of the starting vinylidene complexes.

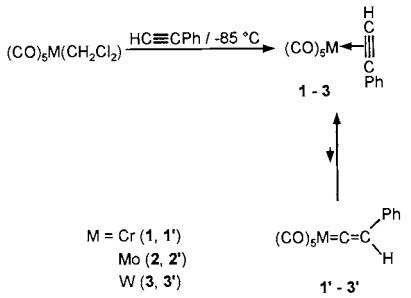
Recently we observed that $[(CO)_5W(HC{\equiv}CR)]$ complexes [readily obtained by reaction of alkynes with photolytically generated $[(CO)_5W(CH_2Cl_2)]$ rapidly react with ynamines, $R^1C{\equiv}CNR^2_2$, to give cyclobutenylidene complexes, $[(CO)_5W{=}\overline{C}{-}CR^1{=}C(NR^2_2){-}\overline{C}(H)R]$ [9]. We proposed that the cyclobutenylidene complex was formed by addition of the C≡C bond of the alkyne to the $C_\alpha{=}C_\beta$ bond of the vinylidene complexes $[(CO)_5W{=}C{=}C(R)H]$ which are in equilibrium with their alkyne complexes tautomers. Apart from their reactions with ynamines, these vinylidene complexes have also been trapped with alcohols to give alkoxycarbene complexes [10]. The facile availability of such monosubstituted vinylidene complexes from the tautomerization of terminal alkyne complexes should offer a convenient route to azetidinylidene complexes.

We now report on a novel approach to 2-azetidin-1-ylidene complexes starting from $[M(CO)_6]$, phenylacetylene and *N*-alkyl benzylideneimines and on the oxidative decomplexation of the azetidinylidene ligand of some representative examples to give β-lactams.

2. Results and discussion

2.1. Generation of pentacarbonyl(phenylvinylidene) complexes

Irradiation of the metal hexacarbonyls $[M(CO)_6]$ in dichloromethane at −85°C gives pentacarbonyl(dichloromethane) complexes. Although, these are unstable and cannot be isolated, solutions of $[(CO)_5M(CH_2Cl_2)]$ can be handled at −80°C for short periods of time. Addition of phenylacetylene affords the phenylacetylene(pentacarbonyl) complexes **1**–**3** by substitution of the alkyne for coordinated dichloromethane (Scheme 2). Presumably, in solution the alkyne complexes are in equilibrium with their vinylidene complex tautomers **1′**–**3′** [9] (Scheme 2). The equilibrium is far on the side of the alkyne complexes since it was not possible to detect the vinylidene complexes by IR or



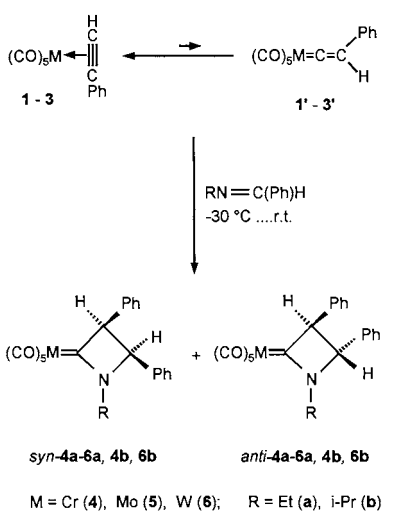
Scheme 2.

NMR spectroscopy. However, 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 [10] and cyclobutenylidene complexes [9], respectively.

The alkyne complexes/vinylidene complexes quickly decompose in solution at temperatures above −20°C (Cr, Mo) and 0°C (W). Therefore, they were not isolated but only characterized by their IR and NMR spectra. For the subsequent reactions with imines, the solutions of the alkyne complexes were immediately used after their volume had been reduced to a few milliliters. The complex $[(CO)_5W(\eta^2\text{-}HC{\equiv}CPh)]$ has already earlier been isolated and fully characterized including an X-ray structural analysis [9].

2.2. Reactions with N-alkyl imines

Addition of two equivalents (relative to the starting metal hexacarbonyls) of *N*-ethyl or *N*-isopropyl benzylideneimine to concentrated solutions of **1**/**1′**, **2**/**2′** and **3**/**3′**, respectively, afforded the 2-azetidin-1-ylidene complexes **4a**–**6a**, **4b** and **6b** by a formal [2 + 2] cycloaddition of the N=C bond of the imine to the C=C bond of the vinylidene complex tautomers **1′**, **2′** and **3′** (Scheme 3).



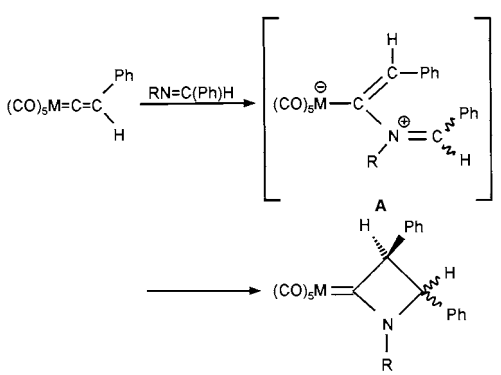
Scheme 3.

The cycloaddition is regiospecific. The formation of the regioisomeric 3-azetidinylidene complexes has not been observed. The ^{1}H-NMR data indicated that the azetidinylidene complexes were obtained as mixtures of two stereoisomers which could not be separated by column chromatography. The ratio of isomers was $\geq$ 9:1 and was almost independent of the metal and the alkyl substituent on nitrogen. The resonances of the protons bonded to the ring C(Ph) atoms of the major isomer appeared as doublets at $\delta = 5.98–6.08$ ppm and 4.37–4.42 ppm ($^3J_{H,H} = 4.2–4.6$ Hz, each) suggesting a *syn* arrangement of these protons. The coupling constants for the corresponding signals of the minor isomer were $^3J_{H,H} = 1.2–1.6$ Hz establishing that these protons are *anti* to each other. Therefore, predominantly the thermodynamically less stable *syn* isomers were formed. An analogous preference for the formation of the *syn* isomers was also observed in the reactions of imines with ketenes to give β-lactams [11]. This suggests that both reactions, the cycloaddition of imines to vinylidene ligands and to ketenes, proceed by a similar mechanism.

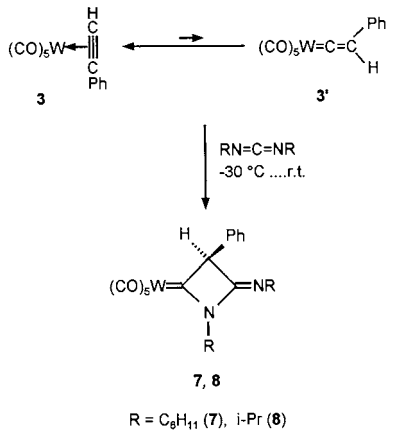
The reaction of the imines with the alkyne complexes is very likely initiated by a nucleophilic addition of the imine via the nitrogen lone electron pair to the C_α atom of the vinylidene ligand to give a dipolar adduct **A**. Adduct formation is followed by ring closure to form the final product (Scheme 4). The synthesis of the azetidinylidene complexes of iron [4–6], manganese [7], rhenium [7], and tungsten [8] has also been suggested to proceed by a similar stepwise mechanism. Two complexes related to the proposed intermediate **A** (Scheme 2) have been isolated [5,6,8].

2.3. Reactions with carbodiimides

Substitution of dialkylcarbodimides for *N*-alkyl benzylideneimines in the reaction with **3**/**3′** afforded the 3-imino-2-azetidin-1-ylidene complexes **7** and **8** (Scheme 5), although in rather low yield [21% (**7**) and 10% (**8**)].



Scheme 4.



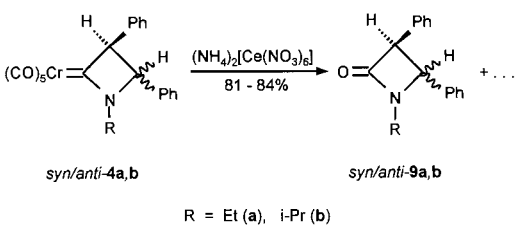
Scheme 5.

In contrast, no reaction was observed between **3**/**3′** and diarylcarbodiimides. This may be attributed to mesomeric effects in these carbodiimides which reduce the nucleophilicity of the nitrogen atom.

Again, the reaction is highly selective, regioisomers of **7** and **8** could not be detected. The ^{1}H-NMR spectrum of **8** shows one singlet for the hydrogen atom bonded to the ring-C(sp^2) atom and two septets and four well-separated doublets for the two isopropyl groups. Analogously, complex **7** exhibits only one singlet for the C(Ph)*H* atom. These data indicate that in solution there is either only one isomer (with respect to the C=N bond) present or there is a rapid interconversion of the isomers.

2.4. Oxidative cleavage of the M=C bond

The oxidative cleavage of the metal–carbon bond and the formation of β-lactams was investigated with the examples of *syn*/*anti*-**4a** and *syn*/*anti*-**4b**. The reaction of *syn*/*anti*-**4a** and *syn*/*anti*-**4b** with ammonium ceric(IV) nitrate in acetone at room temperature afforded the β-lactams *syn*/*anti*-**9a** and *syn*/*anti*-**9b** in 83 and 84% yield (Scheme 6). The progress of the reaction could be followed by IR spectroscopy. The NMR spectra indicated that the decomplexation proceeded without structural changes at the ring. The *syn*/*anti* ratio was at least 9:1.



Scheme 6.

3. Discussion

These results demonstrate that azetidinylidene complexes of chromium, molybdenum and tungsten are readily obtained from commercially available $[M(CO)_6]$, terminal alkynes and imines by a simple reaction sequence. Presumably, the key intermediate is a monosubstituted vinylidene complex formed by tautomerization of $[(CO)_5M(HC{\equiv}CPh)]$. In earlier investigations, hydroxycarbene complexes (M = Cr) [2], acetylchromate [4,5], carbyne complexes (M = Mn, Re) [7], or benzylidene complexes [8] were employed as the starting compounds for the generation of vinylidene intermediates. Subsequent addition of the N=C bond of the imine to the C=C bond of the vinylidene complex in a stepwise fashion affords then the azetidinylidene complexes. A two-step mechanism has also been proposed for the addition of imines to ketenes to give β-lactams. The proposal agrees well with the results of calculations on the ketene/imine system [11]. A two-step mechanism for the reaction of imines and carbodiimides with vinylidene complexes is supported by the isolation of dipolar vinylidene complex/imine adducts in the reaction of $[Cp(CO)\{P(OMe)_3\}Fe{=}C{=}CMe_2]^+$ with MeN=C(Ph)H [5] and of $(CO)_5W{=}C{=}CPh_2$ with PhN=C(Ph)H [8]. On standing in solution, the adducts undergo cyclization.

In former studies usually symmetrically disubstituted vinylidene complexes were employed giving 4-disubstituted complexes. An exception are the reactions of *N*-phenyl benzylideneimine with the manganese complexes $[Cp(CO)_2Mn{=}C{=}C(R)H]$ (R = Me, Ph) derived from carbyne complexes [7]. For R = Me, the diastereoelectivity has been reported to range from 4:1 to 9:1 in favor of the *anti* isomer, the ratio depending on the reaction conditions. For R = Ph, the formation of a single diastereomer (*anti*) was observed. Its configuration was established by an X-ray structural analysis. In contrast, the addition of imines to the complexes **1**–**3** proceeds with a strong preference for the formation of the thermodynamically less stable *syn* isomer.

Analogously to *N*-alkyl benzylideneimines, carbodiimides also add to **3** giving the 3-imino-2-azetidin-1-ylidene complexes **7** and **8**. These results contrast with those obtained with $[Cp(CO)_2Mn{=}C{=}C(Ph)H]$ and $[Cp(CO)_2Re{=}C{=}CH_2]$. The rhenium complex was found to react with RN=C=NR (R = *i*-Pr, *t*-Bu) by C=C/C=N metathesis to give ketenimines, $H_2C{=}C{=}NR$, and the isocyanide complexes $[Cp(CO)_2Re{-}C{\equiv}NR]$. The reaction of $[Cp(CO)_2Mn{=}C{=}C(Ph)H]$ with (*i*-Pr)N=C=N(*i*-Pr) did neither give an azetidin-1-ylidene complex nor an isocyanide complex but rather an *ansa*-carbene complex [9].

The Cr=C bond in **4a**,**b** can be cleaved oxidatively by ammonium ceric(IV) nitrate in acetone to give β-lactams. The oxidative decomplexation proceeds with high yield. Thus, the reaction sequence offers an interesting alternative route to β-lactams.

4. Experimental

4.1. 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-NMR 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 recorded at room temperature (r.t.). IR: Biorad FTS 60 spectrophotometer; MS: Finnigan MAT 312 (EI, 70 eV or FAB, NBOH). 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 [12,13] were prepared according to literature procedures.

4.2. General procedure for the synthesis of the (phenylacetylene)metal complexes (*1*–*3*)

A solution of the hexacarbonyl metals $[M(CO)_6]$ {2.84 mmol of $[W(CO)_6]$, 2.73 mmol of $[Cr(CO)_6]$, 3.79 mmol of $[Mo(CO)_6]$} in ca. 300 ml of dichloromethane was irradiated at −85°C while passing a slight stream of nitrogen through the solution. The progress of the reaction was controlled by IR spectroscopy. After ca. 90 min $[M(CO)_6]$ was converted to pentacarbonyl(dichloromethane)metal complexes as evidenced by the disappearance of the characteristic ν(CO) absorption of $[M(CO)_6]$ at ca. 1980 cm^{-1} and the appearance of those of $[(CO)_5M(CH_2Cl_2)]$ (IR (CH_2Cl_2, 230 K): $[(CO)_5Cr(CH_2Cl_2)]$: ν(CO) = 1885 m, 1936 vs, 2073 w cm^{-1}; $[(CO)_5Mo(CH_2Cl_2)]$: ν(CO) = 1885 m, 1942 vs, 2079 w cm^{-1}; $[(CO)_5W(CH_2Cl_2]$: νCO) = 2076 w, 1934 vs, 1880 m cm^{-1}). The resulting solutions were immediately used for the subsequent reactions with alkynes.

Two equivalents (relative to the starting metal hexacarbonyls) of phenylacetylene were added at −80°C

to the freshly prepared solution of $[(CO)_5M(CH_2Cl_2)]$ (M = Cr, Mo, W). The solution was stirred for 10 min at −80°C. Then the temperature was gradually raised from −80 to −40°C [10°C/10 min]. The resulting brown solution was concentrated at −30°C in vacuo to a volume of ca. 5 ml. These highly concentrated solutions containing the (phenylacetylene)pentacarbonyl complexes **1**–**3** were used for the subsequent reactions with imines. These (phenylacetylene)pentacarbonyl complexes are unstable and quickly decompose at temperature above −20°C (M = Cr, Mo) or 0°C (M = Cr).

*4.2.1. Pentacarbonyl(phenylacetylene)chromium (**1**)*

IR (CH_2Cl_2, 243 K): ν(CO) = 2010 m, 2075 m, 1956 vs, 1889 sh cm^{-1}.

*4.2.2. Pentacarbonyl(phenylacetylene)molybdenum (**2**)*

IR (CH_2Cl_2, 243 K): ν(CO) = 2084 s, 1959 sh, 1939 vs cm^{-1}.

*4.2.3. Pentacarbonyl(phenylacetylene)tungsten (**3**)*

IR (CH_2Cl_2, 243 K): ν(CO) = 2085 m, 1955 vs, 1933 sh cm^{-1}. ^{1}H-NMR ($CDCl_3$, 243 K): δ = 7.52–6.73 (m, 5H, aryl), 6.15 (s, 1H, ≡CH). ^{13}C-NMR ($CDCl_3$, 243 K): δ = 203.4 (*trans*-CO), 195.8 (*cis*-CO), 131.3, 128.9, 128.2, 125.7 (aryl), 64.6 (≡*C*–Ph), 57.5 (≡C–H)

4.3. Reactions of $[(CO)_5M(HC{\equiv}CPh)]$ with N-alkyl imines

At −30°C *N*-ethyl benzylideneimine or *N*-isopropyl benzylideneimine [two equivalents relative to the starting $M(CO)_6$] was added to the highly concentrated solutions of the alkyne complexes **1**, **2**, or **3**. The solution was stirred and gradually warmed to r.t. The reaction was followed by IR spectroscopy. When the ν(CO) absorptions due to the alkyne complexes had disappeared the solvent was removed in vacuo to give a brown oil. The reaction products were chromatographed at −30°C on neutral Al_2O_3 or silica gel. First, unreacted $[M(CO)_6]$ and imine were eluted with pentane. Next, with pentane–dichloromethane (10:3) a yellow band containing the azetidinylidene complexes was eluted. Removal of the solvent in vacuo gave the complexes **4a**–**6a**, **4b**, and **6b** which were characterized by their IR, MS, ^{1}H-NMR and ^{13}C-NMR spectra, and by elemental analysis.

*4.3.1. Pentacarbonyl(N-ethyl-3,4-diphenyl-2-azetidin-1-ylidene)chromium (**4a**)*

Yield 0.59 g (30% relative to $[Cr(CO)_6]$), two isomers: *syn*/*anti* ratio >95:5. M.p. 123°C. IR (CH_2Cl_2): ν(CO) = 2056 m, 1936 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): *syn* isomer: δ = 7.20–6.90 (m, 10 H, 2 Ph), 6.04 (d, J = 4.6 Hz, 1H, 3-CH), 4.42 (d, J = 4.5 Hz, 1H, 4-CH), 4.24 (dq, ^2J = 14.6 Hz, ^3J = 7.3 Hz, 1H, CH*H*Me), 3.80 (dq, ^2J = 14.6 Hz, ^3J = 7.3 Hz, 1H, C*H*HMe), 1.33 (t, J = 7.3 Hz, Me); *anti* isomer: δ = 7.20–6.90 (m, 2 Ph), 5.35 (d, 3-CH), 4.10 (m, CH*H*Me), 3.84 (d, 4-CH), 3.45 (m, C*H*HMe), 1.33 (t, Me). ^{13}C-NMR ($CDCl_3$): δ = 289.0 (C1), 222.9 (*trans*-CO), 217.4 (*cis*-CO, *syn*), 217.2 (*cis*-CO, *anti*), 133.6, 132.6, 130.0, 128.1, 127.7, 127.3, 126.4 (Ph), 79. 5 (C3, *anti*), 77.5 (C3, *syn*), 67.3 (C4, *anti*), 65.5 (C4, *syn*), 45.0 (NCH_2, *syn*), 44.5 (NCH_2, *anti*), 13.5 (CH_3, *anti*), 12.6 (CH_3, *syn*). MS: m/z (%) = 427 (5) [M^+], 343 (5) [M^+-3CO], 287 (76) [M^+–5CO]; 232 (13) [M^+–5CO–CNEt]. Anal. Found: C, 61.82; H, 4.21; N, 3.60. $C_{22}H_{17}CrNO_5$ (427.4) Calc.: C, 61.83; H, 4.01; N, 3.28%.

*4.3.2. Pentacarbonyl(N-isopropyl-3,4-diphenyl-2-azetidin-1-ylidene)chromium (**4b**)*

Yield 0.66 g (33% relative to $[Cr(CO)_6]$), two isomers: *syn*/*anti* >9:1. IR (CH_2Cl_2): ν(CO) = 2056 m, 1936 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): *syn* isomer: δ = 7.56–7.06 (m, 10 H, 2 Ph), 6.07 (d, J = 4.6 Hz, 1H, 3-CH), 4.73 (sept, J = 6.8 Hz, 1H, $CHMe_2$), 4.41 (d, J = 4.6 Hz, 1H, 4-CH), 1.41 (d, J = 6.7 Hz, Me), 1.36 (d, J = 6.8 Hz, 3H, Me); *anti* isomer: δ = 7.56–7.06 (m, 2 Ph), 5.38 (d, J ca. 1.5 Hz, 3-CH), 4.5 (sept, $CHMe_2$), 3.92 (d, J ca. 1.5 Hz, 4-CH), 1.52 (d, J = 6.7 Hz, Me), 1.00 (d, J = 6.8 Hz, Me);. ^{13}C-NMR ($CDCl_3$): *syn* isomer: δ = 290.5 (C1), 222.9 (*trans*-CO), 217.6 (*cis*-CO), 134.1, 133.4, 130.3, 128.4, 128.0, 127.8, 127.5, 127.3 (2 aryl), 77.5 (C3), 65.5 (C4), 54.8 (N-C*H*Me_2), 22.7, 20.5 (2 Me). MS: m/z (%) = 441 (2) [M^+], 357 (2) [M^+–3CO], 301 (41) [M^+–5CO], 259 (45) [M^+–5CO–CMe_2], 206 (48) [M^+–$Cr(CO)_5$–CMe_2H]. Anal. Found: C, 62.55; H, 4.64; N, 3.23. $C_{23}H_{19}CrNO_5$ (441.4) Calc.: C, 62.59; H, 4.34; N, 3.17%.

*4.3.3. Pentacarbonyl(N-ethyl-3,4-diphenyl-2-azetidin-1-ylidene)molybdenum (**5a**)*

Yield 0.25 g (14% relative to $[Mo(CO)_6]$), two isomers: 90% *syn*, 10% *anti*. IR (CH_2Cl_2): ν(CO) = 2064 m, 1934 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): *syn* isomer: δ = 7.70–6.94 (m, 10H, 2 Ph), 6.08 (d, J = 4.4 Hz, 1H, 3-CH), 4.38 (d, J = 4.2 Hz, 1H, 4-CH), 4.15 (dq, ^2J = 14.6 Hz, ^3J = 7.3 Hz, 1H, C*H*HMe), 3.77 (dq, ^2J = 14.6 Hz, ^3J = 7.3 Hz, 1H, CH*H*Me), 1.38 (t, J = 7.3 Hz, 3H, Me). ^{1}H-NMR ($CDCl_3$): *anti* isomer: δ = 7.70–6.94 (m, 10H, 2 Ph), 5.41 (d, J = 1.5 Hz, 3-CH), 4.00 (dq, ^2J = 14.6 Hz, ^3J = 7.3 Hz, C*H*HMe), 3.97 (d, J = 1.5 Hz, 4-CH), 3.47 (dq, ^2J = 14.6 Hz, ^3J = 7.3 Hz, CH*H*Me), 1.36 (t, J = 7.3 Hz, Me). ^{13}C-NMR ($CDCl_3$): δ = 281.5 (C1), 212.8, (*trans*-CO), 206.5 (*cis*-CO, *syn*), 206.4 (*cis*-CO, *anti*), 133.9, 132.6, 132.1, 130.0, 129.8, 129.5, 129.4, 129.0, 128.8, 128.3, 127.8, 127.3, 127.1, 126.6 (4 Ph), 83.6 (C3, *syn*), 77.5 (C3, *anti*), 66.6 (C4, *anti*), 65.0 (C4, *syn*), 45.9 (NCH_2, *syn*), 45.4 (NCH_2, *anti*), 13.2 (Me, *anti*), 12.9 (Me, *syn*). MS: m/z (%) =

473 (6) [M^+], 389 (12) [M^+–3CO], 333 (9) [M^+–5CO], 278 (100) [M^+–5CO–CNEt]. Correct elemental analysis could not be obtained probably due to unseparable impurities.

4.3.4. Pentacarbonyl(N-ethyl-3,4-diphenyl-2-azetidin-1-ylidene)tungsten (**6a**)

Yield 0.49 g (31% relative to [$W(CO)_6$]), two isomers: 90% *syn*, 10% *anti*. M.p. 124°C, IR (CH_2Cl_2): ν(CO) = 2064 m, 1927 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): *syn* isomer: $\delta = 7.43–6.95$ (m, 10H, 2 Ph), 6.03 (d, $J = 4.5$ Hz, 1H, 3-CH), 4.41 (d, $J = 4.4$ Hz, 1H, 4-CH), 4.14 (dq, $^2J = 14.6$ Hz, $^3J = 7.3$ Hz 1H, C*H*HMe), 3.74 (dq, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz 1H, CH*H*Me), 1.39 (t, $J = 7.3$ Hz, 3H, Me). ^{1}H-NMR ($CDCl_3$) *anti* isomer: $\delta = 7.43–6.95$ (m, 2 Ph), 5.42 (d, $J = 1.2$ Hz, 3-CH), 3.95 (m, C*H*HMe), 3.80 (d, 4-CH), 3.40 (m, CH*H*Me), 1.34 (t, $J = 7.3$ Hz, Me). ^{13}C-NMR ($CDCl_3$): $\delta = 267.2$ (C1), 202.9 (*trans*-CO), 197.6 (*cis*-CO, $J_{WC} = 80.4$ Hz, *syn*), 197.3 (*cis*-CO, *anti*), 133.7, 132.7, 130.0, 128.5, 128.3, 127.9, 127.4, 126.5 (2 Ph), 77.5 (C3), 68.4 (C4, *anti*), 65.9 (C4, *syn*), 46.2 (CH_2, *syn*), 45.5 (CH_2, *anti*), 13.1 (Me, *anti*), 12.8 (Me, *syn*). MS: m/z (%) = 559 (7) [M^+], 475 (15) [M^+–3CO], 419 (18) [M^+–5CO], 364 (100) [M^+–5CO–CNEt], 178 (40) [M^+–5CO–CNEt–W–2H]. Anal. Found: C, 47.25; H, 3.06; N, 2.50. $C_{22}H_{17}NO_5W$ (559.2) Calc.: C, 7.12; H, 3.19; N, 2.56%.

4.3.5. Pentacarbonyl(N-isopropyl-3,4-diphenyl-2-azetidin-1-ylidene)tungsten (**6b**)

Yield 0.62 g (38% relative to [$W(CO)_6$]), two isomers: 90% *syn*, 10% *anti*. M.p. 158°C. IR (CH_2Cl_2): ν(CO) = 2068 m, 1925 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): *syn* isomer: $\delta = 7.40–7.02$ (m, 10H, 2 Ph), 5.98 (d, $J = 4.6$ Hz, 1H, 3-CH), 4.57 (sept, 1H, $J = 6.7$ Hz, C*H*Me_2), 4.37 (d, $J = 4.6$ Hz, 1H, 4-CH), 1.41 (d, $J = 6.7$ Hz, 3H, Me), 1.33 (d, $J = 6.8$ Hz, 3H, Me). ^{1}H-NMR ($CDCl_3$) *anti* isomer: $\delta = 7.40–7.02$ (m, 2 Ph), 5.39 (d, $J = 1.6$ Hz, 3-CH), 4.42 (sept, C*H*Me_2), 3.87 (d, $J = 1.6$ Hz, 4-CH), 1.47 (d, $J = 6.7$ Hz, Me), 1.01 (d, $J = 6.8$ Hz, Me). ^{13}C-NMR ($CDCl_3$): $\delta = 267.7$ (C1), 202.9 (*trans*-CO), 197.8 ($J_{WC} = 128.1$ Hz, *cis*-CO, *syn*), 197.4 (*cis*-CO, *anti*), 134.1, 133.4, 130.2, 129.2,129.0, 128.0, 127.6, 127.3 (2 Ph), 77.5 (C3), 67.4 (C4, *anti*), 65.5 (C4, *syn*), 55.9 (*C*HMe_2, *syn*), 53.0 (*C*HMe_2, *anti*), 22.4, 20.4 (2 Me, *syn*), 21.3, 21.0 (2 Me, *anti*). MS: m/z (%) = 573 (3) [(M^+], 489 (10) [M^+–3CO], 364 (100) [M^+–5CO–CNPr], 179 (19) [M^+–$W(CO)_5$–CNPr–H]. Anal. Found: C, 48.19; H, 3.36; N, 2.44. $C_{23}H_{19}NO_5W$ (573.3) Calc.: C, 48.20; H, 3.26; N, 2.42%.

4.4. Reactions of complex **3** with carbodiimides

The reactions of complex **3** with carbodiimides [RN=C=NR; R, R = cyclohexyl, isopropyl] in 3–4 ml of CH_2Cl_2 and the subsequent purification of the reaction products were carried out analogously to those with imines. The resulting complexes **7** and **8** were characterized by IR, MS, ^{1}H-NMR and ^{13}C-NMR spectroscopy and by elemental analysis.

4.4.1. Pentacarbonyl(N-cyclohexyl-3-cyclohexylimino-4-phenyl-2-azetidin-1-ylidene)tungsten (**7**)

Yield 0.38 g (21% relative to [$W(CO)_6$]). M.p. 132°C. IR (CH_2Cl_2): ν(CO) = 2066 m, 1933 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 7.68–7.10$ (m, 5H, aryl), 4.58 (s, 1H, 4-CH), 4.00 (m, br, 1H, NCH), 2.90 (m, br, 1H, NCH), 2.28–0.84 (m, br, 20H, 2 cyclohexyl). ^{13}C-NMR ($CDCl_3$): $\delta = 270.5$ (C1), 203.7 (*trans*-CO), 196.4 (*cis*-CO), 153.5 (C3), 133.4, 129.2, 128.4, 128.1 (Ph), 72.2 (C4), 62.7, 57.2 (NCH), 34.2, 33.0, 30.4, 29.8, 25.5, 25.4, 25.3, 24.9, 24.0, 23.8 (CH_2). MS: m/z (%) = 632 (0.6) [M^+], 548 (2) [M^+–3CO], 492 (1) [M^+–5CO], 327 (3) [M^+–5CO-2 cyclohexyl], 117 (100) [M^+–$W(CO)_5$–2 cyclohexyl]. Anal. Found: C, 48.91; H, 4.78; N, 4.16. $C_{26}H_{28}N_2O_5W$ (632.4) Calc.: C, 49.38; H, 4.46; N, 4.43%.

4.4.2. Pentacarbonyl(N-isopropyl-3-isopropylimino-4-phenyl-2-azetidin-1-ylidene)tungsten (**8**)

Yield 0.16 g (10% relative to [$W(CO)_6$]). IR (CH_2Cl_2): ν(CO) = 2069 m, 1928 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 7.51–7.14$ (m, 5H, aryl), 4.64 (s, 1H, 4-C), 4.45 (sept, $J = 6.8$ Hz, 1H, C*H*Me_2), 3.29 (sept, $J = 6.3$ Hz, 1H, C*H*Me_2), 1.71 (d, 3H, $J = 6.5$ Hz, Me), 1.65 (d, 3H, $J = 6.5$ Hz, Me), 1.09 (d, 3H, $J = 5.8$ Hz, Me) 0.84 (d, 3H, $J = 6.0$ Hz, Me). ^{13}C-NMR ($CDCl_3$): $\delta = 270.6$ (C1), 204.8 (*trans*-CO), 196.3 (*cis*-CO), 153.3 (C3), 133.7, 129.3, 128.5, 128.2 (aryl), 72.4 (C4), 55.0, 49.9 (CHMe_2), 29.7, 24.2, 23.1, 20.4 (Me). MS: m/z (%) = 552 (2) [M^+], 468 (4) [M^+–3CO], 412 (7) [M^+–5CO], 367 (10) [M^+–5CO–H–Pr], 300 (10) [M^+–5CO–H–^{i}Pr], 300 (10) [M^+–5CO–H–^{i}Pr–C=N–^{i}Pr]. Correct elemental analysis could not be obtained probably due to the unseparable impurities.

4.5. Oxidation of **4a**,**b** to form the β-Lactams **9a**,**b**

Ca. 4.0 g of silica gel was added to a solution of 0.30 g *syn*/*anti*-**4a** [0.70 mmol] or *syn*/*anti*-**4b** [0.68 mmol] in 100 ml of acetone. The slurry was vigorously stirred and 0.60 g of ammonium ceric(IV) nitrate was added. The mixture was stirred for 2–3 days at r.t. until the IR spectrum indicated that the complexes **4a** and **4b**, respectively, were completely consumed. The mixture was filtered. The solvent of the filtrate was removed in vacuo to give the β-lactams as colorless oils.

4.5.1. syn/anti-N-Ethyl-3,4-diphenylazetidin-1-one (**9a**)

Yield 0.24 g (81% relative to complex **4a**). IR (CH_2Cl_2): ν(CO) = 1746 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 7.47–6.91$ (m, 10H, 2 aryl), 4.96 (d, 1H, $J = 5.6$ Hz,

3-CH), 4.74 (d, 1H, $J = 7.6$ Hz, 4-CH), 3.60 (dq, $^2J = 15.2$ Hz, $^3J = 5.6$ Hz, 1H, CH_2), 3.00 (dq, $^2J = 15.2$ Hz, $^3J = 7.6$ Hz, 1H, CH_2), 1.09 (t, $J = 7.6$ Hz, 3H, Me). ^{13}C-NMR ($CDCl_3$): $\delta = 167.9$ (*C*=O), 135.2, 132.8, 128.6, 128.0, 127.9, 127.8, 127.4, 126.7 (2 aryl), 60.5 (C3), 59.8 (NCH_2), 35.5 (C4), 12.7 (Me). MS: m/z (%) = 251 (7) [M^+], 180 (100) [M^+–C(O)NEt], 90 (31) [M^+–C(O)NEt–C(H)Ph].

*4.5.2. syn/anti-N-Isopropyl-3,4-diphenylazetidin-1-one (**9b**)*

Yield 0.25 g (84% relative to complex **4b**). IR (CH_2Cl_2): ν(CO) = 1742 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 7.47$–6.91 (m, 10H, 2 aryl), 5.02 (d, 1H, $J = 5.6$ Hz, 3-CH), 4.76 (d, 1H, $J = 5.6$ Hz, 4-CH), 3.87 (s, $J = 6.7$ Hz, 1H, C*H*Me_2), 1.36, 1.15 (2 t, $J = 6.7$ Hz, 3H, Me). ^{13}C-NMR ($CDCl_3$): $\delta = 167.9$ (*C*=O), 135.2, 132.8, 128.6, 128.0, 127.9, 127.8, 127.4, 126.7 (2 Ph), 60.5 (C3), 59.8 ($CHMe_2$), 35.5 (C4), 12.7 (Me). MS: m/z (%) = 265 (3) [M^+], 180 (100) [M^+–C(O)N^{i}Pr].

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