Synthesis and Structures of Low-Valent Tungsten Complexes Bearing Chiral Oxazoline-Derived Ligands

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Dedicated to Prof. Dr. Dr. h. c. mult. Günther Wilke on the occasion of his 70th birthday
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The synthesis of low-valent tungsten (0 and II) complexes bearing chiral bidentate phosphino-oxazoline or bisoxazoline ligands is described. The structures of four of the complexes have been determined by single crystal X-ray analyses. Tungsten(II)-allyl complexes of the type $[\text{W}(\text{CO})_2(\text{PN})(\text{C}_3\text{H}_5)\text{Cl}]$ (PN = phosphino-oxazoline) are fluxional in solution, but can be crystallized as single diastereoisomers. The complex $[\text{W}(\text{CO})_3(\text{PN})(\text{CH}_3\text{CN})]$, which also crystallizes as a single diastereoisomer, is readily oxidized in solution and solid state, in stark contrast to analogous compounds bearing four carbonyl ligands $[\text{W}(\text{CO})_4(\text{PN})]$ or $[\text{W}(\text{CO})_4(\text{NN})]$ (NN = bisoxazoline) which were found to be stable. $[\text{W}(\text{CO})_3(\text{PN})(\text{CH}_3\text{CN})]$ functions as a highly enantioselective catalyst in allylic substitution reactions with dimethyl sodiomalonate, whereas complexes of the type $[\text{W}(\text{CO})_3(\text{PN})(\text{Z}–\text{C}_3\text{H}_4\text{X})]$ (Z = H, Ph; X = Cl, Br) failed to yield allylic alkylation products.

Introduction

Over the last years, enantioselective Pd-catalyzed allylic substitution has developed into an efficient, versatile method for asymmetric synthesis [1]. Very high enantiomeric excesses can now be obtained with several types of substrates [2–6]. Nevertheless, some major problems still remain to be solved, among them the regioselectivity of nucleophilic attack in unsymmetrical allyl systems. Monosubstituted substrates 1, e.g., react with stabilized carbanions preferentially at the unsubstituted allyl terminus, affording mainly the achiral products 3 (eq. (1)). Trost et al. [7] have found a possible solution for this regioselectivity problem, using tungsten instead of palladium catalysts. With achiral tungsten complexes, the racemic products 2 (R = aryl) were formed with high regioselectivity. However, chiral tungsten complexes functioning as enantioselective catalysts for allylic substitutions have not been described so far.

The promising results obtained with chiral bisoxazoline and phosphino-oxazoline ligands of type 4 [3, 8] and 5 [4–6] in Pd-catalyzed enantioselective allylic substitution prompted us to prepare low-valent tungsten complexes with these ligands in order to evaluate their potential as enantioselective catalysts. Here we report the synthesis and structures of a series of chiral W(0) and W(II) carbonyl complexes derived from ligands 4, 5, and 6.

Experimental

All manipulations were performed on a vacuum line (argon) using standard Schlenk techniques or in a glove-box (nitrogen). Solvents for reactions were freshly distilled before use (THF and Et₂O from Na/benzophenone, hexane from Na, CH₃CN

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from CaH₂, CH₂Cl₂ from P₂O₅, degassed (freeze-thaw cycles) and argon-saturated. NMR: Varian Gemini 300 or VXR 400; ¹H and ¹³C; δ values in ppm from TMS; ³¹P: δ in ppm, referenced to (PhO)₃P=O (~18.0 ppm). IR: Perkin-Elmer 1600 FT; samples were prepared as KBr discs or as solutions (CH₃CN, CHCl₃, hexane), ν in cm⁻¹. MS: Varian MAT 212, FAB matrix: 3-nitrobenzyl alcohol (NBA), data reported as m/z (%). Optical rotations: Perkin-Elmer 141 polarimeter (cal rotations: Perkin-Elmer 141 polarimeter).

Materials

Cycloheptatriene (C₇H₈), allyl chloride, 3-phenyl-2-propenyl bromide and W(CO)₆: Fluka AG, used as received. [D₈]THF: Cambridge Isotope Labs; refluxed over and distilled from CaH₂.

Preparation of complexes 7, 8 and 9

The following procedure is typical: [W(CO)₃(CH₃CN)₃] (400 mg, 1.02 mmol) was suspended in THF (25 ml) and treated with C₇H₈ (116 mg, 1.5 mmol). After heating to 60 °C until CO evolution ceased (35 min), the mixture was cooled, then the volatiles removed in vacuo to afford a dark-brown oil. Fresh THF (25 ml) and 5 (392 mg, 1.05 mmol) was added; heating to 60 °C (1 h) afforded a red-orange solution. The solution was cooled, then the solvent evaporated to afford a red-brown oil which was applied to silica gel (42 g, 2 cm column) and eluted first with CH₂Cl₂ (200 ml) to separate small quantities of 10, and then with EtOAc (100 ml). Evaporation of the EtOAc fraction afforded a red-black powder, which was dissolved in CH₂Cl₂ (5 ml) and covered with a layer of hexane (25 ml). Storage at −14 °C for 10 days afforded 7 as dark-orange-red crystals (410 mg); a further crop of 56 mg was obtained by repeating the process with the evaporated mother liquor, total yield 466 mg (60%).

Complex 7: [W(CO)₅(CH₃CN)] P₂O₅ in CH₂Cl₂: m.p. 165–175 °C (dec.).

C₃₅H₁₀₇NO₃BrP₂W (810.38)

Calcd C 51.88 H 4.10 N 1.73%.

Found C 51.63 H 4.12 N 1.70%.
\[ [\alpha]_D^2 = +56.3 \text{ (c = 0.13, CHCl}_3) \]. IR (CHCl\(_3\)): \( \nu_{CO} = 1915, 1815 \text{ cm}^{-1} \). H NMR (CDCl\(_3\)): 8.48 (d, 1H, H - Ar, J = 9.7); 8.43 (d, 1H, H - Ar, J = 12.5); 7.95 (m, 1H, H - Ar); 7.69 (m, 2H, H - Ar); 7.52 (m, 7H, H - Ar); 7.34 (m, 4H, H - Ar); 6.88 (dd, 1H, H - Ar, J = 7.7, 8.0); 6.75 (dd, 1H, H - Ar, J = 8.0, 8.0); 6.69 (dd, 1H, H - Ar, J = 8.0, 8.0); 5.39 (dd, 1H, CHN, J = 9.0, 11.0); 4.13 (d, 1H, CHHO, J = 11.0); 3.84 (d, 1H, CHHO, J = 9.0); 3.42 (d, 1H, CH\(_{syn}\), J = 6.6); 3.31 (d, 1H, CH\(_{syn}\), J = 8.2); 3.05 (m, CH\(_{cent}\)); 1.72 (m, 1H, CH(CH\(_3\))\(_2\)); 1.63 (d, 1H, CH\(_{anti}\), J = 8.0); 0.42 (d, 3H, CH(CH\(_3\))\(_2\), J = 6.3); -0.35 (d, 3H, CH(CH\(_3\))\(_2\), J = 6.0). \(^{13}\)C NMR (CDCl\(_3\)): 218.2 (W - CO); only one W - CO observed due to low s/n; 170.3 (C = N); 139.9, 136.8, 136.3 (arom. C); 135.1 (d, arom. CH, J\(_{CP} = 11.0\)); 134.7, 134.6 (br s, arom. C); 132.6 (d, arom. C, J\(_{CP} = 6.0\)); 132.2 (d, arom. C - P, J\(_{CP} = 43.0\)); 132.1 (d, arom. H, J\(_{CP} = 7.0\)); 131.2 (d, arom. C, J\(_{CP} = 2.0\)); 131.1 (d, arom. C, J\(_{CP} = 2.0\)); 130.7, 130.5 (arom. C); 129.2, 129.1, 128.7, 126.9 (br s, arom. C); 96.5 (br s, allyl CH - Ph); 89.8 (br s, allyl CH); 76.6 (CH(O)); 68.2 (CHN); 39.9 (br s, allyl CH\(_2\)); 29.3 (CH\(_3\))\(_2\)); 18.9, 12.9 (CH\(_3\))\(_2\)). \(^{31}\)P NMR (CDCl\(_3\)): 24.9 (br s), MS (FAB\(^+\), NBA): 811 (M\(^+\), 4); 783 (M\(^+\) - CO, 4); 750 (M\(^+\), 0.37 mmol), 145 mg, 0.39 mmol) and Et\(_2\)O (8 ml) were mixed in a borosilicate test tube (15 x 1.5 cm) to form a colourless suspension. Under a static argon atmosphere and with stirring, the tube was illuminated (366 nm, ca. 10 cm from a TLC visualization lamp, 40 W). The suspension rapidly dissolved resulting in a bright yellow solution and, after 6 h, the solvent was removed under a stream of argon to afford a yellow oily residue that was applied to silica gel (2 x 18 cm). The column was eluted with hexane/Et\(_2\)O (9:1) and a single orange fraction collected. Evaporation afforded a red oil that was triturated with boiling hexane to afford 10 as a yellow microcrystalline solid (134 mg, 55%).

Complex 10: m.p. 195 - 200 °C.

\[ [\alpha]_D^2 = +96.3 \text{ (c = 0.25, CHCl}_3) \]. IR (CHCl\(_3\)): \( \nu_{CO} = 2009, 1880, 1847 \text{ cm}^{-1} \); in hexane: 2012, 1904s, 1886s, 1874s. H NMR (CDCl\(_3\)): 8.04 (m, 1H, H - Ar); 7.5 - 7.29 (m, 12H, H - Ar); 6.79 (m, 1H, H - Ar); 4.32 (dd, 1H, CHHO, J = 8.8, 8.3); 4.22 (dd, 1H, CHHO, J = 8.8, 6.5); 4.10 (m, 1H, CHN), 2.62 (m, 1H, CH(CH\(_3\))\(_2\)); 0.87 (d, 3H, CH(CH\(_3\))\(_2\), J = 7.1); 0.09 (d, 3H, CH(CH\(_3\))\(_2\), J = 6.8). \(^{13}\)C NMR (CDCl\(_3\)): 210.2 (d, W - CO, J\(_{CP} = 5.1\)); 209.5 (d, W - CO, J\(_{CP} = 32.4\)); 203.8 (d, W - CO, J\(_{CP} = 7.0\)); 201.4 (d, W - CO, J\(_{CP} = 6.8\)); 165.4 (C = N); 135.6 (d, arom. C - P, J\(_{CP} = 29.0\)); 134.2 (d, arom. CH, J\(_{CP} = 13.4\)); 133.4 (d, arom. C - P, J\(_{CP} = 39.9\)); 133.0 (d, arom. CH, J\(_{CP} = 12.6\)); 132.3 (d, arom. CH, J\(_{CP} = 5.1\)); 132.1 (d, arom. C - P, J\(_{CP} = 39.8\)); 131.5 (d, arom. CH, J\(_{CP} = 6.5\)); 131.3 (arom. CH); 130.7 (d, arom. CH, J\(_{CP} = 2.3\)); 130.3 (d, arom. CH, J\(_{CP} = 2.0\)); 129.8 (d, arom. C, J\(_{CP} = 13.0\)); 128.8 (d, arom. CH, J\(_{CP} = 9.8\)); 128.7 (d, arom. CH, J\(_{CP} = 10.1\)); 79.3 (CHN); 66.9 (CH(O)); 28.8 (CH(CH\(_3\))\(_2\)); 19.1, 12.2 (CH(CH\(_3\))\(_2\)). \(^{31}\)P NMR (CDCl\(_3\)): 22.5 (s), [D\(_8\)jTHF: 26.0 (s, J\(_{PHPS}^{31P} = 236\)). MS (FAB\(^+\), KCl, NBA): 708 (M\(^+\) + K, 20); 669 (M\(^+\), 99); 641 (M\(^+\) - CO, 85); 613 (M\(^+\) - CO, 80); 585 (M\(^+\) - 3 CO, 7); 557 (M\(^+\) - 4 CO, 11).
isotope cluster 562–553: obs. (calc.) 4.2 (3.1), 21.8 (22.5), 76.2 (83.7), 33.7 (25.7), 100.0 (100.0), 72.5 (60.5), 82.6 (73.7), 22.1 (0.1), 13.9 (0.3).

Following a similar procedure with ligand 4 but omitting chromatography, complex 11 was obtained as a yellow-green solid. Recrystallization from EtOAc afforded bright yellow crystals (50%). M.p. 215–220 °C (darkens at 170 °C).

\[ C_{21}H_{30}N_{2}O_{6}W \] (590.33)

Calcd C 42.73 H 5.12 Found C 42.71 H 4.98 N 4.75 O 16.26%

[\alpha]_D^{27} = -344.6 (c = 0.41, CHCl₃). \nu_{CO} (CHCl₃): 2005 m, 1881 s, 1860 s, 1814 m; in hexane: 2006 m, 1876 s, 1846 s, 1830 s. \text{H NMR (CDCl₃):} 4.52 (dd, 2H, CHHO, J = 2.4, 9.2); 4.35 (dd, 2H, CHN, J = 9.2, 8.4); 4.20 (dd, 2H, CHHO, J = 2.4, 8.4); 1.57 (s, 6H, C(CH₃)₂); 1.03 (s, 18H, C(CH₃)₃). \text{13C NMR (CDCl₃):} 213.1 (W (CO)₂, \nu \gamma = 87); 203.8 (W (CO)₂, W = 67); 173.9 (C=N); 81.5 (CH₂O); 77.3 (CHN); 40.9 (C(CH₃)₂); 35.2 (C(CH₃)₂); 26.5 (C(CH₃)₃); 24.7 (C(CH₃)₃).

MS (FAB+, NBA): 590 (M⁺, 14); 562 (M⁺-CO, 100); isotope cluster 566-558: obs. (calc.) 1.4 (0.1), 0.7 (0.3); 534 (M⁺-2CO, 13); 506 (M⁺-3CO, 5); 295 (4⁺ + H, 76).

Preparation of complex 12

\[ [W(CO)₃(CH₃CN)₃] \] (300 mg, 0.76 mmol) was suspended in a solution of 5 (500 mg, 1.34 mmol) in THF (15 ml) and heated to 60 °C for 3 h with vigorous stirring. After this time, the reaction was cooled to 25 °C and filtered. The deep-red filtrate was covered with a layer of hexane (20 ml), and stored at 20 °C for 9 days. The resultant deep-red solid was separated from the brown-orange mother liquor by filtration and washed with 2 x 20 ml portions of hexane/THF (1:1). Drying in vacuo afforded complex 12-THF as dark-red needles and blocks (364 mg, 63%).

Complex 12-THF: m.p. 112–116 °C (dec. >120 °C).

\[ C_{33}H_{35}N_{2}O_{5}PW \] (754.48)

Calcd C 52.54 H 4.68 N 3.71%

Found C 52.42 H 4.84 N 3.72%

IR (KBr): \nu_{CO} = 1907 s, 1792 s. \text{P NMR ([D₈]THF):} 32.00 (s, J_{N-P-W} = 227), 32.04 (s). MS (FAB⁺, NBA): 669 (M⁺-CH₃CN+CO, 2.2) isotope cluster 672–667: obs. (calc.) 0.6 (0.6), 1.8 (1.8), 0.8 (0.7), 2.2 (2.2), 1.4 (1.4), 1.4 (1.6); 641 (M⁺-CH₃CN, 2.1); 613 (M⁺-CH₃CN-CO, 1.6); 557 (M⁺-CH₃CN-3CO, 2.1); 390 (5⁺ + OH, 100).

Results and Discussion

Synthesis

W(II)-allyl complexes 7, 8 and 9 were prepared in good to moderate yield (7: 60%, 8: 77%, 9: 47%) by a modification of the method of Faller et al. [13] that involves sequential addition of the corresponding allyl halide to a suspension of \[ [W(CO)₅(CH₃CN)] \] in THF and then adding ca. 1 equivalent of ligand 5 or 6. Purification was achieved by chromatography on silica gel and then crystallization or precipitation. Complexes 7 and 8 were air-stable as solids and moderately stable in solution, complex 9 slowly decomposed on storage in air.

W(0) tetracarbonyl complexes 10 and 11 were readily synthesized in moderate yield (50–55%) by low power photolysis (366 nm) of \[ [W(CO)₆] \] in the presence of the corresponding ligand 5 or 4 in Et₂O. Both complexes were remarkably air-stable in the solid state, but slowly decomposed in oxidizing solvents (e.g. CHCl₃). Complex 10 could only be obtained in microcrystalline form.

The W(0) tricarbonyl complex 12 was obtained in 63% yield by displacing two of the three (CH₃CN) ligands from a suspension of \[ [W(CO)₅(CH₃CN)] \] in THF at 60 °C with ligand 5 (1.5 to 1.8 eq.). The product was isolated as a deep-red crystalline complex containing 1 equivalent of THF and was stored at −14 °C under argon. In the solid state at 25 °C the complex decomposed slowly, however, in solution in the presence of oxygen or oxidizing solvents (e.g. CHCl₃) rapid decomposition was observed. Whilst the
more convenient (air-stable, sublimable, highly soluble) precursor \([\text{W(CO)}_3(\text{cycloheptatriene})]\) \([11, 12]\) also reacted with ligand 5, the product was not isolable as a crystalline material, but only as an unstable brown powder which was a mixture (by IR spectroscopy). \([\text{W(CO)}_2(1,3\text{-cyclohexadiene})]\) \([11]\), \([\text{W(CO)}(3\text{-hexyne})_3]\) \([14]\) and \([\text{W(methylvinyl ketone)}_3]\) \([11]\) failed to react with ligand 5 under identical conditions.

**Structure and reactivity**

X-ray analysis of complexes 7 and 9 (Fig. 1 and 2) \([15]\) and comparison of the \(^1\text{H} \text{COSY}\) and \(^{13}\text{C} \text{NMR}\) spectra of 7, 8 and 9 confirmed the proposed \(\text{W(II)(allyl)}\) structures. Complexes 7 and 9 are single diastereoisomers in the solid state and the structures can be described as pseudo-octahedral if the allyl ligand is considered as a single vertex.

In both complexes, the nitrogen atom of the oxazoline ring is located \textit{trans} to the allyl ligand with the phosphine group \textit{trans} to CO and allyl \textit{cis} to the halide. The structures are of similar geometry to complexes of the type \([\text{M(CO)}_2(\text{PP})(\text{C}_3\text{H}_5)X]\) \((\text{M} = \text{Mo, W}; \ X = \text{Cl, Br, I}; \ \text{PP} = \text{diposphine})\) which have been described by Faller et al. \([13]\).

In CDCl\(_3\) solution at ambient temperature, \(^1\text{H}\) and \(^{13}\text{C} \text{NMR}\) signals corresponding to the allyl systems are broad in all three complexes. Despite broad \(^{31}\text{P} \text{NMR}\) signals \((\omega_{1/2} = 120–280 \text{ Hz})\) the \(^1\text{H}\) and \(^{13}\text{C} \text{NMR}\) signals of the phosphino-oxazoline ligand \((5 \text{ or } 6)\) are well resolved (slight broadening in complex 8). On cooling complex 7 in CDCl\(_3\), broadening reached a maximum at 0 °C. Below 0 °C, two species became apparent although they were not fully resolved at \(-60 \degree\text{C} \ (\text{ca. 5:1 ratio at } -60 \degree\text{C}).\) The major species is assumed to be that relating to the solid state structure; the \(^1\text{H} \text{NMR}\) signals of the allyl and phosphino-oxazoline ligand were broad but could be assigned by correlation with the \(^1\text{H} \text{COSY}\) spectrum at 25 °C.

The \(^1\text{H} \text{NMR}\) spectrum of complex 8 at 25 °C was similar in resolution to that of complex 7 at \(-60 \degree\text{C}.\) On cooling, the spectra became increasingly resolved and at \(-60 \degree\text{C} \text{ a minor isomer was also visible (ca. 10:1 ratio). At this temperature, the allyl system of the major isomer ceased to be fluxional at the NMR time scale as evidenced by well resolved signals corresponding to allylic and \textit{ortho/meta}-aryl protons in the phenylallyl unit.

Treatment of complex 8 with excess NaCH\((\text{CO}_2\text{Me})_2\) \((8 \text{ equivalent})\) in THF at 60 °C resulted in complete reaction within 2 h (tlc). However, after aqueous work-up the only organic compound detectable \((^1\text{H} \text{NMR})\) was ligand 5. The reaction of complexes 7 and 8 with NaCH\((\text{CO}_2\text{Me})_2\) was monitored by \(^1\text{H}\) and \(^{31}\text{P} \text{NMR}\) spectroscopy in [D\(_8\)]THF, which revealed that the reaction results in complete displacement of ligand 5 and precipitation of NaCl (or NaBr, respectively) with no detectable allylic alkylation product. The use of a “harder” nucleophile did result in allylic alkylation; hence, treatment of complex 8 with \(n\)-BuLi \((1 \text{ equivalent, } -78 \degree\text{C to } 25 \degree\text{C})\) followed by aqueous work-up resulted in a ca. 50% conversion of 8 to a mixture of 1-phenyl-1-heptene and 3-phenyl-1-heptene \((\text{ca. 1:1, } ^1\text{H} \text{NMR}).\) Ligand displacement with a “soft” nucleo-
phile has also been reported by Brisdon and Griffin [16] for the reaction of 
[Mo(CO)₂(bpy)(C₃H₅)X] (bpy = 2,2'-bipyridine; X = e.g. Cl) with sodium acetylacetonate, however, Trost and Hung [7a] describe the formation of C₃H₅-CH(CO₂Me)₂ in 65% yield by reaction of NaCH(CO₂Me)₂ with [W(CO)₂(dppe)(C₃H₅)Br] (dppe = bis-diphenylphosphinoethane) in the presence of one equivalent dppe.

W(0) tetracarbonyl complexes 10 and 11 are fairly inert towards mild oxidants (e.g. CHCl₃, C₃H₅Cl) or substitution of the carbonyl groups by donor solvents (e.g. CH₃CN, THF) [17]. Both 10 and 11 display similar IR f_CO bands in CHCl₃ or hexane solutions. In the solid state structure of complex 11 (Fig. 3 [15]), the bisoxazoline ligand adopts a distorted, non-symmetric conformation, while the ¹H and ¹³C NMR spectra of 11 in CDCl₃ are consistent with a (presumably time-averaged) C₂-symmetric structure.

The W(0) tricarbonyl complex 12 crystallized as a single diastereoisomer, in which the readily dissociable CH₃CN ligand and the isopropyl group of the oxazoline ring are trans to each other (Fig. 4 [15]). In [D₈]THF solution two species were observed by ³¹P NMR spectroscopy (at 25 °C: 32.00, 32.04 ppm, singlets in ca. 3:1 ratio); addition of excess CH₃CN did not affect the ratio.

Consequently, the reactions of [W(CO)₃(CH₃CN)₃] and [W(CO)₃(cycloheptatriene)] with ligand 5 in [D₈]THF were monitored by ¹H and ³¹P NMR spectroscopy. An equimolar solution of 5 and [W(CO)₃(cycloheptatriene)] (0.034 M) after 35 min at 25 °C displayed the following ³¹P signals: two singlets (32.01, 32.05 ppm, ca. 3:1) and a pair of doublets (37.17, 27.51 ppm, J_PP = 23 Hz) – together with residual free ligand 5 (~2.97 ppm). On heating the mixture (60 °C, 3 min), then cooling back to 25 °C, a CIDNP effect was observed for the signals of the complexes, but not for those of the free ligand 5. The singlets are assigned to two diastereoisomers of [W(CO)₃(5)([D₈]THF)] based on the ³¹P NMR spectrum of complex 12. A possible explanation for the pair of doublets is the formation of an additional complex of the type σac-[W(CO)₃(5)₂] where one of the two phosphino-oxazoline ligands acts as a monodentate phosphine ligand – the 23 Hz P–P coupling being consistent with a mutually cis orientation of the two phosphorus nuclei. With [W(CO)₃(CH₃CN)₃] the reaction was slower but still generated identical major species – together with tetracarbonyl complex 10 as a minor side product in variable yield. In both procedures, additional minor species were observed but structures could not readily be assigned.

Tricarbonyl complex 12 functions as a highly enantioselective catalyst for the allylic substitution of aryl-propenyl phosphates 13 with NaCH(CO₂Me)₂ (eq. (2)) [18]. The regioselectivity is opposite to that of Pd phosphino-oxazoline catalysts which afford, almost exclusively, the achiral product 15 [19]. Significantly, the more stable W(0) tetracarbonyl complexes 10 and 11 were not active as catalysts.
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