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

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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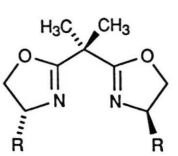
Chiral Tungsten Complexes, Phosphino-oxazoline Ligands, Bisoxazoline Ligands, Tungsten Allyl Complexes, Asymmetric Catalysis

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 $[W(CO)_2(PN)(C_3H_5)Cl]$ (PN = phosphino-oxazoline) are fluxional in solution, but can be crystallized as single diastereoisomers. The complex $[W(CO)_3(PN)(CH_3CN)]$, 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 $[W(CO)_4(PN)]$ or $[W(CO)_4(NN)]$ (NN = bisoxazoline) which were found to be stable. $[W(CO)_3(PN)(CH_3CN)]$ functions as a highly enantioselective catalyst in allylic substitution reactions with dimethyl sodiomalonate, whereas complexes of the type $[W(CO)_2(PN)(Z\text{-}C_3H_4)X)]$ (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.**



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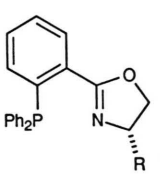

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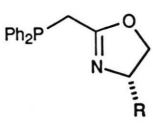
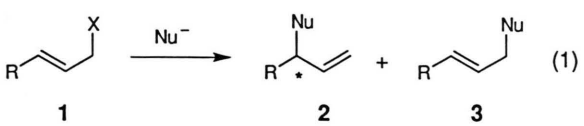


6 R = *i*Pr



1 **2** **3** (1)

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 Et_2O from Na/benzophenone, hexane from Na, CH_3CN

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from CaH_2, CH_2Cl_2 from P_2O_5), degassed (freeze-thaw cycles) and argon-saturated. NMR: Varian Gemini 300 or VXR 400; ^1H and ^{13}C: δ values in ppm from TMS; ^{31}P: 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 (CH_3CN, $CHCl_3$, hexane), $\tilde{\nu}$ in cm^{-1}. MS: Varian MAT 212, FAB matrix: 3-nitrobenzyl alcohol (NBA), data reported as *m/z* (%). Optical rotations: Perkin-Elmer 141 polarimeter (estimated accuracy ± 5%). Flash column chromatography: Chemie Uetikon C560 silica gel (35–70 μm).

Materials

Cycloheptatriene (C_7H_8), allyl chloride, 3-phenyl-2-propenyl bromide and $W(CO)_6$: Fluka AG, used as received. [D_8]THF: Cambridge Isotope Labs; refluxed over and distilled from CaH_2. $[W(CO)_3(CH_3CN)_3]$ [9, 10]: A suspension of $W(CO)_6$ in CH_3CN (*ca.* 40 g/l) was refluxed until IR spectroscopy of reaction samples indicated >95% $[W(CO)_3(CH_3CN)_3]$ (*ca.* 12 to 14 d). Concentration and cooling afforded a yellow solid which was collected by filtration, washed and then recrystallized (CH_3CN, −14 °C). IR (CH_3CN): $\tilde{\nu}_{CO}$ = 1911 s, 1791 s; $[W(CO)_6]$, $[W(CO)_5(CH_3CN)]$ and $[W(CO)_4(CH_3CN)_2]$ were not detected [10]). The isolated complex decomposes on storage, but is indefinitely stable when stored under CH_3CN at −14 °C. $[W(CO)_3(C_7H_8)]$ [11] was prepared from $[W(CO)_3(CH_3CN)_3]$ by a modification of the literature procedures [11, 12]: hexane was replaced by THF since suspensions of crystalline $[W(CO)_3(CH_3CN)_3]$ in refluxing hexane tend to decompose before reacting with C_7H_8. $[W(CO)_3(C_7H_8)]$ can be separated from a minor (unidentified) impurity by fractional sublimation (impurity: ≤ 100 °C, 10^{-1} Torr, $[W(CO)_3(C_7H_8)]$: 120 °C, 4×10^{-2} Torr).

Preparation of complexes **7, 8** *and* **9**

The following procedure is typical: $[W(CO)_3(CH_3CN)_3]$ (400 mg, 1.02 mmol) was suspended in THF (25 ml) and treated with C_3H_5Cl (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 CH_2Cl_2 (200 ml) to separate small quantities of **10,** and then with EtOAc (100 ml). Evaporation of the EtOAc fraction afforded a red-black oil, which was dissolved in CH_2Cl_2 (5 ml) and covered with a layer of hexane (25 ml). Storage at −14 °C for 10 days afforded **7**·CH_2Cl_2 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**·CH_2Cl_2: m.p. 165–175 °C (dec.).

$C_{30}H_{31}NO_3Cl_3PW$ (786.86)

Calcd	C 46.51	H 4.03	N 1.81%,
Found	C 46.42	H 4.01	N 1.83%.

$[\alpha]_D^{27}$ = +53.1 (*c* = 0.31, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}_{CO}$ = 1926 s, 1823 s. ^1H NMR ($CDCl_3$): 8.05 (m, 1H, H–Ar); 7.62–7.28 (m, 12H, H–Ar); 7.04 (m, 1H, H–Ar); 5.31 (s, 2H, CH_2Cl_2); 5.03 (m, 1H, CHN); 4.49 (dd, 1H, C$\underline{H}$HO, *J* = 8.9, 9.1); 4.39 (dd, 1H, CH$\underline{H}$O, *J* = 4.0, 9.1); 3.56 (m, 1H, CH_{syn}); 2.94 (m, 3H, CH_{cent}, CH_{syn}, C$\underline{H}(CH_3)_2$); 1.65 (m, 1H, CH_{anti}); 1.42 (m, 1H, CH_{anti}); 0.99 (d, 3H, $CH(C\underline{H}_3)_2$, *J* = 7.0); 0.00 (d, 3H, $CH(C\underline{H}_3)_2$, *J* = 6.7). ^{13}C NMR ($CDCl_3$): 216.6 (d, W–CO, J_{CP} = 6.8); 214.7 (d, W–CO, J_{CP} = 34.2, $J_{C^{183}W}$ = 76); 168.2 (C=N); 134.6 (arom. CH); 134.4 (d, arom. CH, J_{CP} = 11.5); 133.2 (d, arom. C–P, J_{CP} = 34.9); 132.8, 132.7 (arom. CH); 132.4 (d, arom. CH, J_{CP} = 7.5); 132.3 (d, arom. CH, J_{CP} = 5.7); 131.1, 130.8 (arom. CH); 130.1 (d, arom. C–P, J_{CP} = 37.9); 130.0 (d, arom. C, J_{CP} = 12.3); 129.5 (d, arom. C–P, J_{CP} = 34.4); 129.0 (d, arom. CH, J_{CP} = 9.2); 128.6 (d, arom. CH, J_{CP} = 9.0); 81.0 (allyl CH); 68.5 (allyl CH_2); 67.1 (CH_2O); 56.7 (CHN); 53.4 (CH_2Cl_2); 50.6 (allyl CH_2); 29.3 ($\underline{C}H(CH_3)_2$); 19.2, 12.5 ($CH(\underline{C}H_3)_2$). ^{31}P NMR ($CDCl_3$): 13.4 (br s). MS (FAB$^+$, NBA): 689 (M^+, 0.8); 661 (M^+–CO, 100; isotope cluster 667–659: obs. (calc.) 0.6 (1.1), 6.7 (7.1), 24.5 (25.0), 27.7 (28.6), 93.0 (93.3), 41.2 (40.2), 100 (100), 52.1 (50.5), 59.2 (58.3); 633 (M^+–2 CO, 40); 626 (M^+–CO–Cl, 20); 592 (M^+–C_3H_5–2 CO, 38). Slow evaporation of $CHCl_3$ solutions afforded **7** as bright orange crystals, free of solvent of crystallization.

Complex **8:** precipitated by slow removal of CH_2Cl_2 (rotary evaporation, 45 °C, 560 Torr) from a CH_2Cl_2/*n*-hexane solution, brick-red powder (77%). M.p. 135–140 °C (dec.).

$C_{35}H_{33}NO_3BrPW$ (810.38)

Calcd	C 51.88	H 4.10	N 1.73%,
Found	C 51.63	H 4.12	N 1.70%.

$[\alpha]_D^{27}$ = +56.3 (*c* = 0.13, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}_{CO}$ = 1915 s, 1815 s. ^{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, C<u>H</u>HO, *J* = 11.0); 3.84 (d, 1H, CH<u>H</u>O, *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, C<u>H</u>$(CH_3)_2$); 1.63 (d, 1H, CH_{anti}, *J* = 8.0); 0.42 (d, 3H, CH(C<u>H</u>$_3)_2$, *J* = 6.3); –0.55 (d, 3H, CH(C<u>H</u>$_3)_2$, *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 <u>C</u>H–Ph); 89.8 (br s, allyl <u>C</u>H); 76.6 (CH_2O); 68.2 (CHN); 39.9 (br s, allyl <u>C</u>H_2); 29.3 ($CH_3)_2$<u>C</u>); 18.9, 12.9 (<u>C</u>$H_3)_2$C). ^{31}P NMR ($CDCl_3$): 24.9 (br s). MS (FAB$^+$, NBA): 811 (M^+, 4); 783 (M^+–CO, 44); 755 (M^+–2CO, 8); 730 (M^+–Br, 55); isotope cluster 735–727: obs. (calc.) 1.0 (0.5), 2.7 (3.5), 15.5 (16.8), 43.5 (44.3), 19.6 (19.6), 54.5 (54.5), 36.0 (35.1), 39.6 (37.1); 702 (M^+–CO–Br, 17); 674 (M^+–2CO–Br, 12); 638 (M^+–2CO–$C_6H_5C_3H_4$, 27); 557 (M^+–2CO–$C_6H_5C_3H_4$–Br, 6); 390 (**5**+OH, 100).

Complex **9** crystallized by slow diffusion of *n*-hexane (*ca.* 5:1) into CH_2Cl_2 solution, yellow-orange blocks (47%). M.p. 175–180 °C (dec.). IR ($CHCl_3$): $\tilde{\nu}_{CO}$ = 1934 s, 1831 s. ^{1}H NMR ($CDCl_3$): 7.81–7.75 (m, 2H, H–Ar); 7.60–7.39 (m, 8H, H–Ar); 4.65 (m, 1H, CHN); 4.55 (dd, 1H, C<u>H</u>HO, *J* = 8.9, 8.9); 4.48 (dd, 1H, CH<u>H</u>O, *J* = 4.8, 8.9); 3.77 (dd, 1H, C<u>H</u>HP, J_{HP} = 6.1, J_{HH} = 17.3); 3.37 (m, 1H, CH_{cent}); 3.28 (dd, 1H, CH<u>H</u>P, J_{HP} = 10.2, J_{HH} = 17.3); 3.14 (m, 2H, C<u>H</u>$(CH_3)_2$, CH_{syn}); 2.90 (m, 1H, CH_{syn}); 1.71 (m, 1H, CH_{anti}); 1.43 (m, 1H, CH_{anti}); 1.06 (d, 3H, CH(C<u>H</u>$_3)_2$, *J* = 7.0); 0.69 (d, 3H, CH(C<u>H</u>$_3)_2$, *J* = 6.6). ^{13}C NMR ($CDCl_3$): 214.7 (d, W–CO, J_{CP} = 36.6); only one W–CO observed due to low s/n; 176.9 (d, C=N, J_{CP} = 19.5); 133.9 (d, arom. CH, J_{CP} = 11.9); 131.9 (d, arom. CH, J_{CP} = 10.3); 131.6 (d, arom. CH, J_{CP} = 2.3); 131.0 (d, arom. CH, J_{CP} = 2.3); 130.6 (d, arom. C–P, J_{CP} = 38.1); 129.3 (d, arom. CH, J_{CP} = 9.4); 128.8 (d, arom. CH, J_{CP} = 9.2); 128.7 (d, arom. C–P, J_{CP} = 36.0); 73.7 (br m, allyl CH); 71.2 (CH_2O); 54.6, 45.7 (allyl CH_2); 30.2 (br m, CH_2P), 28.8 (<u>C</u>H$(CH_3)_2$); 19.0, 13.5 (CH(<u>C</u>$H_3)_2$). ^{31}P NMR ($CDCl_3$): 15.9 (br s). MS (FAB$^+$, NBA): 627 (M^+, 10); 599 (M^+–CO, 100); isotope cluster 605–597: obs. (calc.) 0.4 (0.8), 5.3 (5.9), 23.3 (24.2), 23.7 (24.1), 91.8 (93.8), 37.1 (35.6), 100.0 (100.0), 50.0 (48.5), 60.1 (60.0); 592 (M^+–Cl, 33); 569 (M^+–2CO, 56); 536 (M^+–2CO–Cl, 4); 530 (M^+–2CO–C_3H_5, 16).

Preparation of complexes **10** *and* **11**

$[W(CO)_6]$ (129 mg, 0.37 mmol), **5** (145 mg, 0.39 mmol) and Et_2O (8 ml) were mixed in a borosilicate test tube (15×1.5 cm) to form a colourless suspension. Under a static argon atmosphere and with stirring, the tube was irradiated (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 (2×18 cm). The column was eluted with hexane/EtOAc (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.

$C_{28}H_{24}NO_5PW$ (668.32)

Calcd C 50.25 H 3.62 N 2.09 O 11.95%,
Found C 50.20 H 3.61 N 2.07 O 11.83%.

$[\alpha]_D^{27}$ = +96.3 (*c* = 0.25, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}_{CO}$ = 2009 m, 1880 s, 1847 s; in hexane: 2012 m, 1904 s, 1886 s, 1874 s. ^{1}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, C<u>H</u>HO, *J* = 8.8, 8.8); 4.22 (dd, 1H, CH<u>H</u>O, *J* = 8.8, 6.5); 4.10 (m, 1H, CHN); 2.62 (m, 1H, C<u>H</u>$(CH_3)_2$); 0.87 (d, 3H, CH(C<u>H</u>$_3)_2$, *J* = 7.1); 0.09 (d, 3H, CH(C<u>H</u>$_3)_2$, *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_2O); 28.8 (<u>C</u>H$(CH_3)_2$); 19.1, 12.2 (CH(<u>C</u>$H_3)_2$). ^{31}P NMR ($CDCl_3$): 22.5 (s); [D_8]THF: 26.0 (s, $J_{^{31}P^{183}W}$ = 236). MS (FAB$^+$, KCl, NBA): 708 (M^++K, 20); 669 (M^+, 99); 641 (M^+–CO, 85); 613 (M^+–2CO, 80); 585 (M^+–3CO, 7); 557 (M^+–4CO,

100); isotope cluster 562–553: obs. (calc.) 0.2 (0.3), 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 (0.39).

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).

$C_{21}H_{30}N_2O_6W$ (590.33)
Calcd C 42.73 H 5.12 N 4.75 O 16.26%,
Found C 42.71 H 4.98 N 4.70 O 16.63%.

$[\alpha]_D^{27} = -344.6$ (c = 0.41, $CHCl_3$). $\tilde{\nu}_{CO}$ ($CHCl_3$): 2005 m, 1881 s, 1860 s, 1814 m; in hexane: 2006 m, 1876 s, 1846 s, 1830 s. ^1H NMR ($CDCl_3$): 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, $C(CH_3)_2$); 1.03 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): 213.1 ($W(CO)_2$, $J_{C^{183}W}$ = 87); 203.8 ($W(CO)_2$, $J_{C^{183}W}$ = 67); 173.9 (C=N); 81.5 (CH_2O); 77.3 (CHN); 40.9 ($C(CH_3)_2$); 35.2 ($C(CH_3)_2$); 26.5 ($C(CH_3)_3$); 24.7 ($C(CH_3)_3$). MS (FAB$^+$, NBA): 590 (M^+, 14); 562 (M^+–CO, 100); isotope cluster 566–558: obs. (calc.) 4.9 (3.1), 27.0 (19.8), 80.8 (85.0), 33.1 (22.7), 100.0 (100.0), 63.9 (58.6), 72.3 (75.0), 1.4 (0.1), 0.7 (0.3); 534 (M^+–2 CO, 13); 506 (M^+–3 CO, 11) 478 (M^+–4 CO, 5); 295 (**4**$^+$ + H, 76).

Preparation of complex **12**

$[W(CO)_3(CH_3CN)_3]$ (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 2×20 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).

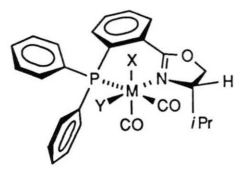
$C_{33}H_{35}N_2O_5PW$ (754.48)
Calcd C 52.54 H 4.68 N 3.71%,
Found C 52.42 H 4.84 N 3.72%.

IR (KBr): $\tilde{\nu}_{CO}$ = 1907 s, 1792 s. ^{31}P NMR ([D_8]THF): 32.00 (s, $J_{^{31}P^{183}W}$ = 227), 32.04 (s). MS (FAB$^+$, NBA): 669 (M^+–CH_3CN+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^+–CH_3CN, 2.1); 613 (M^+–CH_3CN–CO), 1.6); 557 (M^+–CH_3CN–3 CO, 2.1); 390 (**5**$^+$ + OH, 100).

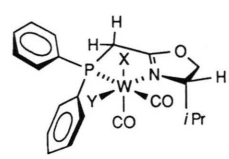
Results and Discussion

Synthesis

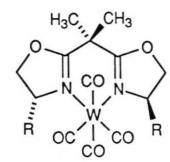
W(II)-allyl complexes **7, 8** and **9** were prepared in good to moderate yield (**7:** 60%, **8:** 77%, **9:** 47%) by a modification of the method of Faller *et al.* [13] that involves sequential addition of the corresponding allyl halide to a suspension of $[W(CO)_3(CH_3CN)_3]$ in THF and then adding *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.



7 X = Cl, Y = allyl
8 X = Br, Y = 1-Ph-allyl
10 X = CO, Y = CO
12 X = CH_3CN, Y = CO



9 X = Cl, Y = allyl



11 R = *t*Bu

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 Et_2O. Both complexes were remarkably air-stable in the solid state, but slowly decomposed in oxidizing solvents (*e.g.* $CHCl_3$). 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 (CH_3CN) ligands from a suspension of $[W(CO)_3(CH_3CN)_3]$ 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.* $CHCl_3$) rapid decomposition was observed. Whilst the

more convenient (air-stable, sublimable, highly soluble) precursor [W(CO)$_3$(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). [W(CO)$_2$(1,3-cyclohexadiene)] [11], [W(CO)(3-hexyne)$_3$] [14] and [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}H COSY and ^{13}C NMR spectra of **7, 8** and **9** confirmed the proposed 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.

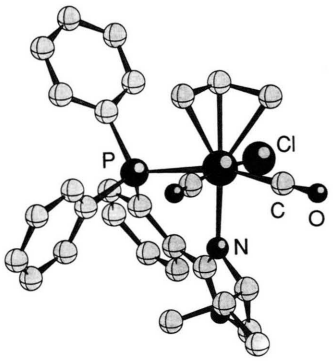


Fig. 1. Crystal structure of complex **7**·CH_2Cl_2 [15]. Ball & stick representation, arbitrary atomic radii, CH_2Cl_2 not shown.

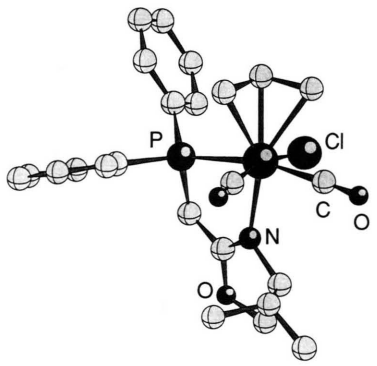


Fig. 2. Crystal structure of complex **9** [15]. Ball & stick representation, arbitrary atomic radii.

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

In $CDCl_3$ solution at ambient temperature, ^{1}H and ^{13}C NMR signals corresponding to the allyl systems are broad in all three complexes. Despite broad ^{31}P NMR signals ($\omega_{1/2} \approx 120-280$ Hz) the ^{1}H and ^{13}C NMR signals of the phosphino-oxazoline ligand (**5** 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 °C (*ca.* 5:1 ratio at −60 °C). The major species is assumed to be that relating to the solid state structure; the ^{1}H NMR signals of the allyl and phosphino-oxazoline ligand were broad but could be assigned by correlation with the ^{1}H COSY spectrum at 25 °C.

The ^{1}H NMR spectrum of complex **8** at 25 °C was similar in resolution to that of complex **7** at −60 °C. On cooling, the spectra became increasingly resolved and at −60 °C 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 *ortho/meta*-aryl protons in the phenylallyl unit.

Treatment of complex **8** with excess $NaCH(CO_2Me)_2$ (8 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}H NMR) was ligand **5.** The reaction of complexes **7** and **8** with $NaCH(CO_2Me)_2$ was monitored by ^{1}H and ^{31}P 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 equivalent, −78 °C to 25 °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 (*ca.* 1:1, ^{1}H NMR). Ligand displacement with a "soft" nucleo-

phile has also been reported by Brisdon and Griffin [16] for the reaction of $[Mo(CO)_2(bpy)(C_3H_5)X]$ (bpy = 2,2′-bipyridine; X = *e.g.* Cl) with sodium acetylacetonate, however, Trost and Hung [7a] describe the formation of $C_3H_5-CH(CO_2Me)_2$ in 65% yield by reaction of $NaCH(CO_2Me)_2$ with $[W(CO)_2(dppe)(C_3H_5)Br]$ (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.* $CHCl_3$, C_3H_5Cl) or substitution of the carbonyl groups by donor solvents (*e.g.* CH_3CN, THF) [17]. Both **10** and **11** display similar IR $\tilde{\nu}_{CO}$ bands in $CHCl_3$ 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 ^{13}C NMR spectra of **11** in $CDCl_3$ are consistent with a (presumably time-averaged) C_2-symmetric structure.

The W(0) tricarbonyl complex **12** crystallized as a single diastereoisomer, in which the readily dissociable CH_3CN ligand and the isopropyl group of the oxazoline ring are *trans* to each other (Fig. 4 [15]). In $[D_8]$THF solution two species were observed by ^{31}P NMR spectroscopy (at 25 °C: 32.00, 32.04 ppm, singlets in *ca.* 3:1 ratio); addition of excess CH_3CN did not affect the ratio.

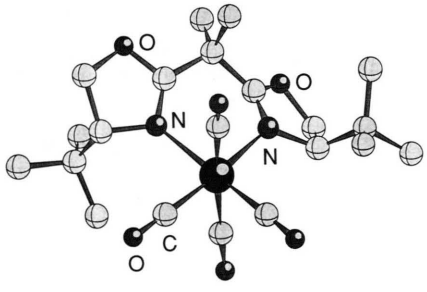


Fig. 3. Crystal structure of complex **11** [15]. Ball & stick representation, arbitrary atomic radii.

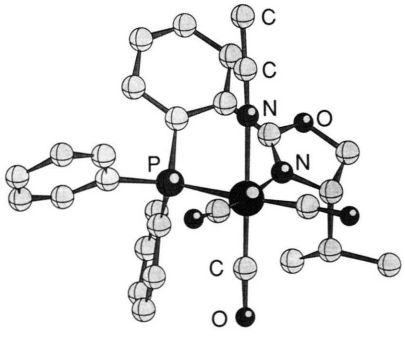
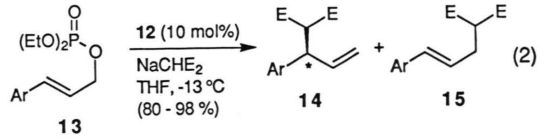


Fig. 4. Crystal structure of complex **12**·THF [15]. Ball & stick representation, arbitrary atomic radii, THF not shown.

Consequently, the reactions of $[W(CO)_3(CH_3CN)_3]$ and $[W(CO)_3$(cycloheptatriene)] with ligand **5** in $[D_8]$THF were monitored by ^1H and ^{31}P NMR spectroscopy. An equimolar solution of **5** and $[W(CO)_3$(cycloheptatriene)] (0.034 M) after 35 min at 25 °C displayed the following ^{31}P 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**)$([D_8]THF)]$ based on the ^{31}P NMR spectrum of complex **12.** A possible explanation for the pair of doublets is the formation of an additional complex of the type *fac*-$[W(CO)_3(\mathbf{5})_2]$ 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 $[W(CO)_3(CH_3CN)_3]$ 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 $NaCH(CO_2Me)_2$ (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.



Ar = Phenyl: 96% ee, 74 : 26
Ar = 1-Naphthyl: 88% ee, 96 : 4
(E = CO_2Me)

Acknowledgements

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