Supplementary Material (ESI) for Chemical Communications

Template synthesis of tungsten complexes with saturated N-heterocyclic carbene ligands

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Supplementary Information

(Synthesis of compounds **1**-**4** and of complexes **5**, **7** and **8**)

2-Azidoethyl amine 2: The compound was prepared according to the method reported by Forster and Newman.[1] Commercially available (Aldrich) 2-bromoethyl amine hydrobromide (25 g, 122 mmol) was dissolved in water (50 ml) and sodium azide (14 g, 215 mmol) dissolved in water (50 mL) was added. The reaction solution was heatated to 70 °C for 5 h. After cooling to ambient temperature 50 g of KOH were added to the reaction mixture and 2-azidoethyl amine was separated together with water by a steam distillation. Addition of KOH to the distillate separated the free amine as a separate phase form the aqueous phase. The free amine was washed from the aqueous phase with diethyl ether. Removal of the diethyl ether at 0 °C under reduced pressure gave crude **2**. Distillation of the crude product from KOH pellets gave **2** as a colorless oil. Yield 5.2 g (60.4 mmol, 49.5 %). ^{1}H NMR (200 MHz, benzene-d_6): δ 2.76 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2-N_3), 2.38 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2-NH_2), 1.38 (s, br, 2H, NH_2); ^{13}C{^{1}H} NMR (50.1 MHz, benzene-d_6): δ 54.6 (s, CH_2-N_3), 41.4 (s, CH_2-NH_2).

2-Azidoethyl formamide 3: A sample of compound **2** (5 g, 58.1 mmol) in THF (50 ml) was reacted with an 1.1 molar amount of the mixed formamide $CH_3C(O)OC(O)H$ obtained from sodium formate and acetyl chloride at 25 °C for 1 h.[2] After removal of the solvent, the crude product was distilled under vacuum (0.07 mbar, 160 °C) to yield **3** as a colorless oil (5.3 g, 46.4 mmol, 80 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.05 (s,1H, NHC*H*O), 7.18 (s, 1H, N*H*CHO), 3.31 (m, 4H, CH_2); ^{13}C{^{1}H} NMR (50.1 MHz, $CDCl_3$): δ 161.5 (s, NHCHO), 49.5 (s, CH_2-N_3), 36.4 (s, CH_2-NHC(O)H); MS (EI): *m/z* 115 (72, $[MH]^+$); IR (KBr): ν 2103 (st, N_3), 1667 (s, CO).

2-Azidoethyl isocyanide 4: The formamide **3** was dehydrated to give the isocyanide **4** using a procedure describend by Casanova.[3] Formamide **3** (5 g, 43.8 mmol) was added to a solution of 1.1. equivalents of *p*-toluenesulfonyl chloride (9.19 g, 48.2 mmol) in 25 ml of chinoline. The clear solution was stirred for 10 min at ambient temperature. The volatile isocyanide **4** was then removed from the reaction mixture under vacuum by distillation into a cold trap (cooled with liquid nitrogen) for 1 h. A colorless, volative oil with an intense smell was obtained (0.85 g, 8.8 mmol, 20 %). **4**: ^{1}H NMR (300 MHz, THF-d_8): δ 3.60 (m, 4H, CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, THF-d_8): δ 160.3 (t, $^1J_{CN}$ = 4.5 Hz, CN), 50.0 (CH_2-N_3), 41.2 (t, $^1J_{CN}$ = 7.0 Hz, CH_2-NC); IR (benzene): ν 2152 (s, CN), 2109 (s, N_3).

[W(4)(CO)$_5$] 5: The tungsten complex **5** was prepared as described for tungsten complexes with the related 2-azidophenyl isocyanide ligand.[4] Tungsten hexacarbonyl (0.7 g, 2 mmol)

dissolved in 500 ml of THF was irradiated in a photoreactor (high-pressure mercury vapor lamp) for 4 h. Complete formation of [$W(CO)_5$(THF)] was assumed after this reaction time. To the solution of the [$W(CO)_5$(THF)] complex was added an excess of isocyanide **4** (0.29 g, 3 mmol). The reaction mixture was stirred for 12 h at ambient temperature. Removal of the solvent and excess isocyanide gave a yellow powder. Complex **5** was purified by column chromatography (neutral Al_2O_3, hexane/diethyl ether 10:1, v:v). A yellow powder was obtained (0.67 g, 1.6 mmol, 80 %). Crystals of **5** could be obtained by recrystallization from hexane at -20 °C. 1H NMR (300 MHz, $CDCl_3$): δ 3.89 (t, $^3J_{HH}$ = 6 Hz, 2H, CH_2-N_3), 3.65 (t, $^3J_{HH}$ = 6 Hz, 2H, CH_2-CN); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 196.3 (CO_{trans}), 194.4 (CO_{cis}), 147.3 (*C*N-CH_2), 50.0 (CH_2-N_3), 44.3 (*C*H_2-NC); IR (KBr): ν 2187 (s, CN), 2104 (s, N_3), 2069 (s, CO), 1923 (s, br, CO); MS (EI): *m/z* 420 (22, $[M]^+$), 392 (5, [M - $CO]^+$), 364 (2, [M - $2CO]^+$), 336 (18, [M - $3CO]^+$), 308 (31, [M - $4CO]^+$), 280 (54, [M - $5CO]^+$).

Complex 7: The intramolecular cyclization of the isocyanide ligand in **5** was carried out in analogy to the method described for the cyclization of coordinated 2-azidophenyl isocyanide.[4] Complex **5** (0.84 g, 2.0 mmol) was dissolved in methanol (10 ml). To this was added PMe_3 (2.2 mmol, 2.2 ml of an 1 *M* solution in THF) and the reaction mixture was stirred at ambient temperature until the gas evolution ceased (2 h). The intermediate iminophosphorane complex **6** was not isolated. The iminophosphorane was hydrolyzed by addition of 0.2 ml of H_2O containing two drops of concentrated HCl. The reaction mixture was stirred for 0.5 h. Then all volatiles were removed and the solid residue was purified by column chromatography (neutral Al_2O_3, hexane/diethyl ether 4:1, v:v). Complex **7** was isolated as a pale yellow powder. Crystals for an X-ray diffraction study were obtained by recrystallization from hexane/diethyl ether at -20 °C. Yield 0.65 g (1.6 mmol, 80 %). ^1H NMR (400 MHz, THF-d_6): δ 7.53 (s, 2H, NH), 3.32 (s, 4H, CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz, THF-d_6): δ 202.2 (NCN), 200.4 (CO_{trans}), 198.8 (CO_{cis}), 45.0 (CH_2); IR (KBr): ν 3475 (s, NH), 2063 (s, CO), 1888 (s, CO); MS (EI): *m/z* 394 (70, $[M]^+$), 366 (36, [M - $CO]^+$), 338 (24, [M - $2CO]^+$), 310 (100, [M - $3CO]^+$) 282 (91, [M - $4CO]^+$), 254 (60, [M -$5CO]^+$). Anal. Calcd. for **7**, $C_8H_6N_2O_5W$ (394.0): C, 24.39; H, 1.53; N, 7.11. Found: C, 24.99; H, 1.63; N, 6.85.

Complex 8: The N,N´-alkylation of complex **7** was carried out in analogy to the method described for the N,N´-alkylation of benzimidazolin-2-ylidenes.[4] A sample of 0.79 g (2.0 mmol) of complex **7** was dissolved in dry DMF (10 ml). To this was added KO*t*Bu (2.2 mmol) and the reaction mixture was stirred for 2 h. Subsequently allyl bromide (0.27 g, 2.2

mmol) was added with a syringe and the reaction mixture was stirred for 4 h. The procedure deprotonation with KO*t*Bu and alkylation with allyl bromide was repeated for the second N-alkylation. Alternatively, alkylation of both N-functions can also be carried simultaneously in one deprotonation/alkylation sequence. All volatiles were removed under reduced pressure and the solid residue was purified by column chromatography (neutral Al_2O_3, hexane). Complex **8** was isolated as a pale yellow powder. Crystals for an X-ray diffraction study were obtained by recrystallization from hexane at -20 °C. Yield 0.57 g (1.2 mmol, 60 %). ^{1}H NMR (400 MHz, THF-d_6): δ 5.81 (ddt, 2H, $^3J_{HH}$ = 16, 10, 4 Hz, CH_2-C*H*=CH_2), 5.24 - 5.21 (m, 4H, CH_2-CH=C*H*$_2$), 4.36 (m, 4H, C*H*$_2$-CH=CH_2), 3.51(s, 4H, N-C*H*$_2$-C*H*$_2$-N); ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 207.7 (NCN), 201.6 (CO_{trans}), 198.9 (CO_{cis}), 134.5 (CH_2-*C*H=CH_2), 118.9 (CH_2-CH=*C*H$_2$), 56.5 (N-*C*H$_2$-CH), 49.0 (N-*C*H$_2$-*C*H$_2$-N); MS (EI): *m/z* 474 (26, $[M]^+$), 446 (18, $[M - CO]^+$), 390 (23, $[M - 3CO]^+$), 362 (100, $[M - 4CO]^+$). Anal. Calcd. for **8**, $C_{14}H_{14}N_2O_5W$ (474.13): C, 35.47; H, 2.98; N, 5.91. Found: C, 35.57; H, 2.84; N, 5.86.

References:

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