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N-Heterocyclic Carbene-Induced Transmethylation in Tungsten Imido Alkylidene Bistriflates: Unexpected Formation of an *N*-Heterocyclic Olefin Complex

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The reaction of [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME)] (DME = 1,2-dimethoxyethane, OTf = CF_3SO_3) with the *N*-heterocyclic carbene (NHC) 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene (IMesH$_2$) leads to DME activation followed by transmethylation and in due consequence to the formation of the N-heterocyclic olefin complex [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(IMesH$_2$CH$_2$)] along with [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)(IMesH$_2$)(κ^2-O(CH$_2$)$_2$OMe)], [1,3-bis(2,4,6-trimethylphenyl)-2-methylimidazolidinium$^+$ (OTf$^-$)] and [1,3-bis(2,4,6-trimethylphenyl)-2-*H*-imidazolidinium$^+$ (OTf$^-$)]. A reaction pathway is proposed and confirmed by the use of ^{13}C-labelled compounds; structures of the products were verified by NMR and/or single-crystal X-ray analysis.

Tungsten imido alkylidene complexes[1-15] complement the corresponding Mo-based systems and have been successfully used in stereoselective ring-opening metathesis polymerization (ROMP)[16] and in Z-selective olefin cross metathesis.[17] We recently accomplished the synthesis of molybdenum imido alkylidene *N*-heterocyclic carbene (NHC) and tungsten oxo NHC complexes,[18-26] which greatly extended the base of both neutral and cationic Mo and W alkylidene catalysts. Their high productivity, especially when supported on silica[27] and their substantial functional group tolerance confirms the high potential of this new class of olefin metathesis catalysts. Upon extension to tungsten imido alkylidene NHC complexes,[28, 29] however, an unexpected reaction occurs in case the synthetic route employed for the synthesis of the analogous molybdenum imido alkylidene NHC complexes is used. Thus, reaction of the bistriflate precursor [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME)][3] with 1 equiv. of 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene (IMesH$_2$)[30] did *not* lead to the desired tungsten imido alkylidene NHC complex; instead, the *N*-heterocyclic olefin (NHO) complex [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(IMesH$_2$CH$_2$)] as well as [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)(IMesH$_2$)(κ^2-O(CH$_2$)$_2$OMe)], [1,3-bis(2,4,6-trimethylphenyl)-2-methylimidazolidinium$^+$ (OTf$^-$)] and [1,3-bis(2,4,6-trimethylphenyl)-2-*H*-imidazolidinium$^+$ (OTf$^-$)] formed. While the formation of tungsten imido alkylidene monoalkoxide complexes from a DME-precursor using thiolate-based ligands in the synthesis of tungsten imido alkylidene complexes has been reported recently by Copéret et al.,[31] formation of a tungsten imido alkylidene *N*-heterocyclic olefin (NHO) complex such as **4** from the corresponding NHC precursor has, to the best of our knowledge, never been demonstrated before. This is surprising since the extent of this reaction suggests that such C-O activation might occur more frequently than expected. Notably, *without* the metal complex, such C-O activation was *not* observed clearly underlining the active role of the metal comlex. In view of this equally unusual and interesting reaction we carried out further investigations to elucidate the underlying reaction mechanism. In order to increase the yield of **2**, **3** and **4**, the bistriflate precursor [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME)] was reacted with 2 equiv. of IMesH$_2$ in benzene. After partial removal of the benzene, compounds **1** - **4** could indeed be isolated and were successfully characterized by single-crystal X-ray analysis. We propose formation of compounds **1** - **4** according to Scheme 1. Thus, reaction of [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME)] with IMesH$_2$ results in the intermediary formation of the corresponding NHC-complex with either free or coordinated DME. DME then reacts with either coordinated or free NHC via C-O activation to yield compounds **3** and **2**. Free NHC then deprotonates compound **3** to form complex **4** and compound **1**. Compound **4** crystallizes in the triclinic space group P$\bar{1}$ a = 1206.93(8) pm, b = 1291.79(9) pm, c = 1882.10(13) pm, α = 79.289(3)°, β = 83.831(4)°, γ = 65.484(3)°, Z = 2. Relevant bond lengths and angels are summarized in Figure 1. In the solid state, complex **4** has a square pyramidal (SP)

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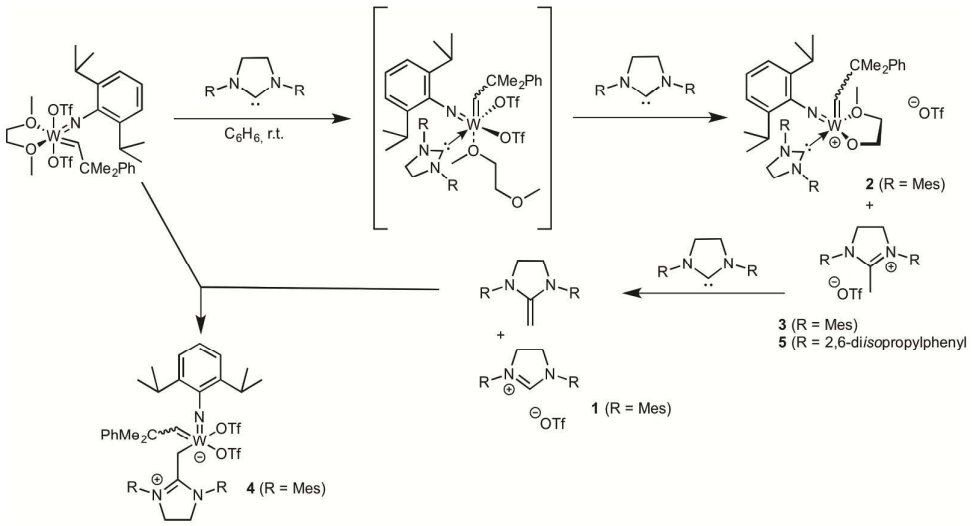

Scheme 1. Formation of compounds **1 – 4** and proposed reaction mechanism.

configuration[32] (τ = 0.02) with the imido ligand in the apex and one triflate *trans* to the alkylidene and the other triflate *trans* to the *N*-heterocyclic olefin (NHO) ligand. The NHO ligand is sp^3-hybridized at the methylene moiety, which indicates full charge separation and formation of a covalent bond to the metal centre, as shown earlier for other NHO complexes by our group[29]. The alkylidene is observed in a *syn*-configuration, both in the solid state and in solution as confirmed by NMR data in CD_2Cl_2 ($^1J_{C-H}$ = 112.2 Hz)[33]. The structure of compound **3** was also confirmed by single-crystal X-ray analysis (see Figure S28, S.I.).

In the reaction of the bistriflate precursor with $IMesH_2$, complex **2** is the main product. Samples of **2** were obtained by extracting the reaction mixture with benzene followed by crystallization form CH_2Cl_2/diethyl ether. It crystalizes in the monoclinic space group $P2_1/n$ a = 1621.73(8) pm, b = 1754.02(9) pm, c = 1719.66(9) pm, α = 90°, β = 109.557(2)°, γ = 90°, Z = 4. Relevant bond lengths and angles are summarized in Figure 2. In the solid state, the alkylidene adopts the *anti* configuration. The complex forms a distorted square pyramidal (SP) configuration[32] (τ = 0.22). The alkylidene forms the apex and the cationic complex is stabilized by the ether moiety of the DME-derived alcoholate *trans* to the NHC. Solution NMR data in CD_2Cl_2 also show the alkylidene in the *anti*-configuration ($^1J_{C-H}$ = 139.3 Hz)[33]. The shift in the ^{19}F NMR (δ = 78.95 ppm, CD_2Cl_2) indicates weakly coordinated triflate and suggests the formation of a highly polar, almost cationic

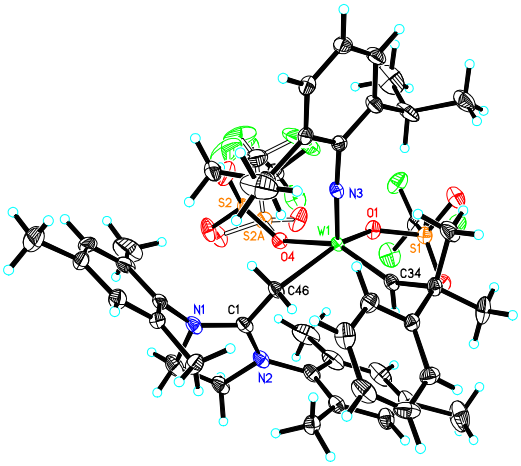

Figure 1. Single crystal X-ray structure of complex **4**. Relevant bond lengths (pm) and angles (°): W(1)-N(3) 172.35(18), W(1)-C(34) 189.0(2), W(1)-O(1) 209.50(14), W(1)-O(4) 219.77(14), W(1)-C(46) 223.7(2), N(3)-W(1)-C(34) 101.68(8), N(3)-W(1)-O(1) 111.10(7), C(34)-W(1)-O(1) 95.43(7), N(3)-W(1)-O(4) 111.07(7), C(34)-W(1)-O(4) 147.20(8), O(1)-W(1)-O(4) 74.97(5), N(3)-W(1)-C(46) 98.77(8), C(34)-W(1)-C(46) 93.84(8), O(1)-W(1)-C(46) 146.07(7), O(4)-W(1)-C(46) 79.64(6).

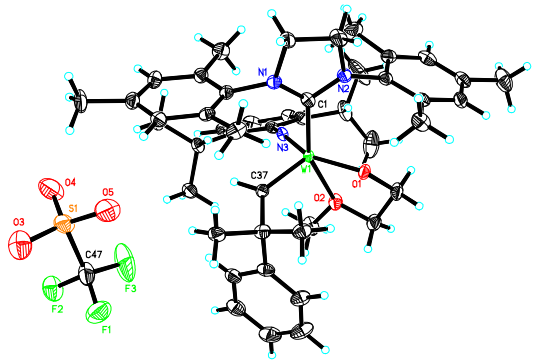

Figure 2. Single crystal X-ray structure of complex **2**. Relevant bond lengths (pm) and angles (°): W(1)-N(3) 1.779(3), W(1)-O(1) 1.906(3), W(1)-C(37) 1.939(4), W(1)-C(1) 2.207(4), W(1)-O(2) 2.233(3), N(3)-W(1)-O(1) 144.09(14), N(3)-W(1)-C(37) 100.63(16), O(1)-W(1)-C(37) 111.81(16), N(3)-W(1)-C(1) 100.02(16), O(1)-W(1)-C(1) 89.20(14), C(37)-W(1)-C(1) 100.35(16), N(3)-W(1)-O(2) 87.40(15), O(1)-W(1)-O(2) 73.05(13), C(37)-W(1)-O(2) 99.07(15), C(1)-W(1)-O(2) 157.51(14).

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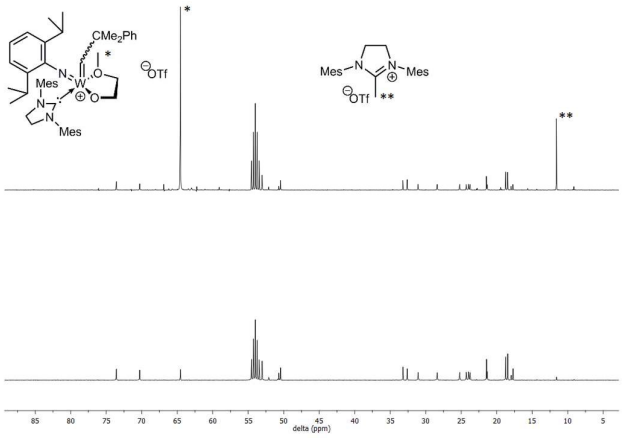

Figure 3. Comparison of unlabelled **2** (bottom) with ^{13}C-labelled **2** (top). * ^{13}C-labelled carbon in **2**. ** ^{13}C-labelled carbons of **3** (impurity).

species at room temperature with weakly coordinated triflate. Notably, both **1** and **3** crystallize together with **2**. As a consequence of this particular crystallization behaviour, it was impossible to isolate pure samples of **2** for NMR measurements or elemental analysis.

In order to confirm the proposed reaction mechanism, the ^{13}C-labelled version of the bistriflate precursor was synthesized[3] using 9 equiv. of 30% ^{13}C-labelled DME and reacted with 2 equiv. of $IMesH_2$ in benzene as described before. All products were isolated and compared to the non-labelled ones. In the ^{13}C labelled precursor the methyl groups of DME are clearly visible at δ = 64.4 and 67.8 ppm (Figure S17, S.I.). For compound **3**, the ^{13}C-reinforced signal for the 2-methyl group is observed at δ = 11.6 ppm (Figure 3), which makes it clear that it forms via reaction of the NHC with DME. The second methyl group of the DME in compound **2** is still visible at δ = 64.6 ppm (Figure 3).

Formation of the 2-methylimidazolidinium salt **5** was also observed in case 1,3-bis(2,6-$^{i}Pr_2C_6H_3$)imidazolidin-2-ylidene ($IDippH_2$)[30] was used as NHC; however, with this particular NHC the by-products could no be isolated in pure form. However, removal of one methyl group of the DME ligand in the precursor by $IDippH_2$ was again verified using the ^{13}C labelled precursor (Figure S27, S.I.). Complementary, the structure of compound **5** was also confirmed by single-crystal X-ray analysis (Figure S29, S.I.).

In conclusion, the reaction of [W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME)] with either $IMesH_2$ or $IDippH_2$ results in C-O activation, transmethylation, and formation of the NHO- instead of the NHC complex. Transmethylation from the DME ligand during the reaction with an NHC was unambiguously demonstrated by following this untypical reaction pathway of a bistriflate precursor and an NHC through ^{13}C labelling. Our experiments allow for a deeper insight into the syntheses of tungsten imido alkylidene NHC complexes. This knowledge will help for prospective synthesis of both, molybdenum and tungsten imido alkylidene NHC and NHO complexes in terms of understanding reaction pathways and for avoiding unwanted side reactions.

Experimental

1,3-Bis(2,4,6-trimethylphenyl)-2-H-imidazolidinium triflates (**1**). W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (292 mg, 0.33 mmol) was dissolved in 5 mL benzene. To this stirred solution, 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene ($IMesH_2$) (204 mg, 0.67 mmol) dissolved in 1 mL benzene, was added drop wise. The reaction mixture was stirred for 3 h at room temperature. After partial removal of the benzene under reduced pressure the reaction mixture was filtered. The obtained white solid was crystallized from CH_2Cl_2 and diethyl ether to get analytical pure product (15.3 mg, 10%): ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.22 (s, 1H, N-CH-N), 7.04 (s, 4H, Ar), 4.47 (s, 2H, CH_2), 4.46 (s, 2H, CH_2), 2.35 (s, 12H, Me), 2.33 (s, 6H, Me) ppm; ^{19}F NMR (376 MHz, CD_2Cl_2) δ = -79.21 ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 159.8 (N-C=N), 141.6 (*ipso*-N-Mes), 135.6 (CAr), 130.6 (CAr), 130.5 (CAr), 52.1 (CH_2-CH_2), 21.4 (MeAr), 18.0 (MeAr) ppm; elemental anal. calcd. (%) for $C_{22}H_{27}F_3N_2O_3S$: C, 57.88; H, 5.96; N, 6.14. found: C, 57.83; H, 5.883; N, 6.10.

1,3-Bis(2,4,6-trimethylphenyl)2-methylimidazolidinium triflate (**3**). W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (292 mg, 0.33 mmol) was dissolved in 5 mL benzene. To this stirred solution, $IMesH_2$ (204 mg, 0.67 mmol) dissolved in 1 mL benzene, was added drop wise. The reaction mixture was stirred for 3 h at room temperature. After partial removal of the benzene under reduced pressure, the reaction mixture was filtered through a pad of celite and the residual solvent was removed *in vacuo* from the obtained clear solution. The yellow solid was suspended in 1 mL benzene and filtered. The resulting white solid was dried *in vacuo* and crystallized from CH_2Cl_2 and diethyl ether to get analytically pure compound (208 mg, 66 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.08 (s, 4H, Ar), 4.42 (s, 4H, CH_2), 2.34 (s, 6H, Me), 2.30 (s, 12H, Me), 1.77 (s, 3H, Me) ppm; ^{19}F NMR (376 MHz, CD_2Cl_2) δ = -78.97 ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 167.9 (N-C=N), 141.8 (*ipso*-N-Mes), 135.6 (CAr), 130.9 (CAr), 130.2 (CAr), 50.7 (CH_2-CH_2), 21.4 (MeAr), 17.7 (MeAr), 11.6 (N=C-Me) ppm; HRMS (ESI): *m/z* calc. for $C_{22}H_{29}N_2^+$: 321.2325, found: 321.2325.

W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$($IMesH_2CH_2$) (**4**). W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (292 mg, 0.33 mmol) was dissolved in 5 mL benzene. To this stirred solution, $IMesH_2$ (204 mg, 0.67 mmol), dissolved in 1 mL benzene, was added drop wise. The reaction mixture was stirred for 3 h at room temperature. After partial removal of the benzene under reduced pressure, the reaction mixture was filtered over a pad of celite and the residual solvent was removed *in vacuo* from the obtained clear solution. The residual yellow solid was dissolved in 1 mL CH_2Cl_2 and a mixture of W(*N*-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)($IMesH_2$)(κ^2-O(CH$_2$)$_2$OMe) (**2**) and 1,3-bis(2,4,6-trimethylphenyl)-2-methylimidazolidinium triflate (**3**) was precipitated with diethyl ether. The liquid phase was decanted off and the solvent was removed *in vacuo* from the obtained clear solution. The residual yellow solid was suspended in diethyl ether and passed over a pad of celite to

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remove residual **2** and **3**. The solvent was again removed *in vacuo* and the residual yellow compound was crystallized in diethyl ether and *n*-pentane to get the product as yellow crystals (36.6 mg, 10 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.18 (s, 1H, W=CH), 7.36 - 7.31 (m, 2H, Ar), 7.25 - 7.20 (m, 2H, Ar), 7.11 - 7.04 (m, 4H, Ar), 6.99 (s, 2H, Ar), 6.89 (s, 2H, Ar), 4.23 - 3.98 (m, 4H, CH_2), 3.26 (sept, 2H, ^{i}Pr, $^3J_{H-H}$ = 6.81 Hz), 2.32 (s, 3H, Me), 2.31 (s, 9H, Me), 2.09 (s, 6H, Me), 1.91 (dd, 2H, CH_2, $^2J_{H-H}$ = 12.67, $^4J_{H-H}$ = 23.13 Hz), 1.40 (s, 3H, Me), 1.31 (s, 3H, Me), 0.99 (d, 6H, ^{i}Pr, $^3J_{H-H}$ = 6.83 Hz), 0.82 (d, 6H, ^{i}Pr, $^3J_{H-H}$ = 6.78 Hz) ppm; ^{19}F NMR (376 MHz, CD_2Cl_2) δ = -76.74 ppm.

1,3-Bis(2,6-^{i}Pr$_2$C$_6$H$_3$)-2-methylimidazolidinium triflate (**5**). W(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (245 mg, 0.281 mmol) was dissolved in 5 mL benzene. To this stirred solution, 1,3-bis(2,6-^{i}Pr$_2$C$_6$H$_3$)imidazolidin-2-ylidene (IDippH$_2$) (220 mg, 0.563 mmol) dissolved in 1 mL benzene was added drop wise. The reaction mixture was stirred for 3 h at room temperature. The resulting white solid was filtered off and dried *in vacuo*. The white solid was crystallized from CH_2Cl_2 and diethyl ether to get analytical pure compound (277 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (t, 2H, Ar, $^3J_{H-H}$ = 7.82 Hz), 7.32 (d, 4H, Ar, $^3J_{H-H}$ = 7.82 Hz), 4.56 (s, 4H, CH_2), 2.89 (sept, 4H, ^{i}Pr, $^3J_{H-H}$ =6.83 Hz), 1.74 (s, 3H, Me), 1.39 (d, 12H, ^{i}Pr, $^3J_{H-H}$ = 6.78 Hz), 1.24 (d, 12H, ^{i}Pr, $^3J_{H-H}$ = 6.88 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -78.33 ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.5 (N-C=N), 146.2 (*ipso*-N-Mes), 131.9 (CAr), 129.2 (CAr), 125.7 (CAr), 53.2 (CH_2-CH_2), 29.2 (MeAr), 24.9 (MeAr), 24.4(N=C-Me) ppm; HRMS (ESI): *m/z* calc. for $C_{28}H_{41}N_2^+$: 405.3270, found: 405.3265.

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