Supporting Information

Deprotonation of a Formato Ligand by a cis-Coordinated Carbyne Ligand in a Bis(phenolate) Tungsten Complex

Tobias Schindler, a Albert Paparo, a‡ Haruka Nishiyama, b Thomas P. Spaniol, a Hayato Tsurugi, b Kazushi Mashima*b and Jun Okuda*a

a Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany
b Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
‡ Current address: School of Chemistry, PO Box 23, Monash University, VIC, 3800, Australia

Corresponding Authors
E-mail for J. O.: jun.okuda@ac.rwth-aachen.de
E-mail for K. M.: mashima@chem.es.osaka-u.ac.jp

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1 General procedures
All manipulations were performed under argon atmosphere using standard Schlenk or glovebox techniques unless otherwise noted. All glassware was dried at 130 °C in an oven overnight. Silylated glassware was prepared through chemical vapor deposition of CSIIME$_3$ and drying at 140 °C in an oven overnight. The solvents used for NMR scale experiments were dried, distilled and degassed by standard methods and stored over 4 Å molecular sieves. Prior to NMR scale experiments, the solvents were filtered through a pad of glass wool. Tetrahydrofuran (THF), toluene, pentane and diethyl ether (Et$_2$O) were dried with a MBraun SPS and stored over 4 Å molecular sieves. All other solvents were dried and degassed by standard methods. Water and D$_2$O were degassed by the freeze-pump-thaw-technique and stored under nitrogen atmosphere. The water content of aprotic solvents was determined by Karl Fischer Titration using a C30 Compact Karl Fischer Coulometer by Mettler Toledo. Hydralan Coulomat AG by Fluka was used as an anolyte reagent and Hydralan Coulomat CG by Fluka as a catholyte reagent. NMR measurements were performed on a Bruker Avance II 400 or on a Bruker DRX 400 spectrometer at 298 K. $^1$H (400 MHz) and $^{13}$C($^1$H) NMR spectra (100 MHz) were referenced to residual proton or carbon signals of the deuterated solvents and reported relative to tetramethylsilane. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constant (J) in hertz (Hz). Standard abbreviations indicating multiplicities were used as follows: s (singlet), d (doublet), t (triplet), m (multiplet). IR spectra were measured on KBr pellets using an AVATAR 360 FT-IR spectrometer. Abbreviations for IR spectra were used as follows: vw (very weak), w (weak), m (medium), s (strong), vs (very strong), br (broad), sh (shoulder). Elemental Analysis were performed at the Institute of Organic Chemistry at the RWTH Aachen University with an Elementar Analysesysteme GmbH Elementar EL device. Lower carbon content than calculated is presumably caused by tungsten carbide formation during combustion analysis. The starting materials [(OSSO)W(CEt)Cl] (2)$^{35}$, [(OSSO)W(CEt)(O'Bu)] (1a)$^{33}$ were prepared according to or by modification of literature procedures. NaOCHO and NaOCDO were dried at 60 °C under reduced pressure or in a drying oven at 120 °C. All other chemicals were purchased form commercial sources and used as received without further purification.

2 Preparation of compounds
NaO$^{13}$CHO. The following procedures were performed under ambient atmosphere. $^{13}$C-formic acid (5.00 g, >95 wt% in water, 103 mmol, 1.00 equiv.) was added dropwise to a stirred suspension of sodium hydroxide (4.13 g, 103 mmol, 1.00 equiv.) in water (3.5 mL) cooled by ice/water bath and the reaction mixture stirred for 10 min at r.t.. NaO$^{13}$CHO was recrystallized from hot water. The white crystals were dried at 120 °C in a drying oven to afford NaO$^{13}$CHO as a white solid (6.64 g, 96.2 mmol, 93%). $^1$H NMR (D$_2$O): 8.51 (d, $^2$J$_{CH}$ = 195 Hz, 1H, OCHO). $^{13}$C($^1$H) NMR (D$_2$O): 171.3 (s, OCHO). IR (KBr pellet): (ν, cm$^{-1}$) 2992 (m sh), 2819 (s), 2719 (m), 2688 (w), 1557 (vs, sh), 1365 (vs), 1053 (w), 980 (w), 766 (vs).

$\text{Formato}(1,4$-$\text{dithiabutanediyl}-2,2'$-$\text{bis}(4,6$-$\text{di-tert}-\text{butyl-phenolato}))$propyldinitungsten(vi)
[(OSSO)W(CEt)(OCHO)] (3). Silylated glassware was used to synthesize, purify and store 2. A red solution of [(OSSO)W(CEt)Cl], 2, (1.80 g, 2.36 mmol, 1.00 equiv) in THF (100 mL) was added to sodium formate (611 mg, 8.99 mmol, 3.81 equiv). The suspension was stirred for 3 days at 60 °C. Sodium chloride was removed via filtration through a pad of glass wool. The solvent was removed under reduced pressure, the orange residue extracted with diethyl ether and filtered again. Removal of the solvent under reduced pressure and drying gave
[(OSSO)W(C(=O)O)] as an orange/brown solid. Recrystallization from THF/n-hexane at -35 °C afforded [(OSSO)W(C(=O)O)] as an orange/brown solid (1.03 g, 1.34 mmol, 48%). 1H NMR (CD3OD): 9.35 (s, 1H, OCHO), 7.55 (d, JHH = 2.4 Hz, 1H, Haryl), 7.50 (d, JHH = 2.4 Hz, 1H, Haryl), 7.22 (d, JHH = 2.4 Hz, 1H, Haryl), 7.07 (d, JHH = 2.4 Hz, 1H, Haryl), 4.47 (m, 2H, C(CH3)2CH), 2.69 (dt, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHCHS), 2.51 (dt, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.81 (td, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.71 (td, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.66 (s, 9H, C(CH3)3), 1.62 (s, 9H, C(CH3)3), 1.22 (s, 9H, C(CH3)3), 1.20 (s, 9H, C(CH3)3), 0.87 (t, JHH = 7.5 Hz, 3H, CCH2CH), 15C NMR (CD3OD): 303.6 (C(CH3)2), 172.3 (OCHO), 169.3 (Caryl), 166.0 (Caryl), 144.0 (Caryl), 140.9 (Caryl), 139.9 (Caryl), 128.0 (Caryl), 127.3 (Caryl), 126.8 (Caryl), 125.1 (Caryl), 117.2 (Caryl), 111.9 (Caryl), 40.0 (C(CH3)2), 38.6 (SCH2CH2S), 36.1 (C(CH3)3), 35.7 (C(CH3)3), 34.6 (C(CH3)3), 34.5 (C(CH3)3), 33.6 (SCH2CH2S), 31.7 (C(CH3)3), 31.6 (C(CH3)3), 29.8 (C(CH3)3), 29.7 (C(CH3)3), 17.7 (CCH2CH), 1H NMR ([D5]-THF): 9.20 (s, 1H, OCHO), 7.42 (d, JHH = 2.4 Hz, 1H, Haryl), 7.38 (d, JHH = 2.4 Hz, 1H, Haryl), 7.36 (d, JHH = 2.4 Hz, 1H, Haryl), 7.28 (d, JHH = 2.4 Hz, 1H, Haryl), 4.60 (m, 2H, C(CH3)2CH), 3.60 (dt, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHCHS), 3.43 (dt, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.47 (s, 9H, C(CH3)3), 1.40 (s, 9H, C(CH3)3), 1.30 (s, 9H, C(CH3)3), 1.28 (s, 9H, C(CH3)3), 0.86 (t, JHH = 7.5 Hz, 3H, CCH2CH), 15C NMR (CD3OD): 304.1 (C(CH3)2), 172.3 (OCHO), 169.3 (Caryl), 166.3 (Caryl), 144.9 (Caryl), 143.2 (Caryl), 139.5 (Caryl), 129.2 (Caryl), 127.7 (Caryl), 176.2 (Caryl), 126.6 (Caryl), 118.4 (Caryl), 112.8 (Caryl), 40.1 (C(CH3)2), 39.4 (SCH2CH2S), 36.5 (C(CH3)3), 36.2 (C(CH3)3), 35.3 (C(CH3)3), 34.3 (SCH2CH2S), 32.1 (C(CH3)3), 32.0 (C(CH3)3), 30.0 (C(CH3)3), 29.9 (C(CH3)3), 18.4 (CCH2CH), IR (KBr pellet): (ν, cm-1) 2960 (vs), 2906 (s), 2868 (s), 1706 (s), 1593 (w), 1477 (m), 1464 (m), 1452 (m), 1434 (vs), 1400 (m), 1362 (m), 1288 (s), 1242 (vs), 1201 (m), 1151 (m), 1103 (s), 1047 (w), 1021 (w), 955 (m), 917 (m), 875 (m, sh), 839 (s), 806 (m), 776 (w), 763 (w), 746 (m), 645 (m), 550 (m), 492 (m). Calculated for C31H26O13S2: C: 52.98, H: 6.54; found: C: 51.66, H: 6.66.

13C-Formato[1,4-dithiabutanediyl-2,2’-bis(4,6-di-tert-butyl-phenolato)]propylidynetungsten(vi)

[(OSSO)W(C(=O)C(=O))](13C-3). Silylated glassware was used to synthesize, purify and store 13C-3. The synthesis was performed analogously to 3 with NaO13CHO (68.9 mg, 999 μmol, 3.80 equiv) and 2 (200 mg, 263 μmol, 1.00 equiv) in THF (10 ml). The compound was obtained as an orange/brown solid (165 mg, 214 μmol, 81%) and used without further purification. 1H NMR (CD3OD): 9.35 (d, JCH = 214 Hz, 1H, OCHO), 7.55 (d, JHH = 2.4 Hz, 1H, Haryl), 7.49 (d, JHH = 2.4 Hz, 1H, Haryl), 7.22 (d, JHH = 2.4 Hz, 1H, Haryl), 7.07 (d, JHH = 2.4 Hz, 1H, Haryl), 4.46 (m, 2H, C(CH3)2CH), 2.69 (dt, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHCHS), 2.51 (dt, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.81 (td, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.71 (td, JHH = 14 Hz, JHH = 3 Hz, 1H, SCHCHHS), 1.66 (s, 9H, C(CH3)3), 1.62 (s, 9H, C(CH3)3), 1.22 (s, 9H, C(CH3)3), 1.20 (s, 9H, C(CH3)3), 0.87 (t, JHH = 7.5 Hz, 3H, CCH2CH2), 15C NMR (CD3OD): 303.6 (C(CH3)2), 172.3 (OCHO), 169.3 (Caryl), 168.9 (Caryl), 143.7 (Caryl), 142.4 (Caryl), 141.0 (Caryl), 139.9 (Caryl), 128.0 (Caryl), 127.3 (Caryl), 126.8 (Caryl), 125.1 (Caryl), 117.2 (Caryl), 40.0 (C(CH3)2), 38.6 (SCH2CH2S), 36.1 (C(CH3)3), 35.7 (C(CH3)3), 34.6 (C(CH3)3), 34.5 (C(CH3)3), 33.6 (SCH2CH2S), 31.7 (C(CH3)3), 31.6 (C(CH3)3), 29.8 (C(CH3)3), 18.4 (CCH2CH), IR (KBr pellet): (ν, cm-1) 2960 (vs), 2906 (s), 2869 (s), 1776 (w), 1667 (vs), 1593 (w), 1531 (w), 1461 (m), 1433 (s), 1400 (m), 1362 (m), 1263 (s), 1249 (vs), 1202 (m), 1126 (s), 1102 (s), 1047 (w), 957 (w), 916 (m), 839 (s), 800 (m), 763 (m), 745 (m), 645 (m), 550 (m), 493 (m). Calculated for C31H26O13S2: C: 53.03, H: 6.54; found: C: 52.14, H: 6.98.
D-Formato[1,4-dithiabutanediy]-2,2′-bis[4,6-di-tert-butyl-phenolato]propyldiynetungsten(vi) [(OSSO)W(CEt)(OCDO)] (D-3). The synthesis was performed analogously to 3 with NaOCDO (68.9 mg, 999 μmol, 3.80 equiv) and 2 (200 mg, 263 μmol, 1.00 equiv) in THF (15 mL). The compound was obtained as an orange/brown solid (176 mg, 229 μmol, 87%) and used without further purification. 1H NMR (C6D6): 7.55 (d, 4JH= 2.4 Hz, 1H, Haryl), 7.49 (d, 4JH= 2.4 Hz, 1H, Haryl), 7.22 (d, 4JH= 2.4 Hz, 1H, Haryl), 7.07 (d, 4JH= 2.4 Hz, 1H, Haryl), 4.46 (m, 2H, CCH3CH3), 2.69 (dt, 2JH,trans = 14 Hz, 1H, SCHHCH3S), 2.51 (dt, 2JH = 14 Hz, 1H, 2JH = 3 Hz, 1H, SCH2CH3S), 1.81 (td, 2JH = 14 Hz, 1H, SCH2CH3S), 1.71 (td, 2JH = 14 Hz, 1H, SCH2CH3S), 1.66 (s, 9H, C(CH3)3), 1.22 (s, 9H, C(CH3)3), 1.20 (s, 9H, C(CH3)3), 0.87 (t, 2JH = 7.5 Hz, 3H, CCH3CH3). 13C[1H] NMR (C6D6): 303.5 (CCH3CH3), 169.3 (Caryl), 166.0 (Caryl), 143.7 (Caryl), 142.4 (Caryl), 140.9 (Caryl), 139.9 (Caryl), 128.0 (Caryl), 127.3 (Caryl), 126.8 (Caryl), 125.1 (Caryl), 117.2 (Caryl), 112.0 (Caryl), 40.0 (CCH3CH3), 38.6 (SCH2CH3S), 36.1 (C(CH3)3), 35.8 (C(CH3)3), 34.6 (C(CH3)3), 34.5 (C(CH3)3), 33.6 (SCH2CH3S), 31.8 (C(CH3)3), 29.8 (C(CH3)3), 29.7 (C(CH3)3), 17.7 (CCH3CH3). IR (KBr pellet): (ν, cm⁻¹) 2960 (vs), 2906 (s), 2869 (s), 2112 (m), 1759 (w), 1678 (vs), 1593 (w), 1555 (w), 1461 (s), 1433 (vs), 1400 (s), 1362 (s), 1200 (s), 1253 (vs), 1241 (vs), 1201 (m), 1141 (s), 1103 (s), 1047 (w), 998 (w), 965 (w), 916 (m), 839 (s), 802 (m), 776 (m), 763 (m), 746 (m), 645 (m), 550 (m), 493 (m). Calculated for C45H36O5S2W: C: 52.92, H: 6.66; found: C: 52.14, H: 6.99.

Dioxo[1,4-dithiabutanediy]-2,2′-bis[4,6-di-tert-butyl-phenolato]tungsten(vi) [(OSSO)WO₄] (4). A solution of 3 (19.8 mg, 25.7 μmol, 1.00 equiv) in C6D6 (0.6 mL) was heated in a nitrogen glovebox at 60 °C for 3 days with intermittent freeze-pump-thaw cycles to shift the equilibrium toward 4. All volatiles were removed under reduced pressure to afford 4 as a dark brown solid (15.3 mg, 21.4 μmol, 83%). 1H NMR (C6D6): 7.51 (d, 4JH= 2.3 Hz, 2H, Haryl), 7.05 (d, 4JH= 2.3 Hz, 2H, Haryl), 2.54 (d, 3JH = 11 Hz, 2H, SCH2CH3S), 1.98 (d, 3JH = 11 Hz, 2H, 2JH = 2.4 Hz, 1H, SCH2CH3S), 1.52 (s, 18H, C(CH3)3), 1.17 (s, 18H, C(CH3)3). 13C[1H] NMR (C6D6): 165.8 (Caryl), 145.5 (Caryl), 141.6 (Caryl), 127.9 (Caryl), 127.8 (Caryl), 115.3 (Caryl), 37.3 (SCH2CH3S), 36.1 (C(CH3)3), 34.9 (C(CH3)3), 31.9 (C(CH3)3), 30.0 (C(CH3)3). IR (KBr pellet): (ν, cm⁻¹) 2960 (vs), 2907 (m), 2869 (m), 1592 (v.w.), 1465 (m), 1455 (m), 1435 (vs), 1400 (m, sh), 1362 (m), 1287 (m), 1240 (vs, sh), 1203 (m), 1140 (w), 1104 (m), 983 (v.w.), 958 (m), 920 (s), 868 (w), 843 (s), 777 (w), 752 (m), 679 (w), 641 (w, sh), 557 (m), 492 (w). Calculated for C₃₀H₄₀O₅S₂W: C: 50.28, H: 6.19; found: C: 45.46, H: 6.13.

3 Experiments of decomposition

Decomposition of 3

Typical Procedure: A solution of 1a, 2, 3, 13C-3 or D-3 (5-20 mg) in the respective solvent was heated for a minimum of 24 h at 60 °C in a Young tube. The reaction was monitored via NMR spectroscopy.

Decomposition of [(OSSO)W(CEt)[O'Bu]] (1a) under air

A solution of 1a in C6D6 (0.6 mL) was heated at 80 °C under air for 3 h. The reaction was monitored by 1H NMR spectroscopy, revealing the formation of the main product 4 and some pro-ligand H2(OSSO). Crystals suitable for X-ray diffraction analysis were grown from the reaction mixture.

Hydrolysis of 3

Typical Procedure: H2O (1 equiv.) was added via microliter-syringe to a solution of 3, 13C-3 or D-3 (5-15 mg) in C6D6 inside of a nitrogen glovebox and heated for 12 h at 60 °C in a syliyalted Young tube. The reaction was monitored via NMR spectroscopy.
Hydrolysis of 1a

Typical Procedure: H$_2$O (1 equiv.) was added via microliter-syringe to a solution of 1a (5-15 mg) in [D$_8$]-THF with the internal standard trimethoxybenzene inside of a nitrogen glovebox and heated for 12 h at 60 °C in a silylated Young tube. The reaction was monitored via NMR spectroscopy.

4 Spectroscopic data of by-products
Ethylene: $^1$H NMR (C$_6$D$_6$): 5.25 (s, 4H, CH$_2$).$^{52}$ Propylene: $^1$H NMR (C$_6$D$_6$): 5.71 (m, 1H, CH), 4.96 (m, 2H, CH$_2$), 1.55 (m, 3H, CH$_3$).$^{52}$ H$_2$(OSSO): $^1$H NMR (C$_6$D$_6$): 7.46 (d, 4$^H$H$_2$H = 2.2 Hz, 2H, $H_{aryl}$), 7.43 (d, 4$^H$H$_2$H = 2.5 Hz, 2H, $H_{aryl}$), 7.13 (m, 2H, OH), 2.44 (s, 4H, SCH$_2$), 1.55 (s, 18H, C(CH$_3$)$_3$), 1.22 (s, 18H, C(CH$_3$)$_3$). Butanal: $^1$H NMR (C$_6$D$_6$): 9.30 (s br, 1H, CHO), 1.80 (s br, 2H, CH$_2$), 1.28 (s br, 2H, CH$_2$), 0.65 (s br, 3H, CH$_2$). 2-Methylpropanal: $^1$H NMR (C$_6$D$_6$): 9.26 (m, 1H, CHO), 1.85 (m, 1H, CH), 0.75 (d, 4$^H$H$_3$ = 7.1 Hz, 6H, CH$_3$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): 203.4 (CHO), 40.9 (CH$_2$), 15.3 (CH$_3$). Tert-butyl alcohol: $^1$H NMR (C$_6$D$_6$): 1.05 (s, 9H, C(CH$_3$)$_3$), 0.63 (s, 1H, OH).$^{52}$ Formic acid: $^1$H NMR (C$_6$D$_6$): 11.21 (s, 1H, HCOOH), 7.30 (s, 1H, HCOOH). Isobutylene: $^1$H NMR (C$_6$D$_6$): 4.75 (m, 2H, H$_2$CC(CH$_3$)$_2$), 1.60 (m, 6H, H$_2$CC(CH$_3$)$_2$).$^{52}$ Carbon monoxide: $^{13}$C{$^1$H} NMR (C$_6$D$_6$): 184.5 (CO).$^{52}$
Proposed mechanism of formation of ethylene and propylene

Scheme S1. Proposed mechanism of formation of ethylene and propylene starting from \( B ([W] = \text{OSSO}W, \ H = H \) or \( D \) and alternative formation of \( B \) via a concerted five-centered transition state.
Figure S1. $^1$H NMR spectrum of NaO$^{13}$CHO in D$_2$O.
Figure S2. $^{13}$C($^1$H) NMR spectrum of NaO$^{13}$CHO in D$_2$O.
Figure S3. $^1$H NMR spectrum of [(OSSO)W(CEt)(OCHO)] (3) in CsD$_6$. 
Figure S4. $^{13}$C(1H) NMR spectrum of [(OSSO)W(CEt)(OCHO)] (3) in C$_6$D$_6$. 
Figure S5. 1H NMR spectrum of [(OSSO)W(CEt)(O\textmetallic{13}CHO)](\textmetallic{13}C\textmetallic{3}) in C6D6 with impurities of [(OSSO)WO2] and H2(OSSO).
Figure S6. $^{13}$C(1H) NMR spectrum of [(OSSO)W(CEt)(O$^{13}$CHO)] ($^{13}$C-3) in C$_6$D$_6$ with impurities of [(OSSO)WO$_2$] and H$_2$(OSSO).
Figure S7. $^1$H NMR spectrum of [(OSSO)W(CEt)(OCDO)] (D-3) in CsD$_6$. 
Figure S8. $^{13}$C($^1$H) NMR spectrum of [(OSSO)W(CEt)(OCDO)] (D-3) in C$_6$D$_6$. 

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Figure S9. $^1$H NMR spectrum of [(OSSO)WO$_2$] (4) with traces of pro-ligand H$_2$(OSSO) in C$_6$D$_6$. 
Figure S10. $^{13}$C{H} NMR spectrum of [[OSSO]WO$_3$] (4) with traces of pro-ligand H$_2$(OSSO) in C$_6$D$_6$. 
Figure S11. $^1$H NMR spectrum of 1a (bottom) before and (top) after heating at 60 °C for 35 h in C$_6$D$_6$ (*) in non-silylated glassware.
Figure S12. $^1$H NMR spectrum of 1a (bottom) before and (top) after heating under ambient atmosphere for 3h at 80 °C in C$_6$D$_6$ (*) in non-silylated glassware.
Figure S13. $^1$H NMR spectrum of 1a (bottom) before and (top) after addition of H$_2$O and heating at 60 °C in [D$_8$]-THF (*) in non-silylated glassware with the internal standard trimethoxybenzene (#): Formation of ethylene, propylene, H$_2$(OSSO) and tert-butyl alcohol with a ratio of ethylene to propylene of 1 : 2.
Figure S14. $^1$H NMR spectrum of 2 (bottom) before and (top) after heating at 60 °C for 35 h in C$_6$D$_6$ (*) in non-silylated glassware.
Figure S15. Comparison of the $^1$H NMR spectra of 3 in C$_6$D$_6$ (top) and (bottom) of 3 after heating at 60 °C for 62 h in C$_6$D$_6$ (*) in non-silylated glassware with a ratio of ethylene to propylene of 1 : 2.
Figure S16. $^1$H NMR spectrum of 3 (top) before and (bottom) after heating at 60 °C for 44 h in [D$_8$]-THF (*) in silylated glassware with trimethoxybenzene (#) as internal standard.
Figure S17. $^1$H NMR spectrum of 3 (bottom) before and (top) after heating at 60 °C for 24 h in C$_6$D$_6$ (*) in silylated glassware with trimethoxybenzene (#) as internal standard.
Figure S18. Comparison of the $^1$H NMR spectra of $^{13}$C-3 (bottom) in C$_6$D$_6$ (*) and (top) after heating $^{13}$C-3 in C$_6$D$_6$ (*) at 60 °C for 12 d in non-silylated glassware.
Figure S19. Comparison of the $^{13}$C($^1$H) NMR spectra of $^{13}$C-3 (bottom) and (top) after heating $^{13}$C-3 in C$_6$D$_6$ (* at 60 °C for 12 d in non-silylated glassware.
Figure S20. Comparison of $^1$H NMR spectra of (top) $^{13}$C-3 in C$_6$D$_6$ (*) after heating at 60 °C for 12 d in C$_6$D$_6$ (*) with a ratio of ethylene to propylene of 1 : 1.1 and (bottom) after addition of water and heating at 60 °C for 20 h in C$_6$D$_6$ (*) with a ratio of ethylene to propylene of 1 : 2.5.
Figure S21. Comparison of the $^{13}\text{C}^1\text{H}$ NMR spectra of (top) $^{13}\text{C}-3$ in $\text{C}_6\text{D}_6$ (*) after heating at 60 °C for 12 d and (bottom) after addition of water and heating at 60 °C for 20 h in $\text{C}_6\text{D}_6$. 
Figure S22. $^1$H NMR spectrum of (top) $\mathbf{3}$ in $\text{C}_6\text{D}_6$ (*) after heating at 60 °C for 62 h with a ratio of ethylene to propylene of 1 : 2 and (bottom) $^1$H NMR spectrum of (OSSO)W(CEt)(OCDO), $\mathbf{D-3}$, after heating at 60 °C for 13 d in $\text{C}_6\text{D}_6$ (*) with a ratio of ethylene to propylene of 1 : <0.4.
Figure S23. $^1$H NMR spectrum of (top) D-3 in C$_6$D$_6$ (*) after heating at 60 °C for 13 d with a ratio of ethylene to propylene of 1 : <0.4 and (bottom) $^1$H NMR spectrum of D-3 after addition of H$_2$O and heating at 60 °C for 17 h in C$_6$D$_6$ (*) with a ratio of ethylene to propylene of 1 : 6.7.
Figure S24. $^1$H NMR spectrum of (top) D-3 in C$_6$D$_6$ (*) after addition of H$_2$O and heating at 60 °C for 17 h with a ratio of ethylene to propylene of 1 : 6.7 and (bottom) $^1$H NMR spectrum of 3 after addition of D$_2$O and heating at 60 °C for 4 h in C$_6$D$_6$ (*) with a ratio of ethylene to propylene of 1 : <0.4.
Figure S25: $^1$H NMR spectrum of 3 after addition of H$_2$O and heating for 17 h at 60 °C in [D$_8$]-THF (*) with a ratio of ethylene to propylene of 1 : 8.3.
7  IR Spectra

Figure S26. IR spectrum of \([\text{OSSO}]^2\text{W}(\text{CEt})(\text{OCHO})\) (3) in KBr
Figure S27. IR spectrum of \([\text{OSSO}](\text{Et})(\text{O}^{13}\text{CHO})] \text{ (13C-3)}\) in KBr.
Figure S28. IR spectrum of [(OSSO)W(CEt)(OCDO)] (D-3) in KBr.
Figure S29. IR spectrum of [(OSSO)WO₂] (4) in KBr.
8 Molecular structure of 3

Figure S30. Molecular structure of 3 in the solid state. Hydrogen atoms except the formate proton are omitted for clarity.

9 Crystallographic data

Diffraction data of 3 were collected at 100 K on a Eulerian 4-circle diffractometer (STOE STRADIVARI) with Cu Kα radiation (graded multilayer mirror, \( \lambda = 1.54186 \) Å) using \( \omega \) scans. The programs X-Area and STOE X-Red32 were used for data reduction and absorption correction. Diffraction data of 4 were collected at 100 K on a Bruker CCD area-detector diffractometer with Mo Kα radiation (monolayer optics, \( \lambda = 0.71073 \) Å) at 100 K using \( \omega \) scans. The SMART program package was used for data collection and unit cell determination; processing of the raw frame data was performed using SAINT; the absorption correction was applied with SADABS. The structure s were solved by direct methods (SIR-92). All non-hydrogen atoms were refined anisotropically using all reflections with the program SHELXL-2013 as implemented in the program system WinGX. In 3, the carbon atoms C8, C9, C28, C29, C30, C33 and C34 as well as the carbon atoms C24, C25 and C26 in 4 that belong to methyl groups of tert-butyl units are disordered. This disorder was modelled with split positions and these atoms are refined with isotropic displacement parameters. All hydrogen atoms were placed in calculated positions and treated as riding with \( U_H = 1.2 \cdot U_C \) or with \( U_H = 1.5 \cdot U_C \) for the hydrogen atoms of methyl groups, respectively. The structure of 3 contains co-crystallized solvent molecules that could not be refined. The SQUEEZE routine as implemented in the program system PLATON has been applied to account for the large solvent accessible void. Due to the high sensitivity of the crystals of 3, the crystals quickly decomposed and data were measured only up to a \( \theta \) value of 60.22° (corresponding to a value for \( \sin(\theta)/\lambda \) of 0.56). For this reason, details about the molecular structure of 3 are not discussed. The graphical representations were performed with the program DIAMOND.
### Table S1. Crystallographic and refinement data of 3 and 4.

<table>
<thead>
<tr>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical formula</strong></td>
<td>C₃₄H₅₀O₄S₂W</td>
</tr>
<tr>
<td><strong>M_w (g·mol⁻¹)</strong></td>
<td>770.71</td>
</tr>
<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.11 x 0.12 x 0.13</td>
</tr>
<tr>
<td><strong>Crystal color and habit</strong></td>
<td>block, red</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>trigonal</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>R̅3</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>21.333(3)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>14.4457 (18)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>45.902(9)</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>18091(6)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>18</td>
</tr>
<tr>
<td><strong>D(calc.) (g·cm⁻³)</strong></td>
<td>1.273</td>
</tr>
<tr>
<td><strong>µ(Mo Kα) (mm⁻¹)</strong></td>
<td>6.522</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>7056</td>
</tr>
<tr>
<td><strong>θ range, deg</strong></td>
<td>4.54 – 60.22</td>
</tr>
<tr>
<td><strong>Refins collected</strong></td>
<td>20555</td>
</tr>
<tr>
<td><strong>Independent refns (R(int)</strong></td>
<td>5730, 0.0669</td>
</tr>
<tr>
<td><strong>Observed refns ([I ≥ 2σ(I)])</strong></td>
<td>3410</td>
</tr>
<tr>
<td><strong>Data/restraints/params</strong></td>
<td>5730 / 0 / 364</td>
</tr>
<tr>
<td><strong>R1, wR2 ([I ≥ 2σ(I)]</strong></td>
<td>0.0623, 0.1601</td>
</tr>
<tr>
<td><strong>R1, wR2 (all data)</strong></td>
<td>0.0968, 0.1957</td>
</tr>
<tr>
<td><strong>GoF (F²)</strong></td>
<td>1.049</td>
</tr>
<tr>
<td><strong>Δρmax/min, e·Å⁻³</strong></td>
<td>0.544, -1.323</td>
</tr>
</tbody>
</table>

#### References

4. a) X-Area Pilatus3_SV 1.31.131.0, STOE, 2017; b) X-Area Recipe 1.33.0.0, STOE, 2015; c) X-Area Integrate 1.71.0.0, STOE, 2016; X-Area LANA 1.71.4.0, STOE, 2017.