

SUPPLEMENTARY INFORMATION

A MULTI-DIMENSIONAL APPROACH COMBINING HPLC, ION MOBILITY AND HIGH RESOLUTION MASS SPECTROMETRY FOR INVESTIGATING TRANSITION METAL COMPLEXES

Laura Zellner^{1*}, Julian Süß^{2,3}, Samuel Vorbach³, Uwe Monkowius^{2,4}, Markus Himmelsbach¹,
Stephan Hann⁵, Christian Klampfl¹

¹ Johannes Kepler University Linz, Institute of Analytical and General Chemistry, Altenberger
Strasse 69, 4040 Linz, Austria

² Johannes Kepler University Linz, School of Education, Chemistry, Altenberger Strasse 69,
4040 Linz, Austria

³ Johannes Kepler University Linz, Institute of Catalysis, Altenberger Strasse 69, 4040 Linz,
Austria

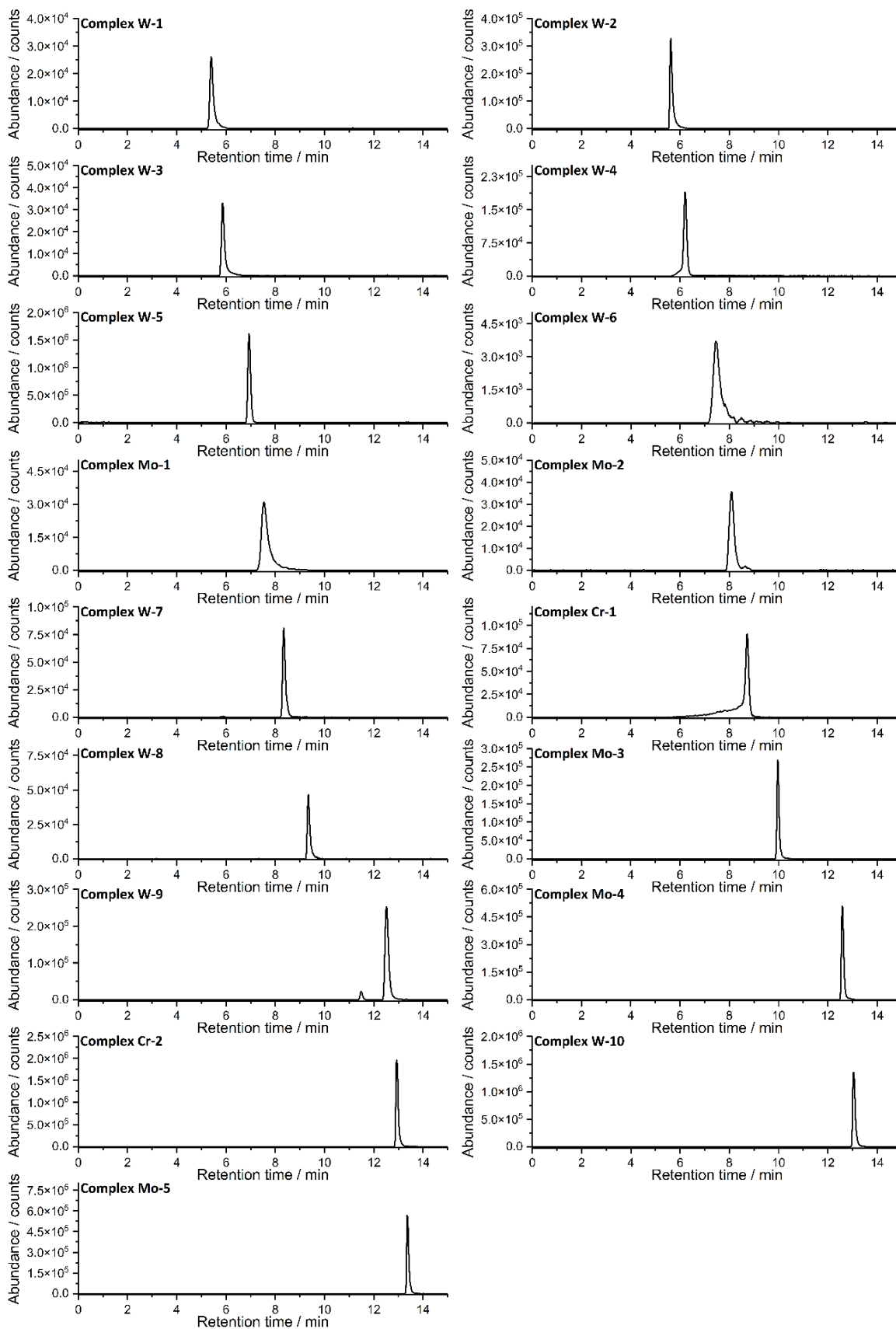
⁴ Johannes Kepler University Linz, Institute of Inorganic Chemistry, Altenberger Strasse 69,
4040 Linz, Austria

⁵ BOKU University, Institute of Analytical Chemistry, Department of Natural Sciences and
Sustainable Resources, Muthgasse 18, Vienna 1190, Austria

*Correspondence to Laura Zellner (E-mail: laura.zellner@jku.at), Tel +43 732 2468 9707

Supplementary Table S1: Sum formulas and monoisotopic masses (calculated using *enviPat* ¹) of the herein investigated group six transition metal complexes.

Abbreviation	Complex	Sum formula	Monoisotopic mass / Da
W-1	CpW(CO) ₂ PN	C ₂₁ H ₂₁ NO ₂ PW	534.0819
W-2	CpW(CO) ₂ PP	C ₃₃ H ₂₉ O ₂ P ₂ W	703.1152
W-3	CpW(CO) ₂ PPP*	C ₄₁ H ₃₈ O ₂ P ₃ W	839.1594
W-4	W(ACN) ₃ (CO) ₃	C ₉ H ₉ N ₃ O ₃ W	391.0153
W-5	W(Py) ₂ (CO) ₄	C ₁₄ H ₁₀ N ₂ O ₄ W	454.0150
W-6	CpW(CO) ₂ PPP	C ₄₈ H ₄₄ O ₂ P ₃ W	929.2063
Mo-1	CpMo(CO) ₂ PPP	C ₄₈ H ₄₄ O ₂ P ₃ Mo	843.1608
Mo-2	Mo(Py) ₂ (CO) ₄	C ₁₄ H ₁₀ N ₂ O ₄ Mo	367.9695
W-7	W(CO) ₄ PN	C ₁₈ H ₁₆ NO ₄ PW	525.0326
Cr-1	Cr(CO) ₄ PN	C ₁₈ H ₁₆ NO ₄ PCr	393.0222
W-8	W(iPrBiOx)(CO) ₄	C ₁₆ H ₂₀ N ₂ O ₆ W	520.0831
Mo-3	Mo(iPrBiOx)(CO) ₄	C ₁₆ H ₂₀ N ₂ O ₆ Mo	434.0375
W-9	IndPhosW	C ₂₈ H ₂₂ ClO ₂ PW	640.0555
Mo-4	IndPhosMo	C ₂₈ H ₂₂ ClO ₂ PMo	554.0100
Cr-2	Cr(dppm)(CO) ₄	C ₂₉ H ₂₂ O ₄ P ₂ Cr	548.0398
W-10	W(dppm)(CO) ₄	C ₂₉ H ₂₂ O ₄ P ₂ W	680.0503
Mo-5	Mo(dppm)(CO) ₄	C ₂₉ H ₂₂ O ₄ P ₂ Mo	595.0047

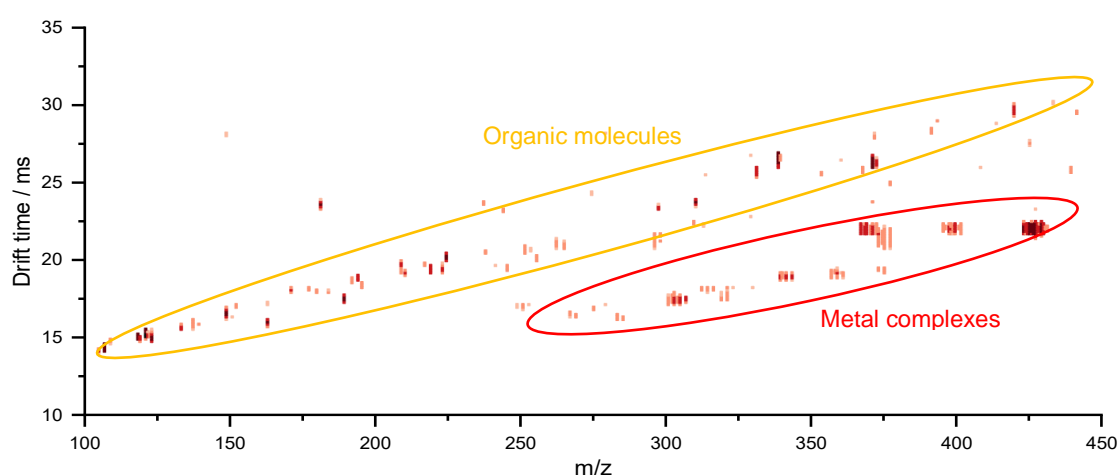


Supplementary Figure S1: Extracted ion chromatograms of the herein investigated complexes.

Supplementary Table S2: Charged species, drift times and $^{DT}CCS_{N_2}$ of the herein investigated complex species (n=5).

Complex	Charged species	DT / ms	$^{DT}CCS_{N_2} / \text{\AA}^2$	STDEV / \AA^2
W-1	$[M]^+$	25.0	184.6	0.1
W-2	$[M]^+$	30.0	219.5	0.3
W-3	$[M-CO]^+$	32.8	240.0	0.3
W-4	$[M-ACN+H]^+$	20.5	153.2	0.2
W-5	$[M+H]^+$	22.0	163.3	0.2
W-6	$[M]^+$	36.9	269.9	0.1
Mo-1	$[M]^+$	36.2	264.9	0.2
Mo-2	$[M-CO+H]^+$	21.8	164.2	0.2
W-7	$[M]^+$	24.5	181.4	0.1
Cr-1	$[M]^+$	24.3	180.2	0.1
W-8	$[M+H]^+$	24.6	180.9	0.2
Mo-3	$[M-CO+H]^+$	23.5	173.7	0.3
W-9	$[M+H]^+$	28.2	206.0	0.1
Mo-4	$[M+NH_4]^+$	28.7	211.1	0.1
Cr-2	$[M+H]^+$	29.1	214.5	0.2
W-10	$[M+H]^+$	29.5	216.2	0.2
Mo-5	$[M+H]^+$	29.4	216.1	0.2

DT: drift time; $^{DT}CCS_{N_2}$: collision cross section; STDEV: standard deviation; ACN: acetonitrile

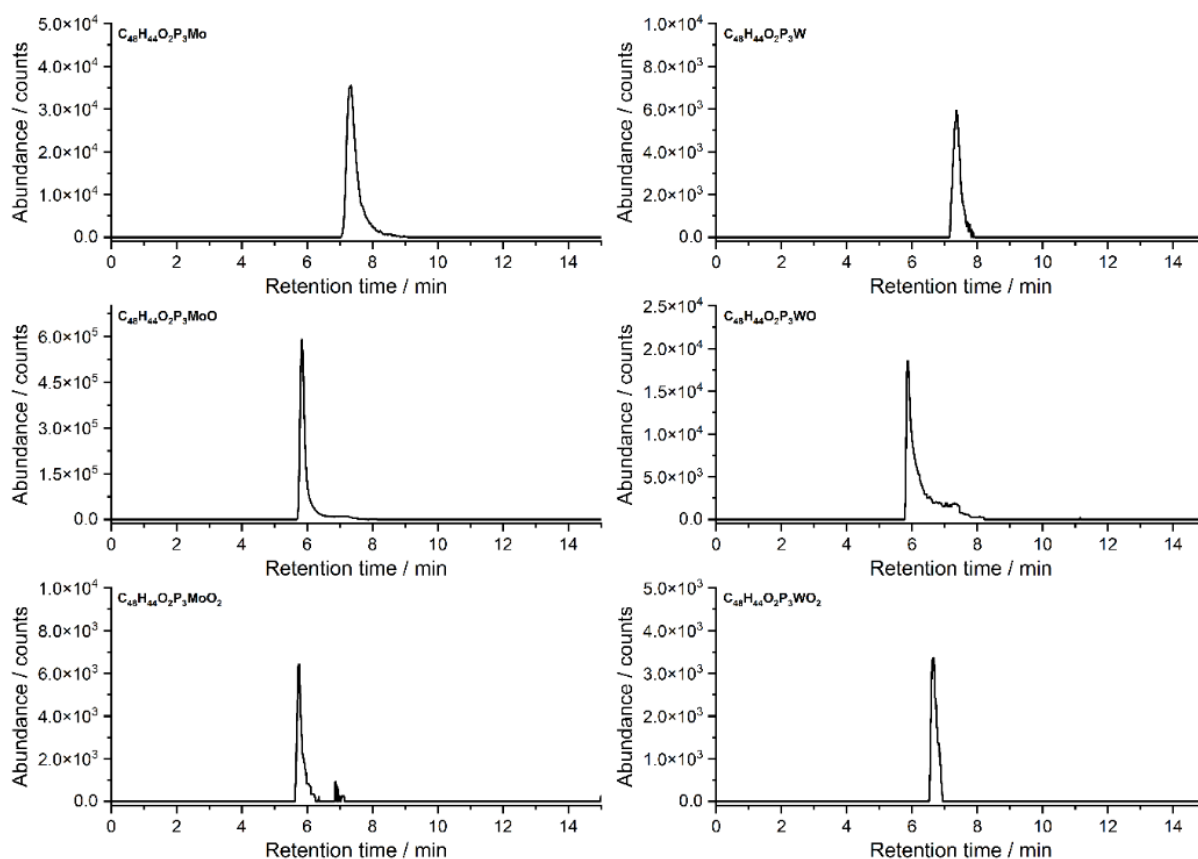


Supplementary Figure S3: Drift time versus m/z spectrum. Metal complex signals deviate from the main organic molecule trend, appearing at shorter drift times for comparable m/z values.

Supplementary Table S3: Isotopologue pattern and assigned metal center according to the trends seen in Figure 7 for unknown products / by-products / contaminations of several W or Mo reaction mixtures.

Reaction mixture	m/z	RT / min	DT / ms	$^{DT}CCS_{N_2} / \text{\AA}^2$	Isotopologue pattern	Metal according to trend
1 - Mo	328.00	4.7	21.0	156.6	Mo	Mo
	540.07	5.9	27.1	199.1	Mo	Mo
	747.06	9.1	31.6	243.9	Mo	Mo
	696.13	7.8	32.0	234.2	Mo	Mo
	668.13	7.8	31.2	228.7	Mo	Mo
	640.14	7.8	31.0	226.8	Mo	Mo
	457.02	7.8	26.1	192.6	Mo	Mo
	547.08	7.8	28.4	208.4	Mo	Mo
2 - Mo	431.00	7.8	24.0	177.3	Mo	Mo
3 - Mo	386.89	5.8	20.5	152.3	inconclusive	W
	425.05	12.0	24.4	180.3	Mo	Mo
	481.03	12.0	25.7	189.8	Mo	Mo
4 - Mo	345.91	7.6	19.1	142.2	inconclusive	W
5 - Mo	321.92	4.8	19.9	148.3	inconclusive	Mo
6 - W	782.17	8.1	32.1	234.4	W	W
	663.13	7.4	28.8	210.9	W	W
	577.14	7.4	26.3	193.2	W	W
	489.08	7.2	23.2	170.7	W	W
	523.10	5.8	24.4	179.4	W	W
	412.03	5.8	20.6	152.3	W	W
	437.05	6.9	24.1	178.3	Mo	Mo

RT: retention time; DT: drift time; $^{DT}CCS_{N_2}$: collision cross section;



Supplementary Figure S4: Extracted ion chromatograms of once and twice oxidized species of Mo-1 (left) and W-6 (right).

References:

1. Loos, M., Gerber, C., Corona, F., Hollender, J. & Singer, H. Accelerated Isotope Fine Structure Calculation Using Pruned Transition Trees. *Anal. Chem.* **87**, 5738–5744 (2015).