Supplementary Information

Fig. SF1:
XANES region of pure **1** in **2** (solid line), as well as containing three equivalents of ^{i}PrOH (short dashed line) or THF (dotted dashed line), and monoclinic HfO_2 (dotted line).

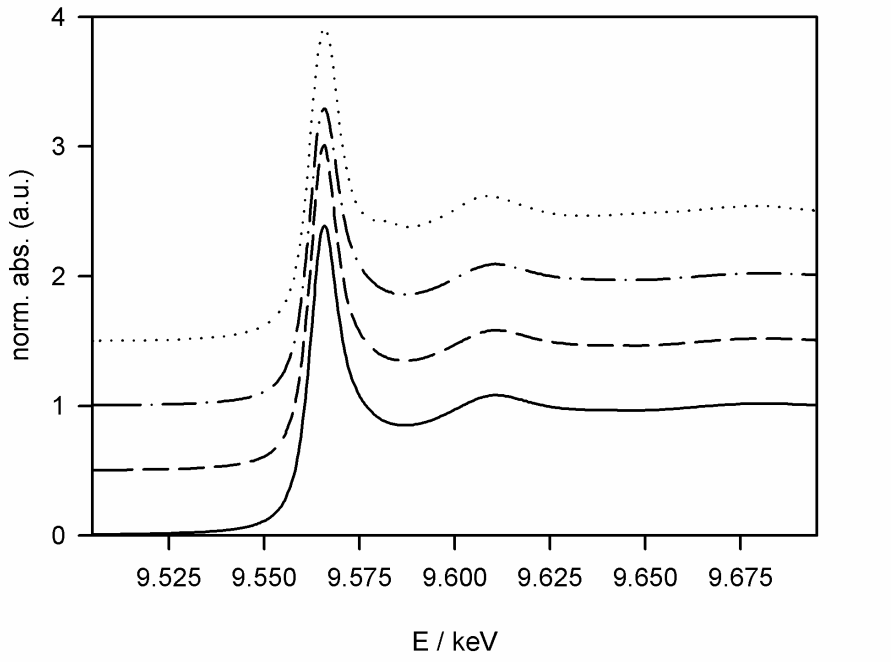

Fig. SF2:
Development of the integral absorption of the C=O stretching vibration in dependence of the added equivalents acetylacetone Hacac (see also table ST1).

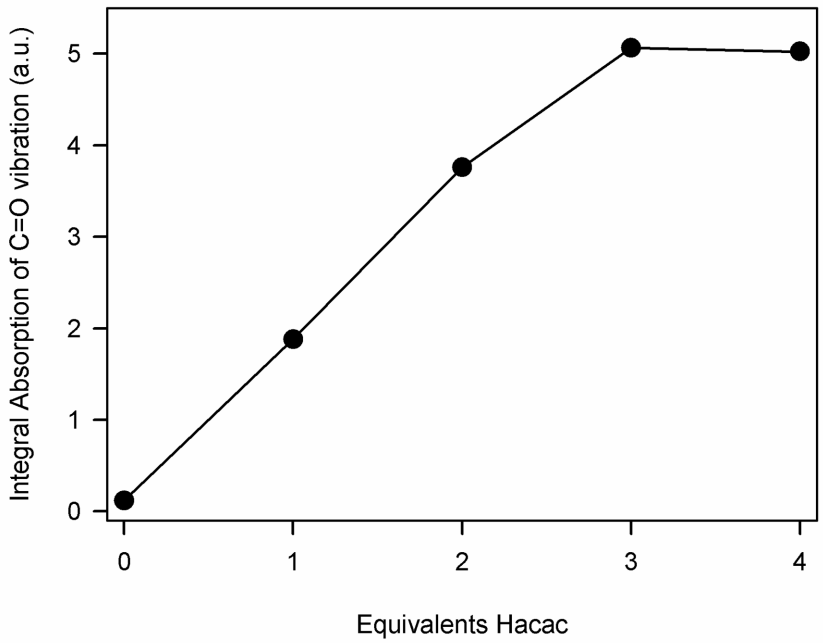

Fig. SF3:
Comparison of the IR-spectra of **1** in **2** (solid line), **1** in **2** with two equivalents Hacac (double dotted dashed line), and a solution of only Hacac in toluene (dashed line) in the region of the characteristic vibrations of coordinated Hacac.

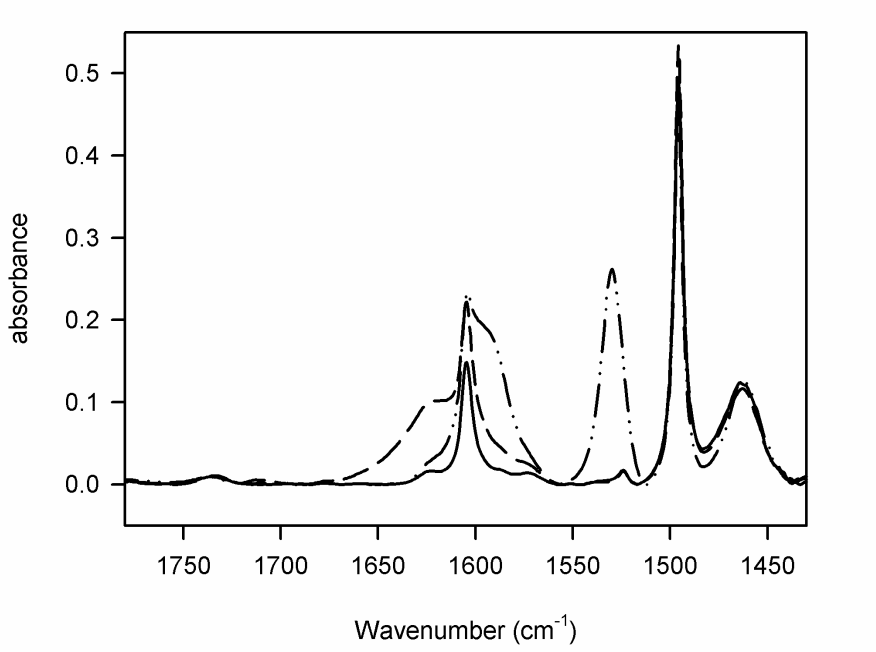

Fig. SF4:
IR-spectra of **1** in **2** with one (solid line), two (dotted line), three (dotted dashed line) and four (short dashed line) equivalents Hacac. Only for four Hacac characterstic vibrations of free acetylacetone are visible.

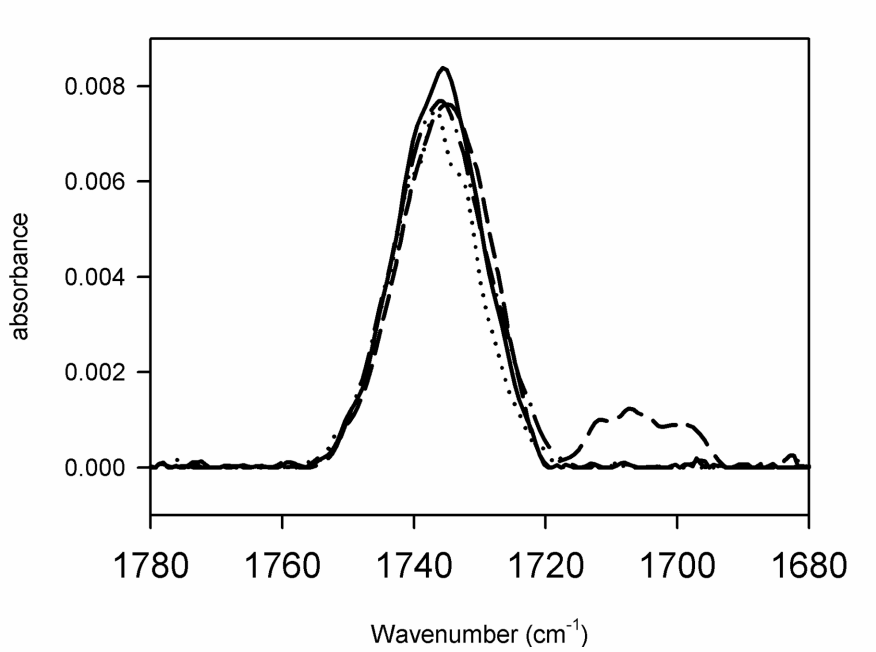

Table ST1 Characteristic values (their integrated intensity, band intensity and energies) of the C=C- and C=O-vibration bands of coordinated acetylaetone for solutions of **1** in **2** that contain one to four equivalents Hacac.

Sample	C=C			C=O		
	Vibrational energy [cm^{-1}]	Signal height (a.u.)	Integrated Intensity (a.u.)	Vibrational energy [cm^{-1}]	Signal height (a.u.)	Integrated Intensity (a.u.)
1 eq. Hacac	1599.3	0.151	2.817	1528.9	0.151	1.880
2 eq. Hacac	1593.7	0.167	4.411	1529.9	0.257	3.758
3 eq. Hacac	1590.9	0.248	6.319	1530.03	0.332	5.064
4 eq. Hacac	1593.1	0.278	7.097	1530.4	0.331	5.026

Scheme SS1: Possible reactions with one equivalent Hacac under consideration of the fact, that *all* Hacac molecules coordinate and electroneutrality is maintained. The reactions mentioned in the paper are marked in yellow, with the enumeration of the paper in squared parentheses.

(a1):	II + 3 Hacac	→	IV + 3 ^{n}BuOH	[(1)]
(a2):	2 II + 6 Hacac	→	3 V + 6 ^{n}BuOH	[(2)]
(a3):	4 II + 12 Hacac	→	2 IV + 3 V + 12 ^{n}BuOH	[(3)]
(b4):	2 II + 6 Hacac	→	II + 3 VI + 3 ^{n}BuOH	
(b5):	4 II + 12 Hacac	→	2 II + 3 VII + 12 ^{n}BuOH	[(4)]
(b6):	3 II + 9 Hacac	→	2 II + 3 VIII + 9 ^{n}BuOH	
(c7):	3 II + 9 Hacac	→	II + IV + 3 VI + 6 ^{n}BuOH	
(c8):	5 II + 15 Hacac	→	2 II + IV + 3 VII + 15 ^{n}BuOH	
(c9):	4 II + 12 Hacac	→	2 II + IV + 3 VIII + 12 ^{n}BuOH	
(c10):	4 II + 12 Hacac	→	II + 3 V + 3 VI + 9 ^{n}BuOH	
(c11):	6 II + 18 Hacac	→	2 II + 3 V + 3 VII + 18 ^{n}BuOH	
(c11.1):	8 II + 24 Hacac	→	2 II + 6 V + 3 VII + 24 ^{n}BuOH	
(c12):	5 II + 15 Hacac	→	2 II + 3 V + 3 VIII + 15 ^{n}BuOH	
(c12.1):	8 II + 24 Hacac	→	4 II + 3 V + 6 VIII + 24 ^{n}BuOH	
(d13):	6 II + 18 Hacac	→	II + 2 IV + 3 V + 3 VI + 15 ^{n}BuOH	
(d13.1):	5 II + 15 Hacac	→	II + IV + 3 V + 3 VI + 12 ^{n}BuOH	
(d13.2):	8 II + 24 Hacac	→	II + 2 IV + 6 V + 3 VI + 21 ^{n}BuOH	
(d13.3):	7 II + 21 Hacac	→	2 II + IV + 3 V + 6 VI + 15 ^{n}BuOH	
(d14):	8 II + 24 Hacac	→	2 II + 2 IV + 3 V + 3 VII + 24 ^{n}BuOH	[(5)]
(d14.1):	7 II + 21 Hacac	→	2 II + IV + 3 V + 3 VII + 21 ^{n}BuOH	
(d14.2):	10 II + 30 Hacac	→	2 II + 2 IV + 6 V + 3 VII + 30 ^{n}BuOH	
(d14.3):	11 II + 33 Hacac	→	4 II + IV + 3 V + 6 VII + 33 ^{n}BuOH	
(d15):	7 II + 21 Hacac	→	2 II + 2 IV + 3 V + 3 VIII + 21 ^{n}BuOH	
(d15.1):	6 II + 18 Hacac	→	2 II + IV + 3 V + 3 VIII + 18 ^{n}BuOH	
(d15.2):	12 II + 36 Hacac	→	2 II + 2 IV + 6 V + 3 VIII + 36 ^{n}BuOH	
(d15.3):	9 II + 27 Hacac	→	4 II + IV + 3 V + 6 VIII + 27 ^{n}BuOH	
(e16):	2 II + 6 Hacac	→	II + VI + VII + 5 ^{n}BuOH	
(e17):	5 II + 15 Hacac	→	3 II + 3 VI + 3 VIII + 12 ^{n}BuOH	
(e18):	10 II + 30 Hacac	→	3 II + 3 VII + 6 VIII + 30 ^{n}BuOH	
(e19):	7 II + 21 Hacac	→	4 II + 4 VI + VII + 3 VIII + 17 ^{n}BuOH	
(e19.1):	12 II + 36 Hacac	→	7 II + VI + 4 VII + 6 VIII + 35 ^{n}BuOH	

Table ST2 Calculated structural parameters of the possible reaction with one equivalent Hacac. The reaction which reflect the results of the EXAFS analysis best are marked in yellow.

Equation	N(O1)	N(O2)
(a1)	1.0	6.0
(a2)	1.0	6.0
(a3)	1.0	6.0
(b4)	1.0	6.0
(b5)	1.0	6.0
(b6)	1.3	5.3
(c7)	1.0	6.0
(c8)	1.0	6.0
(c9)	1.3	5.5
(c10)	1.0	6.0
(c11)	1.0	6.0
(c11.1)	1.0	6.0
(c12)	1.2	5.6
(c12.1)	1.4	5.1
(d13)	1.0	6.0
(d13.1)	1.0	6.0
(d13.2)	1.0	6.0
(d13.3)	1.0	6.0
(d14)	1.0	6.0
(d14.1)	1.0	6.0
(d14.2)	1.0	6.0
(d14.3)	1.0	6.0
(d15)	1.1	5.7
(d15.1)	1.2	5.7
(d15.2)	1.1	5.8
(d15.3)	1.2	5.6
(e16)	1.0	6.0
(e17)	1.2	5.6
(e18)	1.2	5.6
(e19)	1.1	5.7
(e19.1)	1.2	5.7
(e19.2)	1.2	5.6

(e19.2): 15 II + 45 Hacac → 9 II + 3 VI + 3 VII + 9 VIII + 42 ^{n}BuOH

Table ST3 Results of the XANES fit of **1** in **2**, **1** in **2** with one to three equivalents Hacac, HfO_2 and $Hf_4O_2(OMc)_{12}$.

Sample		**1** in **2**	1 eq. Hacac	2 eq. Hacac	3 eq. Hacac	HfO_2	$Hf_4O_2(OMc)_{12}$
Edge step	Function	arctan	arctan	arctan	arctan	arctan	arctan
	Position	9.5604	9.5620	9.5621	9.5624	9.5620	9.5619
	Height	0.81	0.80	0.77	0.77	0.87	0.79
	FWHM	0.0047	0.0044	0.0040	0.0046	0.0046	0.0041
	Area	0.024	0.023	0.021	0.022	0.025	0.021
White line	Function	asym. P-Voigt	asym. P-Voigt	asym. P-Voigt	asym. P-Voigt	asym. P-Voigt	asym. P-Voigt
	Position	9.5658	9.5660	9.5655	9.5659	9.5659	9.5666
	Height	1.67	1.44	1.79	1.46	1.65	1.34
	left FWHM	0.0079	0.0104	0.0097	0.0106	0.0102	0.0118
	right FWHM	0.0084	0.0084	0.0069	0.0075	0.0083	0.0075
	Gaussian part	0.044	0.403	0.416	0.521	0.465	0.459
	Area	0.020	0.018	0.019	0.017	0.020	0.017
Signal ~ 9.58 keV	Function	asym. Gaussian	asym. Gaussian	asym. Gaussian	asym. Gaussian	asym. Gaussian	asym. Gaussian
	Position	--	9.5791	9.5801	9.5803	9.5819	9.5800
	Height	--	0.050	0.095	0.103	0.018	0.070
	left FWHM	--	0.0252	0.0284	0.0316	0.0038	0.0092
	left FWHM	--	0.0047	0.0048	0.0056	0.0037	0.0059
	Area	--	$7.97 \cdot 10^{-4}$	$1.68 \cdot 10^{-3}$	$2.04 \cdot 10^{-3}$	$7.11 \cdot 10^{-5}$	$5.61 \cdot 10^{-4}$