

Exothermal effect in the thermal decomposition of $[\text{IrCl}_6]^{2-}$ containing salts with $[\text{M}(\text{NH}_3)_5\text{Cl}]^{2+}$ cations: $[\text{M}(\text{NH}_3)_5\text{Cl}][\text{IrCl}_6]$ ($\text{M} = \text{Co}, \text{Cr}, \text{Ru}, \text{Rh}, \text{Ir}$)

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SUPPLEMENTARY MATERIALS

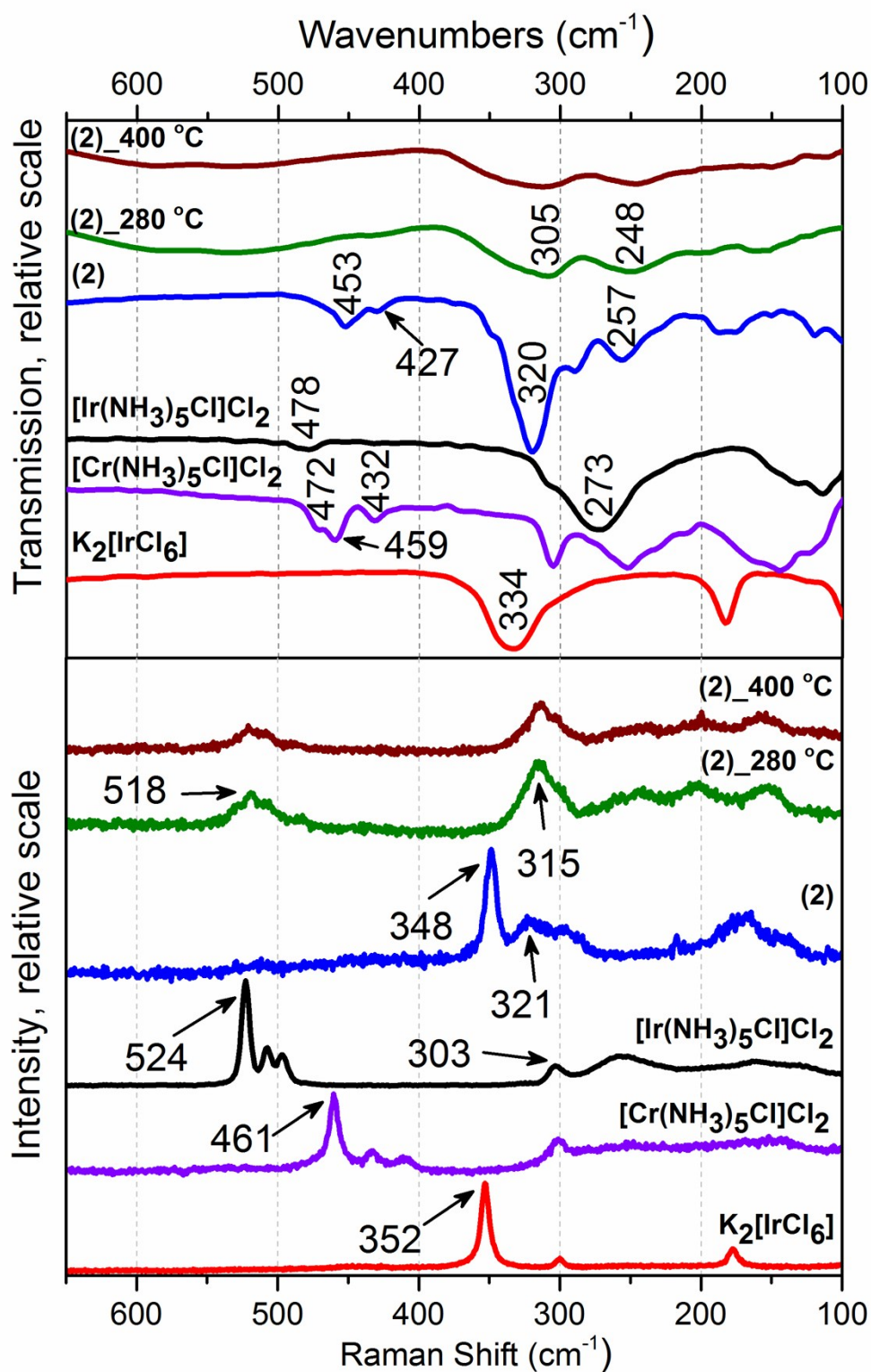


Fig. S1. IR (top) and Raman (bottom) spectra of **(2)** collected *ex situ* after heating to various temperatures in helium.

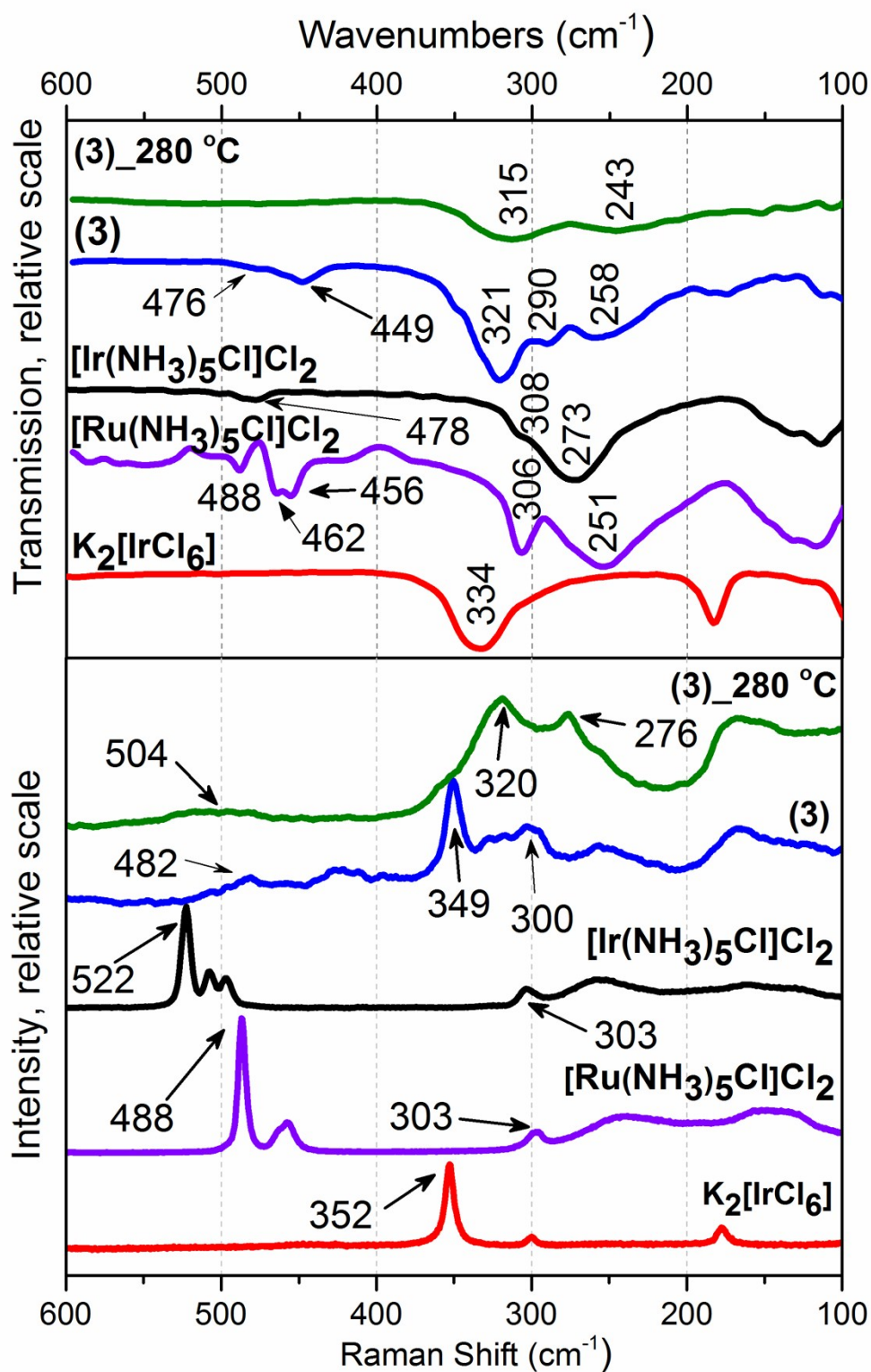


Fig. S2. IR (top) and Raman (bottom) spectra of **(3)** collected *ex situ* after heating to various temperatures in helium.

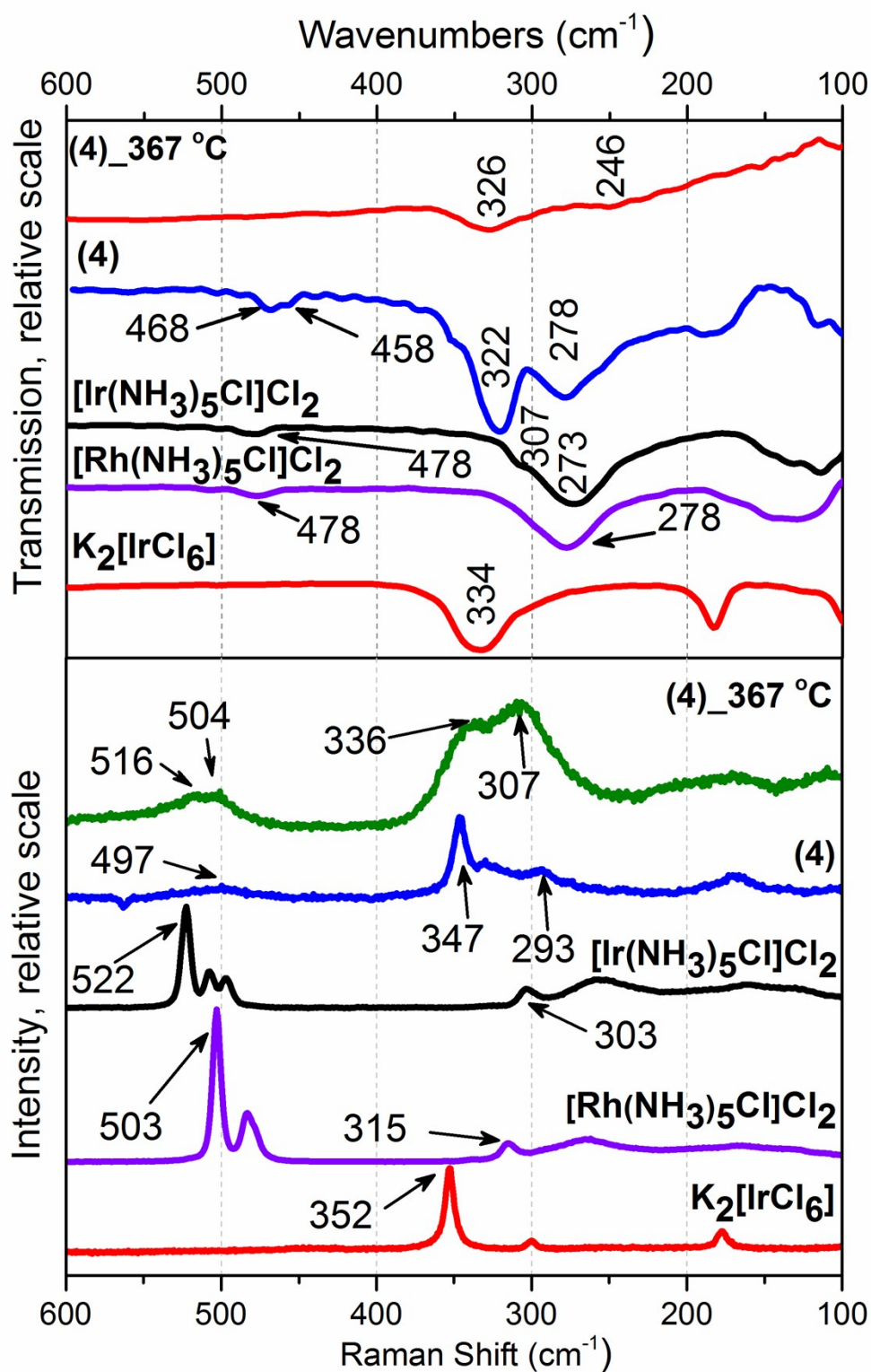


Fig. S3. IR (top) and Raman (bottom) spectra of **(4)** collected *ex situ* after heating to various temperatures in helium.

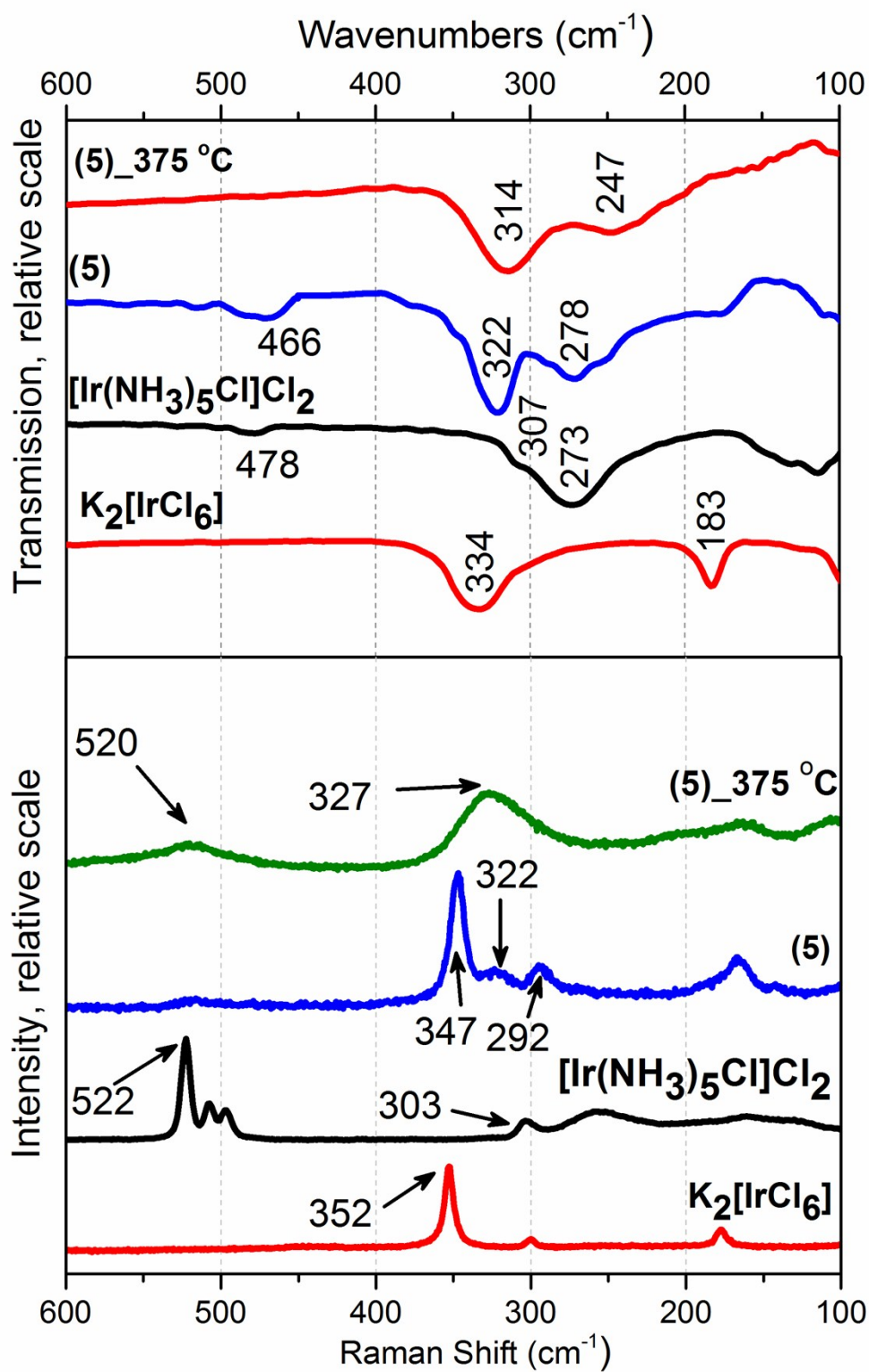


Fig. S4. IR (top) and Raman (bottom) spectra of **(5)** collected *ex situ* after heating to various temperatures in helium.

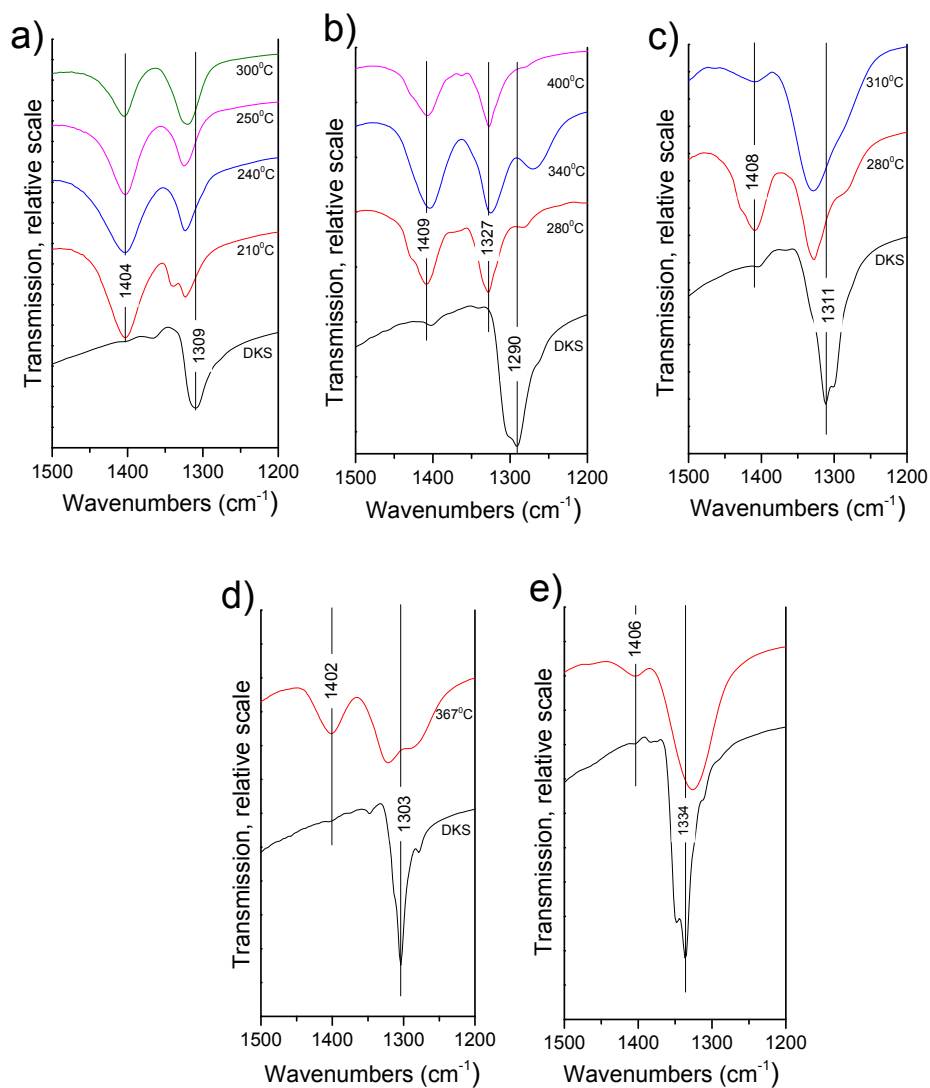


Fig. S5. The region of IR spectra of $\delta(\text{HNH})$ of NH_4^+ and NH_3 of $[\text{M}(\text{NH}_3)_5\text{Cl}][\text{IrCl}_6]$ compounds and intermediate products: a) **(1)**, b) **(2)**, c) **(3)**, d) **(4)**, e) **(5)**.

Tabel S1. Lines IR and Raman spectra of $[M(\text{NH}_3)_5\text{Cl}][\text{IrCl}_6]$ compounds and intermediate products.

	Compound	Method of vibrational spectroscopy							
		IR (cm^{-1})				Raman (cm^{-1})			
		$\rho_r(\text{NH}_3)$	$\nu(\text{MN})$	$\nu(\text{MCl})$	$\delta(\text{NMN})$	$\nu(\text{MN})$	$\nu(\text{MCl})$	$\nu(\text{MCl})$	$\delta(\text{ClMCl})$
	$\text{K}_2[\text{IrCl}_6]$	—	—	334			352	298	178
Co	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	841	490	330	282	461 465 443	332	276	—
	(1)	818	478	321	290	478	346 326	294	172
	(1)_210°C	846		327	297	483	346 315	295	171
	(1)_240°C	832		305	240-191	512 505	364 315	292	182
	(1)_300°C	832		308	239	519 502	317	247	200 153
Cr	$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	774 722	472 459 432	304	250	461 432 408	301	—	—
	(2)	752	453 427	320 289	257	459 429	348 321	294	167
	(2)_280°C	851 721		305	248	518	315	244 203	151
	(2)_400°C	848		312	246	521	314	238 198	157
Ru	$[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	802	488 462 456	306	251	488 457	303	238	143
	(3)	792	476 449	321 290	258	482	349 327	300 255	163
	(3)_280°C	850		315	243	504	320	276	165
Rh	$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	847	478	300	278	503 482	315	263	—
	(4)	829	468 458	322	278	497	347 331	293	168
	(4)_367°C	835	488	326	246	516 504	336 307	—	173
Ir	$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	870	478	307	273	522 507 496	303	254	—
	(5)	856	480 466	322	278	518	347 322	292	165
	(5)_375°C	842	498	314	247	520	327	—	163

Table S2. Elemental composition according to XPS for **(5)** and its intermediate.

	Atomic composition				
	Ir	Cl	N	O	C
Starting salt					
(5)	1.0	3.6	3.4	0.8	3.2
(5)*	1.0	3.4	3.2	1.7	4.3
Intermediate with 7 wt. % weight-loss					
[Ir ₂ (NH ₃) ₅ Cl ₇]	1.0	3.0	2.2	0.6	3.0
[Ir ₂ (NH ₃) ₅ Cl ₇]*	1.0	3.0	2.1	0.7	4.5

* second run after one night in high vacuum.