

Cr(III) Complexes Bearing a β -Ketoimine Ligand for Olefin Polymerization: Are There Differences between Coordinative and Covalent Bonding?

Alessia Amodio ¹, Giorgia Zanchin ^{2*}, Fabio De Stefano ³, Alessandro Piovano ¹, Benedetta Palucci ², Virginia Guiotto ¹, Rocco Di Girolamo ³, Giuseppe Leone ² and Elena Groppo ¹

¹ Dipartimento di Chimica, NIS Interdepartmental Research Center and INSTM Reference Center, Università degli Studi di Torino, I-10135 Torino, Italy; alessia.amodio@unito.it (A.A.); alessandro.piovano@unito.it (A.P.); virginia.guiotto@edu.unito.it (V.G.); elena.groppo@unito.it (E.G.)

² Consiglio Nazionale delle Ricerche, Istituto di Scienze e Tecnologie Chimiche “Giulio Natta” (SCITEC), I-20133 Milano, Italy; benedetta.palucci@scitec.cnr.it (B.P.); giuseppe.leone@scitec.cnr.it (G.L.)

³ Dipartimento di Scienze Chimiche, Università di Napoli “Federico II”, Complesso Monte S. Angelo, I-80126 Napoli, Italy; fabio.destefano@unina.it (F.D.S.); rocco.digirolamo@unina.it (R.D.G.)

* Correspondence: giorgia.zanchin@scitec.cnr.it

SUPPORTING INFORMATION

Table of contents

Figure S1: ¹H-NMR spectrum of ligand L.

Table S1: Polymerization of ethylene

Figure S2: X-ray powder diffraction profiles of PE samples.

Figure S3: IR of poly(norbornene).

Figure S4: IR of poly(diciclopentadiene) and poly(5-ethylidene-2-norbornene).

Figure S5: ¹H and ¹³C-NMR of poly(diciclopentadiene).

Figure S6: ¹H and ¹³C-NMR of poly(5-ethylidene-2-norbornene).

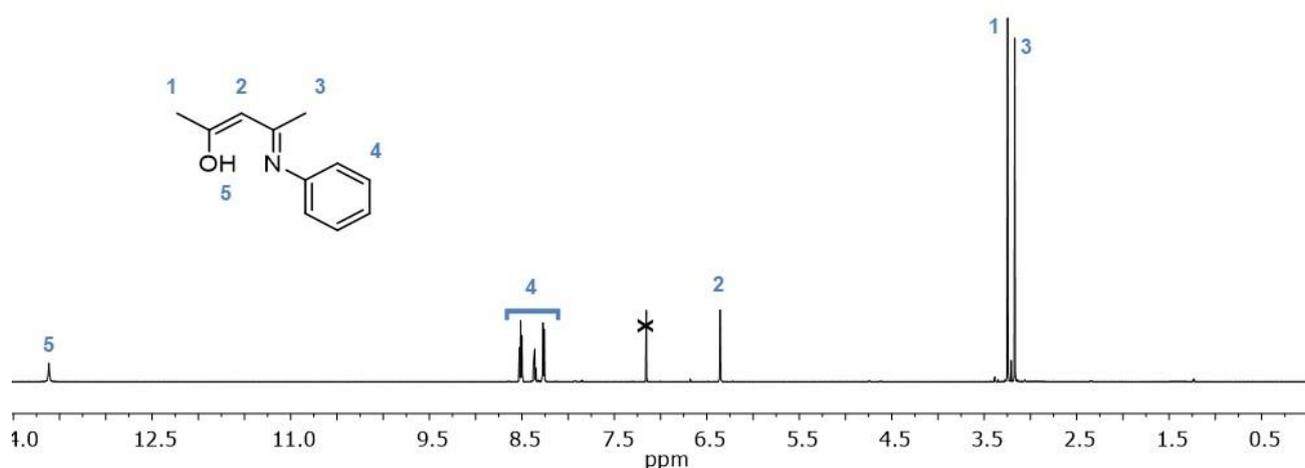
Figure S7: TGA curves of the poly(norbornene) samples.

Figure S8: IR of poly(norbornadiene).

Figure S9: TGA curves of the poly(diciclopentadiene) and poly(norbornadiene) samples.

Scheme S1: polymerization of norbornadiene, mechanistic pathway.

Figure S10: Evolution of the UV-Vis spectra of complexes **1** and **2** in the presence of TEAL.

Figure S1. $^1\text{H-NMR}$ spectrum of ligand L.Table S1. Polymerization of ethylene^a.

entry	complex	co-cat	Al/Cr	T (°C)	time (min)	yield (mg)	act ^b	T _m ^c (°C)	T _c ^c (°C)	ΔH_m^c (J g ⁻¹)	M _w ^d (g mol ⁻¹)	M _n ^d (g mol ⁻¹)	M _w /M _n ^d
9	1	MAO	250	20	24	42	11	134.9	113.3	199.7	519500	66000	7.9
10	1	Et ₃ Al	250	20	8	0	0						
11	1	Et ₂ AlCl	250	20	12	52	26	135.7	115.8	198.6	769900	126000	6.1
12	1	dMAO ^e	250	20	11	91	50	136.2	116.7	198.3			
13	1	Et ₂ AlCl	50	20	10	87	52	137.5	114.6	184.2		<i>n.a.</i>	
14	1	dMAO ^e	50	20	11	0	0						
15 [#]	1	Et ₂ AlCl	50	20	10	32	19	132.2	115.7	182.2	1138600	120300	9.5
16	1	Et ₂ AlCl	50	50	7	8	7						
17	2	MAO	250	20	5	27	32						
18	2	Et ₂ AlCl	250	20	5	3	4						

^a polymerization conditions: ethylene pressure, 1.01 bar; total volume, 25 mL (toluene); Cr complex, 10 μmol , complex solution in dry toluene; ^b activity in $\text{kg}_{\text{pol}} \text{mol}_{\text{Cr}}^{-1} \text{h}^{-1}$; ^c determined by DSC; ^c crystallinity degree calculated from DSC; ^d determined by SEC; ^e dMAO was prepared removing toluene and free AlMe₃ from commercially available MAO. [#] reaction performed in dry dichloromethane.

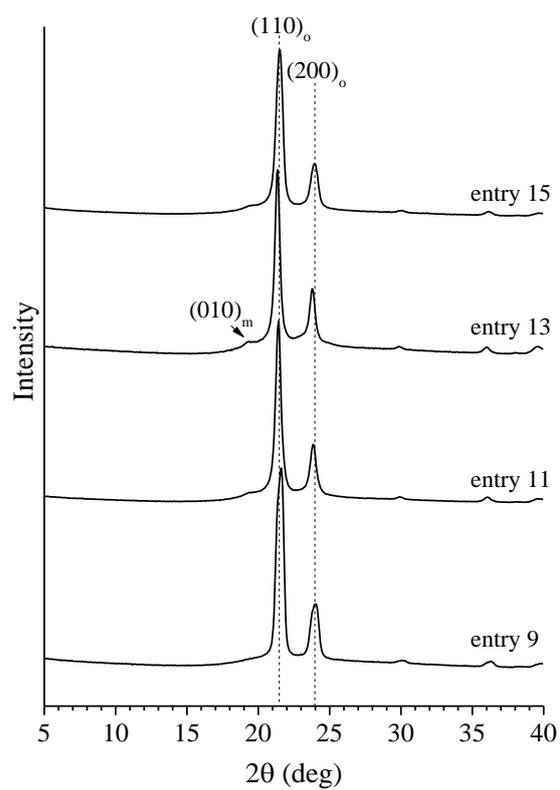


Figure S2. X-ray powder diffraction profiles of some of the PE samples reported in Table S1.

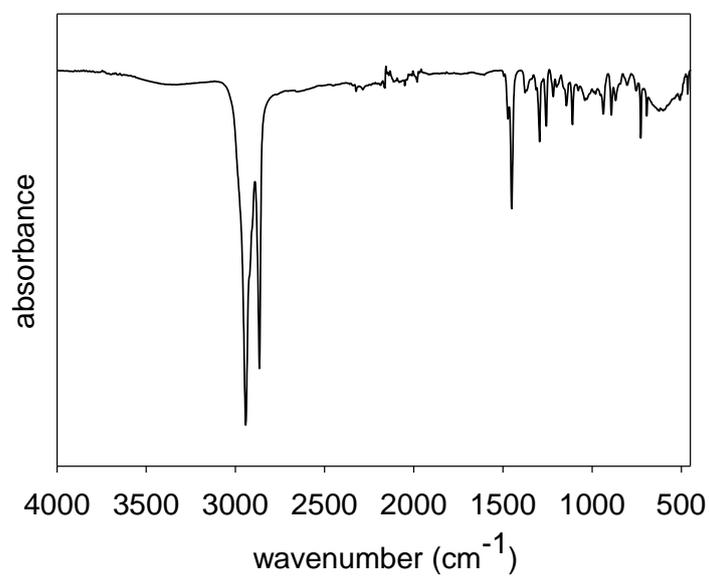


Figure S3. IR of poly(norbornene) (Table 1, entry 4).

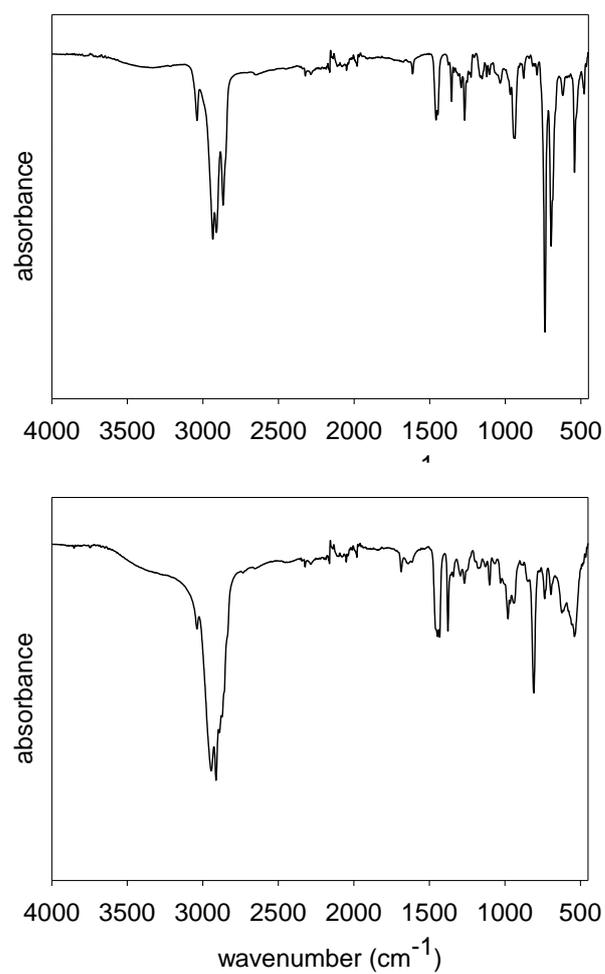
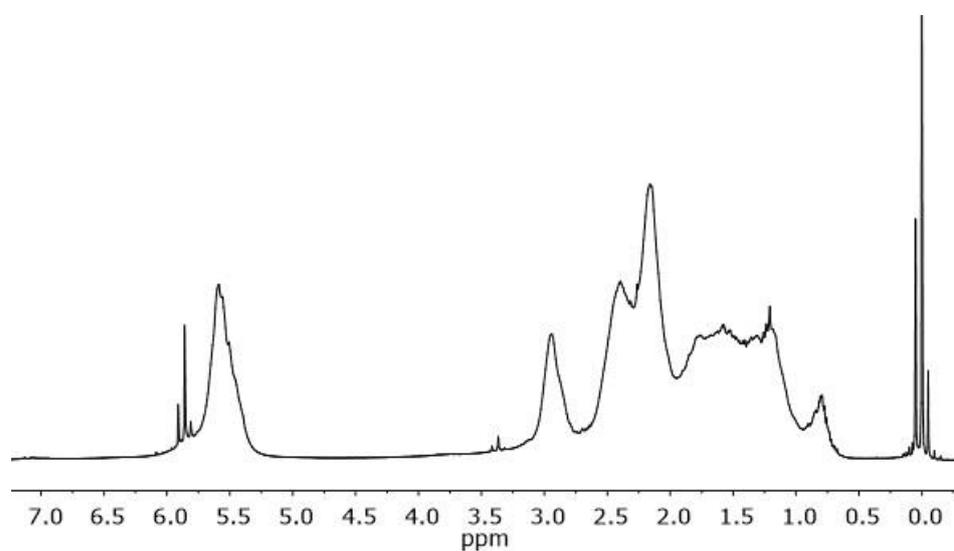


Figure S4. IR of poly(dicyclopentadiene) (*left*) and poly(5-ethylidene-2-norbornene) (*right*) (Table 1, entries 6 and 7, respectively).



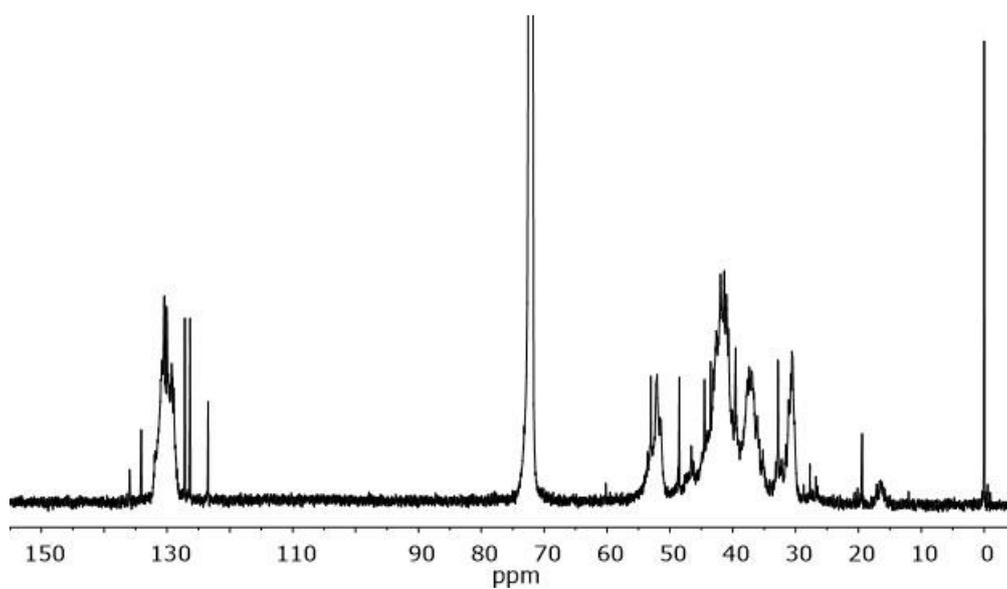


Figure S5. ^1H (top) and ^{13}C (bottom) NMR of poly(dicyclopentadiene) (Table 1, entry 6).

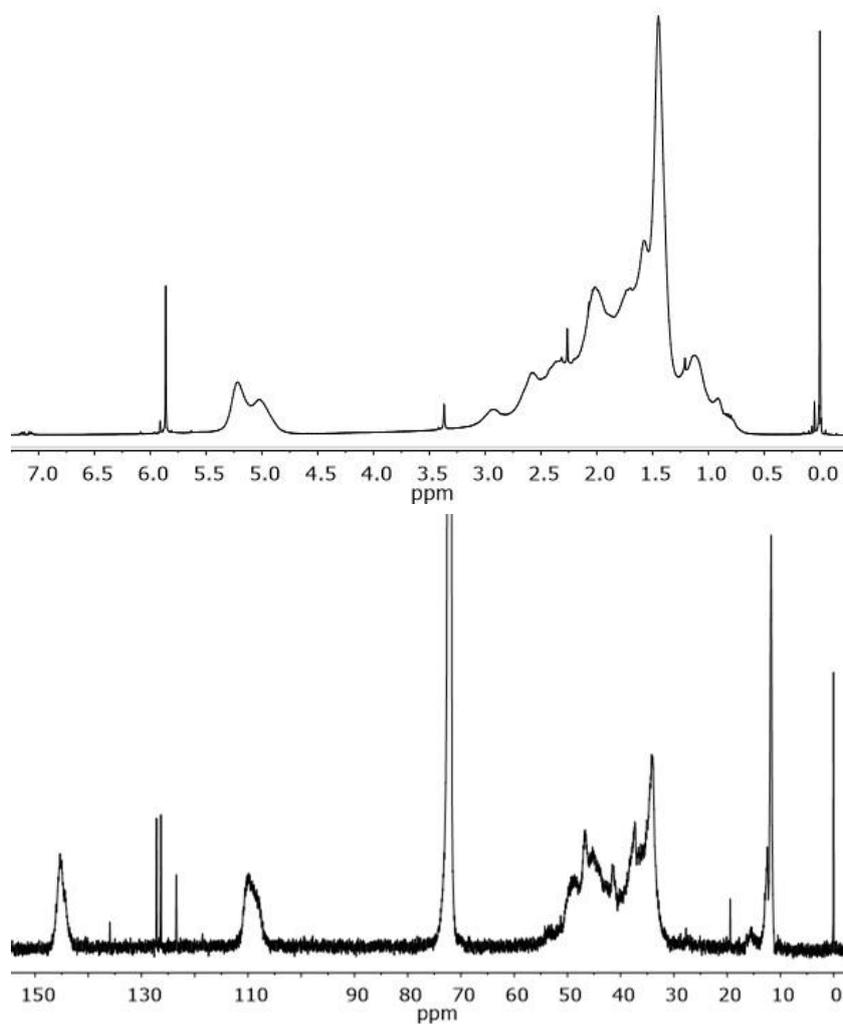


Figure S6. ^1H (top) and ^{13}C (bottom) NMR of poly(5-ethylidene-2-norbornene) (Table 1, entry 7).

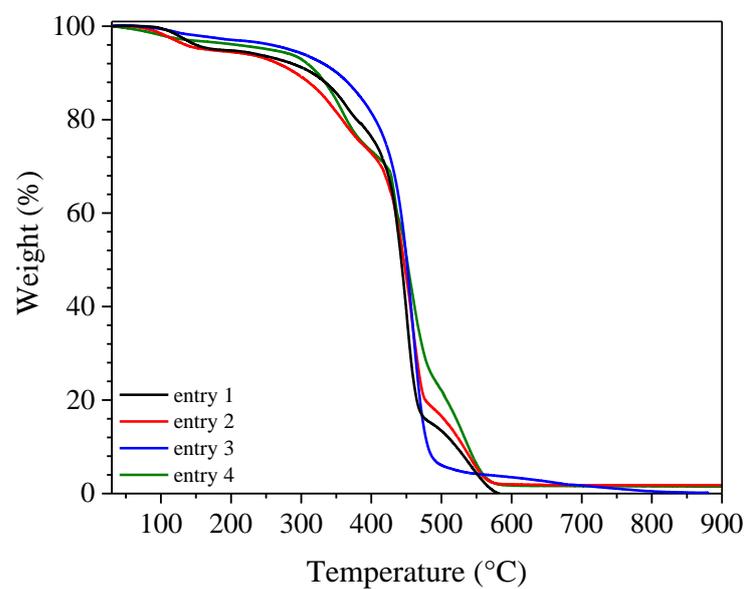


Figure S7. TGA curves of the as-prepared NB oligomer samples reported in Table 1 acquired under a flowing N₂ atmosphere by heating the sample at 10 °C min⁻¹.

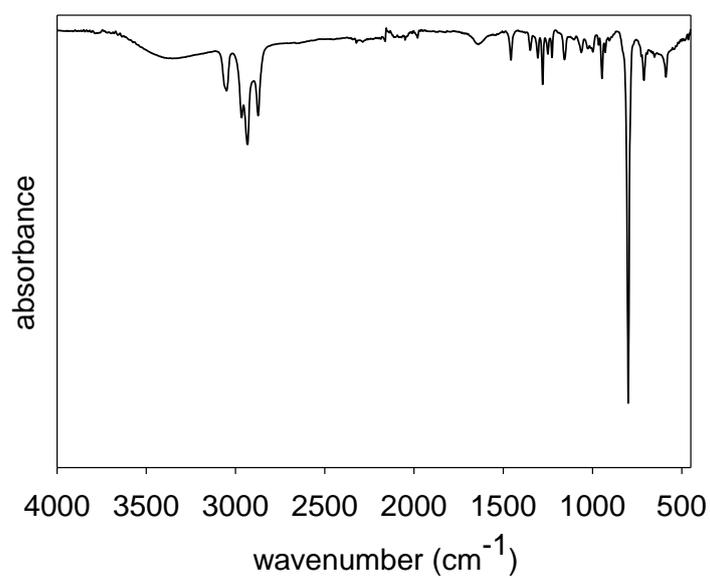


Figure S8. IR of poly(norbornadiene) (Table 2, entry 8).

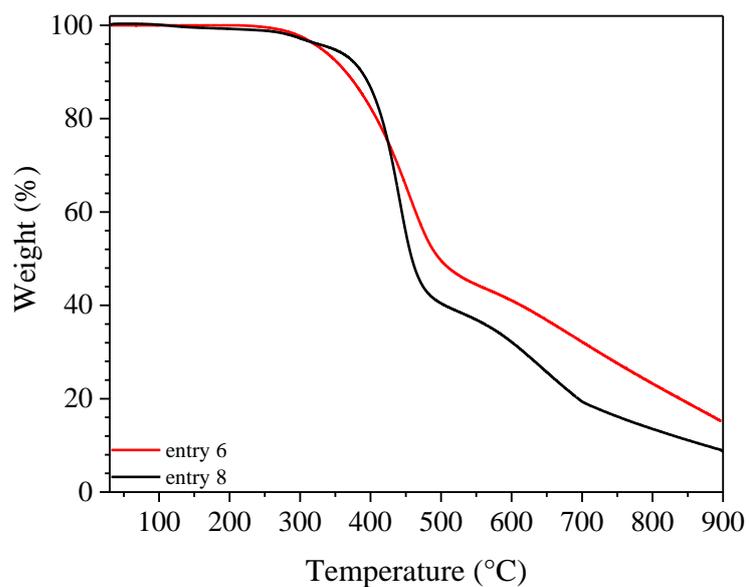
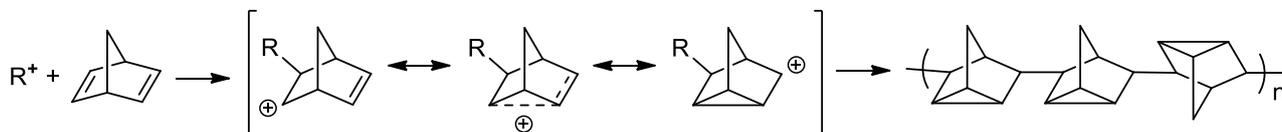


Figure S9. TGA curves of samples 6 and 8 reported in Table 1 acquired under a flowing N₂ atmosphere by heating the sample at 10 °C min⁻¹.



Scheme S1. The possible cationic mechanism involved in the polymerization of NBD.

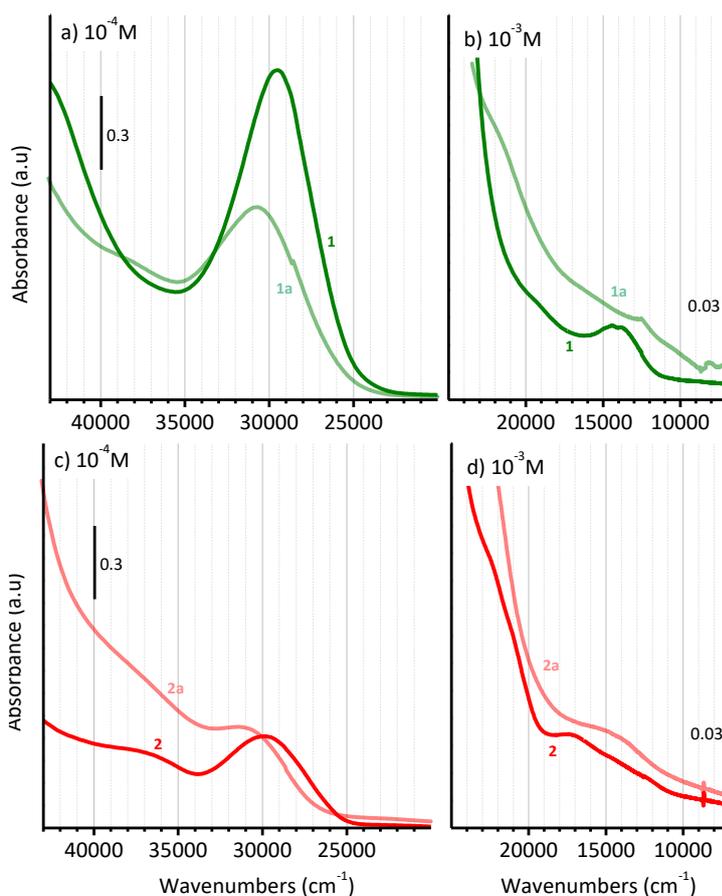


Figure S10. Evolution of the UV-Vis spectra of complex **1** (parts a and b) and complex **2** (parts c and d) in the presence of TEAL (10 μ l) in the region of intra-ligand π - π^* transitions (parts a and c) and in the region of d-d transitions (parts b and d). The spectra have been collected in chloroform at the concentration of 10^{-4} M (part a and c) and 10^{-3} M (part b and d), respectively.

After the addition of 10 μ l of TEAL to complex **1**, relevant changes are observed in the UV-Vis spectrum, both in the region of intra-ligand π - π^* transitions (Figure S10a) and in the region of d-d transitions (Figure S10b). In the former region, the main π - π^* transition decrease in intensity and shifts at higher energy, accompanied by the appearance of a band at about 37000 cm^{-1} . A band at a similar position is also present in the spectrum of complex **2** (spectrum **2** in Figure S10c) and it was assigned to a ligand-to-metal charge-transfer transition of the type O \rightarrow Cr, diagnostic for the presence of a covalent bond between Cr and O. Therefore, observation of this band in spectrum **1a** confirms that TEAL is able to reduce the ligand **L** in complex **1**, promoting the formation of a covalent Cr-O bond. In the region of d-d transitions (Figure S10b), the bands observed in spectrum **1** are both split in two components in spectrum **1a**, which is very much similar to the spectrum of complex **2** (spectrum **2** in Figure S10d).

Addition of 10 μ l of TEAL to complex **2** causes much less changes in the UV-Vis spectrum in both regions. In the region of intra-ligand π - π^* transitions (Figure S10c) a shift of the main π - π^* transition at higher energy is observed, while in the region of d-d transitions the spectrum becomes slightly broader. Both changes are compatible with the exchange of a chlorine atom with an alkyl group in the coordination sphere of the chromium center.