ORGANOMETALLICS

Phenylchromium(III) Chemistry Revisited 100 Years after Franz Hein (Part II): From $\text{Li}_n \text{CrPh}_{3+n}(\text{thf})_x$ (n = 1, 2, 3) to Dimeric Triphenylchromate(II) Complexes

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ABSTRACT: Polyphenylchromium(III) organometallics with various phenylation degrees and stabilized by diverse Lewis bases with various donor strengths and denticity were investigated in order to better understand the formation of (η^6 -arene)chromium complexes according to the procedure of Franz Hein (1892–1976) [*Organometallics* 2019, 38, 498–511, DOI: 10.1021/acs.organomet.8b00811]. Part II focuses on hexa-, penta-, and tetraphenylchromates(III). Chromium(III) compounds with a lower phenylation degree will be discussed in a future part III. The numbering scheme of the complexes relates to the number of Cr-bound phenyl substituents. *Hexaphenylchromate(III)*: The reaction of Ph₃Cr(thf)₃·0.25dx (3) (dx = 1,4-dioxane) with an ethereal solution of phenyllithium yields yellow-orange [Li₃CrPh₆(thf)_{2.3}(OEt₂)_{0.7}] (6-thf-OEt₂) which slowly degrades in contact with the reaction solution leading to emerald-green crystals of [{(Et₂O)Li₃Ph₃Cr(μ -O)]₂ (3-Li₂O). <u>Pentaphenylchromate(III)</u>: Compound 6-thf-OEt₂ reacts with 1 equiv of HCl– OEt₂ solution to turquoise [{(thf)₂Li}{(Et₂O)Li}CrPh₅] (5-thf-OEt₂) that reacts with THF



to the green contact in pair [{(thf)₂Li]₂CrPh₅] (**5-thf**) and with 12-crown-4 (12C4) to the light green solvent-separated ion pair [(12C4)Li(thf)]₂ [CrPh₅] (**5-thf-12C4**). Refluxing of **5-thf-OEt**₂ in diethyl ether leads to ether degradation and formation of **3**-Li₂O, whereas **5-thf-12C4** liberates biphenyl under similar reaction conditions. <u>*Tetraphenylchromate*(*III*)</u>: The reaction of **3** with 1 equiv of phenyllithium in THF leads to a green reaction mixture. At $-50 \ ^{\circ}$ C, red [(thf)₄Li] [*cis*-(thf)₂CrPh₄]·2THF (**4-thf**) crystallizes which reversibly transforms into a green oil above $-50 \ ^{\circ}$ C. Upon acidolysis of **5-thf-OEt**₂ with 1 equiv of HCl–OEt₂ at $-20 \ ^{\circ}$ C, the intermediately formed red complex is reduced to the dinuclear chromate(II) [{(thf)Li}CrPh₃]₂ (**3-Cr^{II}-thf**) (Cr–Cr 187.66(8) pm). Recrystallization of this product from THF yields solvent-separated [(thf)₄Li]₂ [(CrPh₃)₂] (**3-Cr^{II}-thf**) with a Cr–Cr quadruple bond (Cr–Cr 183.7(2) pm) without contacts between the lithium ions and Cr-bound phenyl groups. Complex **3**-Cr^{II}-**thf** reacts at room temperature in diethyl ether to the sandwich complexes bis(biphenyl)chromium(0) [(η^6 -Ph₂)₂Cr⁰] (π -**4**) and benzene-biphenylchromium(0) [(η^6 -C₆H₆)(η^6 -Ph₂)Cr⁰] (π -**3**). Compounds in bold letters are authenticated by X-ray structure determinations.

■ INTRODUCTION

In the year 1919, Franz Hein (1892-1976) presented in his first publication on "polyphenylchromium" compounds and described the synthesis of the crude bromide " $(H_5C_6)_5$ CrBr" besides large amounts of biphenyl.² An ethereal solution of phenylmagnesium bromide was reacted with anhydrous CrCl₃, $CrCl_2$ ³ and CrO_2Cl_2 with molar ratios of 3:1, 3:1, and 6:1, respectively, and the reaction mass, the so-called black product, was degraded in air with cold diluted sulfuric acid, leading to yields of the crude bromide of approximately 20, 4, and 8-13%, respectively. In these reaction mixtures chromium(II) and chromium(I) were detected.⁴ Hein could separate the crude bromide into three components which he interpreted as "penta-",⁵ "tetra-",⁶ and "triphenyl"-chromium halides.⁷ These compounds were moderately sensitive toward light, water, and air. Particularly, these complexes showed the same orange color and the same magnetic moment of 1.7 $\mu_{\rm B}$.⁸ These substances were interpreted as Cr(V) complexes according to

the knowledge at that time. The polyphenylchromium compounds were studied exclusively by Hein's group for the first 30 years after their discovery. Elucidation of the unusual properties and bonding situations of these mysterious substances kept Hein busy nearly for his whole life.⁹ Hein was born in Grötzingen, Baden, near Karlsruhe (Germany), and studied chemistry at the University Leipzig from 1912 to 1917, where he also finished his dissertation and his habilitation with the title "Polyphenylchrombasen und ihre Salze" (Polyphenylchromium Bases and their Salts). Thereafter

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he became a professor at the University Leipzig (Figure 1). In 1942, he moved to Jena, Germany, and was professor for inorganic chemistry at the Friedrich Schiller University Jena until his retirement in 1959.



Figure 1. Franz Hein in his office during his time in Leipzig (Germany) at the Laboratorium für Angewandte Chemie. Reproduced with permission of the Archive of the Faculty of Chemistry and Mineralogy of the University Leipzig.

The (η^{6} -arene)chromium(I) structure was discovered in the 1950s after establishing new preparative methods and the discovery of the sandwich structure of ferrocene.¹⁰ Zeiss and Tsutsui obtained deuterium-free aromatics (phenol, biphenyl, benzene) during the reaction of the three Hein's complexes with the new reagent LiAlD₄. Therefore, and following a thought of Onsager, these complexes were interpreted as (η^{6} -arene)chromium(I) compounds.¹¹ Fischer isolated according to the reducing Friedel–Crafts reaction the missing bis(η^{6} -benzene)chromium(0).¹² In the year 1956, the identity of (η^{6} -Ph₂)₂CrI,¹³ prepared according to a variant of Fischer, and of "Ph₄CrI",¹⁴ synthesized following a procedure of Hein, was verified.

At the beginning of the pioneering work of Hein, phenylmagnesium bromide was used as a solution in diethyl ether. Only later was the stronger Lewis basic THF established as an ideal solvent for Grignard reagents. Thus, Herwig and Zeiss isolated Ph₃Cr(thf)₃, the first true phenylchromium complex with Cr–C σ -bonds.¹⁵ The thf ligands block the coordination sites at Cr^{III} much more effectively than diethyl ether, preventing subsequent reactions to the (η^6 -arene) chromium complexes. This complex with thf ligands allowed for the first time to temporally separate phenylation of CrCl₃, reductive elimination and σ – π rearrangement finally leading to η^6 -arene complexes.

The early investigations of Hein to clarify the mechanism of the synthesis of (η^{6} -arene)chromium complexes were performed during a time where modern spectroscopic methods were unknown or still in its infancy. Chromium(III) compounds require sophisticated NMR and EPR spectroscopic methods for characterization.¹⁶ Therefore, the determination of the crystal structure is of enormous importance. The subsequent products with chromium in the oxidation states of +2, +1, and 0 are easier to characterize by spectroscopy.

In part I of this work we could show that the reaction of $CrCl_3(thf)_3$ with diphenylmagnesium in THF solution allowed

the syntheses of pure phenylchromium(III) complexes.¹ After addition of 1,2-dimethoxyethane (dme), the tetraphenylchromate(III) [PhMg(dme)₂(thf)] [Ph₄Cr(dme)] (4-Mg) was also accessible. However, the reaction sequence following Hein's route to $(\eta^6$ -arene)chromium complexes remained confusing and unclear. Therefore, in this part we systematically studied the potential model substrates of hexa-, penta-, and tetraphenylchromates(III) with respect to the ability to form (η^6 -arene)chromium complexes. Here we report (i) the synthesis and characterization of phenylchromates(III) with stabilizing neutral ligands L with diverse donor strength and denticity (L = 12-crown-4, DME, THF, and Et₂O), (ii) experiments to initiate reduction and $\sigma - \pi$ -rearrangements by dissolution of stabilized phenylchromate(III) complexes in poorly donating Lewis bases, and (iii) the isolation and characterization of intermediates on the route to Hein's (η^6 arene)chromium complexes.

RESULTS AND DISCUSSION

Today, crystal structures of σ -arylchromium complexes are known for chromium in the oxidation states of +1 to +6 (Cr(I),¹⁷ Cr(II),¹⁸ Cr(III),¹ Cr(IV),¹⁹ Cr(V),²⁰ and Cr-(VI)²¹). Until today, organic chromium(III) chemistry has been a scarcely investigated topic, mainly focused on alkyl- and cyclopentadienylchromium(III) complexes.¹⁶

Hexaphenylchromate(III) Complex [Li₃CrPh₆(thf)_{2.3}(OEt₂)_{0.7}] (6-thf-OEt₂). Hein noticed no formation of (η^{6} -arene)chromium complexes during heating of the isolated hexaphenylchromate(III) [{(Et₂O)Li}₃CrPh₆] but the elimination of the majority of the coordinated diethyl ether bases. He concluded that the attached phenyllithium units stabilize this structure type.²² In contrast to Hein who prepared this complex from anhydrous CrCl₃, we reacted CrPh₃(thf)₃·0.25dx (dx = 1,4-dioxane) (**3**) with phenyllithium in diethyl ether and obtained yellow-orange [Li₃CrPh₆(thf)_{2.3}(OEt₂)_{0.7}] (6-thf-OEt₂, Scheme 1). The molecular structure is depicted in Figure 2 and very similar to [{(Et₂O)Li}₃CrPh₆];²³ however, the diethyl ether ligands are partly substituted by thf molecules.

Within 3 days at room temperature, the majority of the solid of **6-thf-OEt**₂ dissolved in the mother liquor and a green solution developed. From this solution emerald green crystals of the composition of $\text{Li}_2\text{OCrPh}_3(\text{OEt}_2)_2$ (**3-Li**₂**O**) precipitated. This transformation was similar to the reaction of $[\text{Li}(thf)_4]$ [{(thf)Li}₂CrPh₆] in THF at -40 °C yielding [{(thf)_3Li}_2(\mu-O)}CrPh_3]_2.¹ Molecular structure and atom labeling scheme of **3-Li**₂**O** are depicted in Figure 3. The molecule is centrosymmetric and symmetry-related atoms are marked with the letter "A".

The penta-coordinate chromium atoms are bound to three phenyl groups and two bridging oxygen atoms with only slightly distorted square pyramidal coordination spheres, verified by the structure index parameter τ of 0.06 (τ is defined as $(\beta - \alpha)/60^{\circ}$ for penta-coordinate complexes with β being the largest and α being the second largest angle).²⁴ For ideal trigonal bipyramids and square pyramids, values of $\tau = 1$ and 0, respectively, are expected. The μ -oxo atoms form the joint edge of the square pyramids. The Cr–C bond lengths to the phenyl groups in the square plane are approximately 6 pm larger than those to the tip of the pyramid.

Pentaphenylchromate(III) Complexes. During the reaction of 6-thf-OEt₂ with hydrogen chloride in diethyl ether (HCl-OEt₂) sparingly soluble lithium chloride pre-

Scheme 1. Synthesis of 6-thf-OEt₂ via Phenylation of $Ph_3Cr(thf)_3$ with Phenyllithium in Diethyl Ether and Subsequent Formation of 3-Li₂O due to Ether Degradation





Figure 2. Molecular structure and atom labeling scheme of molecule A of $[{Li_3(OEt_2)_{0.7}(thf)_{2.3}}CrPh_6]$ (6-thf-OEt₂). Hydrogen atoms are not depicted for clarity reasons. For representation of molecule B, see the Supporting Information. Selected bond lengths of molecule A [molecule B] (pm): Cr1-C1 222.2(3) [223.0(3)], Cr1-C7 232.2(3) $[221.4(3)], \bar{Cr1}-C13 265.2(3)$ [226.7(3)], Cr1-C19 262.2(3) [225.7(3)], Cr1-C25 221.9(3)[221.1(3)], Cr1-C31 226.9(3) [226.5(3)], Li1-O1 191.4(6) [191.7(6)], Li1-13 228.0(6) [232.9(7)], Li1-C19 232.6(7) [229.8(6)] Li1-C25 221.3(6) [223.7(6)], Li2-O2 195.7(8) [187.8(8)], Li2-O2T 1.86.0(9) [197.2(8)], Li2-C7 227.4(6) [225.4(7)], Li2-C13 233.8(6) [232.6(7)], Li2-C31 224.6(6) [232.6(7)], Li3-O3 188.2(7) [185.9(10)], Li3-O3T 204.5(10) [193.7(7)], Li3-C1 225.8(7) [226.1(6)], Li3-C19 228.5(7) [233.7(7)], Li3-C31 234.1(7) [228.9(6)], nonbonding distances (pm): Cr1-Li1 264.1(5) [266.8(6)], Cr1-Li2 266.5(5) [265.9(6)], Cr1-Li3 267.8(6) [268.5(5)]; bond angles (deg.): C1-Cr1-C13 178.63(12) [179.32(12)], C7-Cr1-19 179.07(11) [178.9(12)], C25-Cr1-C31 178.59(12) [178.03(12)], Li1-Cr-Li2 110.66(17) [110.30(19)], Li1-Cr-Li3 110.30(1) [110.50(17)], Li2-Cr-Li3 109.17(17) [109.94(19)].



Figure 3. Molecular structure of $[\{(Et_2O)Li\}_2\{Ph_3Cr(\mu - O)\}]_2$ (3-Li₂O) with selected atom labeling. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths (pm): Cr1–C1 213.4(2), Cr1– C7 207.0(2), Cr1–C13 214.4(2), Cr1–O1 195.00(15), Cr1–O1A 194.41(15), Li1–O1 183.1(4), Li1–O2 189.8(4), Li1–C7 247.0(5), Li1–C13 243.2(5), Li2–O1 181.5(5), Li2–O3 186.3(5), Li2–C1A 226.4(5), Li2–C7A 282.2(6); bond angles (deg): O1–Cr1–C1 167.30(8), O1A–Cr1–C13 163.62(8), O1–Cr1–O1A 87.39, Cr1– O1–Cr1A 92.61(6), O1–Cr1–C13 89.26(8), O1–Cr1–C7 93.91(8), C1–Cr1C7 98.92(9), C7–C1–C13 97.63(9), Li1–O1– Li1A 112.6(2); nonbonding distances (pm): Cr1…Cr1A 281.55(6), Cr1…Li1 254.0(4), Li1…Li2 303.4(6), Cr1A…Li2 257.2(4).

cipitated (Scheme 2). Cooling of the filtrate to -20 °C led to precipitation of turquoise crystals of [{(th)₂Li}{(Et₂O)Li}-

Scheme 2. Synthesis of 5-thf-OEt₂ via Acidolysis of 6-thf-OEt₂ with Hydrogen Chloride in Diethyl Ether



 $CrPh_5$] (5-thf-OEt₂). Molecular structure and atom labeling scheme of this complex are depicted in Figure 4.

The penta-coordinate chromium atom is σ -bound to five phenyl groups, leading to a distorted square pyramid ($\tau = 0.25$). Complex **5-thf-OEt**₂ is one of the rather rare examples for mononuclear chromium(III) organometallics with the coordination number of 5.^{1,25} The deformation of the square pyramid is caused by the different coordination environments of Li1 and Li2. The Cr1–C1 bond length to the tip of the pyramid is approximately 10 pm smaller than the Cr1–C distances to the ipso-carbon atoms of the square plane. The free coordination site opposite to the apical C1 atom is shielded by the *ortho*-hydrogen atoms of the phenyl groups of the square plane.

The corresponding thf-adduct $[{(thf)_2Li}_2CrPh_5]$ (5-thf) that had been prepared by Hein following another procedure²⁶ could be obtained by quenching of a boiling solution of 5-thf-OEt₂ in cold THF. It seemed likely that the temperature-dependent equilibrium favored the left side at elevated temperatures as depicted in Scheme 3. The immediate cooling



Figure 4. Molecular structure of $[\{(Et_2O)Li\}CrPh_5\{Li(thf)_2\}]$ (5-thf-OEt₂) with selected atom labeling. Hydrogen atoms are neglected for clarity reasons. Selected bond lengths (pm): Cr1–C1 206.6(2), Cr1–C7 216.9(2), Cr1–C13 217.8(2), Cr1–C19 214.2(2), Cr1–C25 215.2(2), Li1–O1 94.5(5), Li1–O2 195.7(5), Li1–C19239.6(5), Li1–C25 215.2(5), Li2–C13 191.2(5), Li2–C1 244.9(5), Li2–C7 230.5(5), Li2–C13 223.6(5); nonbonding distances (pm): Cr1…Li1 301.0(5), Cr1…Li2 260.0(4); bond angles (deg.): C1–Cr1–C7 95.33(9), C1–Cr1–C13 98.46(9), C1–Cr1–C19 97.36(9), C1–Cr1–C19 167.28(9), C7–Cr1–C25 82.92(8), C7–Cr1–C19 167.28(9), C13–Cr1–C19 89.14(9), C13–Cr1–C25 151.99(9), C19–Cr1–C25 92.15(9), Li1–Cr1–Li2 148.21(48).

Scheme 3. Temperature-Dependent Equilibrium between 5thf on the One Side and a Mixture of 6-thf and $\text{LiCrPh}_4(\text{thf})_x$ on the Other



of this hot solution slowed equilibration down enabling crystallization of metastable **5-thf**.²⁷ Slow cooling of the green solution to room temperature led to the thermodynamically controlled ligand exchange, and only sparingly soluble yellow **6-thf** crystallized. The nature of the green species $\text{LiCrPh}_4(\text{thf})_x$, which remained in the mother liquor, will be discussed in the next chapter.

The molecular structure and atom labeling scheme of **5-thf** are depicted in Figure 5. The penta-coordinate chromium(III) atom is bound to five phenyl groups with a distorted square planar coordination sphere giving a structure index parameter of $\tau = 0.23$. The C1 atom is located at the tip of the pyramid, whereas the carbon atoms C7, C13, C19, and C25 form the square plane. The lithium atoms bind only to the ipso-carbon atoms of the square plane. The bridging Li–C–Cr positions enhances the Cr1–C bond lengths by 9.3–12.0 pm compared to the apical Cr1–C1 bond.

A pentaphenylchromate(III) of the type $\text{Li}_2\text{CrPh}_5(\text{OEt}_2)_{xy}$ only stabilized by diethyl ether ligands, could not be isolated as of yet. Dissolving **5-thf-OEt**₂ in refluxing diethyl ether led to emerald-green compound **3-Li**₂**O** with bridging oxide moieties due to accompanying ether cleavage reactions (Scheme 4).²⁸ This μ -oxochromium(III) product was unable to create free



Figure 5. Molecular structure of $[{(thf)_2Li}_2CrPh_5]$ (5-thf) with selected atom labeling. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths (pm): Cr1–C1 205.4(2), Cr1–C7 215.4(2), Cr1–C13 217.4(2), Cr1–C19 214.7(2), Cr1–C25 216.2(2), Li1–C7 239.1(4), Li1–C13 227.0(4), Li1–O1 196.3(4), Li1–O2 192.7(4), Li2–C19 229.1(4), Li2–C25 230.2(4), Li2–O3 195.9(5), Li2–O4 194.8(4); nonbonding distances (pm): Cr1…Li1 287.1(4), Cr1…Li2 291.9(4); bond angles (deg.): C1–Cr1–C7 103.43(9), C1–Cr1–C13 98.30(8), C1–Cr1–C19 106.58(9), C1–Cr1–C25 97.47(8), C7–Cr1–C13 92.65(8), C7–Cr1–C19 149.94(8), C7–Cr1–C25 86.50(8), C13–Cr1–C19 81.49(8), C13–Cr1–C25 163.96(8), C19–Cr1–C25 91.24(8), O1–Li1–O2 96.66(19), C7–Li1–C13 84.33(15), O3–Li2–O4 94.72(19), C19–Li2–C25 84.20(15), Li1–Cr1–Li2 157.27(11).

coordination sites and hence also unable to react to (η^6 -arene) chromium complexes.

Scheme 4. Attempt to Produce $Li_2CrPh_5(OEt_2)_x$ without thf Ligands from 5-thf-OEt₂ Failed and Instead Ether Cleavage Occurred Yielding 3-Li₂O



The perfluorinated pentaphenylchromate(III) $[nBu_4N]_2$ [Cr(C₆F₅)₅] is known as a light green solid stable below 0 °C and explosive at room temperature.²⁹ We were interested if thermolysis of pentaphenylchromate(III) derivatives without stabilizing Li–C contacts would yield (η^6 -arene)chromium complexes. Therefore, compound **5-thf-OEt**₂ was reacted with 12-crown-4 (12C4) with a molar ratio of 1:2. This procedure led to formation of a light green and only sparingly soluble substance. Careful recrystallization from warm THF yielded small crystals of the composition "Li₂CrPh₅(thf)₂(12C4)₂". Due to the very small crystal size we were only able to elucidate the structural motif of [Li(thf)(12C4)]₂ [CrPh₅] (**5thf-12C4**) that is depicted in Figure 6. Indeed, there are no short contacts between the lithium ions and the ipso-carbon atoms of the pentaphenylchromate(III) anion.

The formation of a 2:1 ionic lattice explains the poor solubility of **5-thf-12C4** in THF. The penta-coordinate lithium



Figure 6. Motif of the molecular structure of $[(thf)(12\text{-crown-4})\text{Li}]_2[CrPh_5]$ (5-thf-12C4).

ions are in distorted square pyramidal environments of a 12crown-4 and a thf ligand. In the anion, the Cr1 atom is in a trigonal bipyramidal coordination sphere ($\tau \approx 1$). The hight thermo- and light-sensitivity suggests that this bonding situation is disadvantageous compared to the contact ion pairs. This observation is in agreement with homometallic phenyllithium complexes. Donor-free $[(PhLi)_2]_{\infty}$ shows bridging phenyl groups leading to PhLi pairs that form chainlike structures in the solid state via interactions of the lithium atoms with the phenyl π -systems of neighboring dimers.³⁰ Lewis base L leads to deaggregation and formation of $[(L)LiPh]_2^{31}$ before solvent-separated ion pairs are formed.³²

Dissolving complex **5-thf-12C4** in $[D_8]$ THF at 40 °C led to formation of biphenyl within a few minutes. However, (η^{6} arene)chromium complexes could not be detected in this reaction mixture via ¹H and ¹³C NMR spectroscopy. In Scheme 5, a reaction scheme is presented showing the structure–reactivity relationship between the verified compounds.

Scheme 5. Reactions of 5-thf-OEt₂ with THF at -40° C to 5thf and with THF in the Presence of 12-crown-4 Yielding 5thf-12C4^{*a*}



^{*a*}At higher temperatures, the equilibrium depicted in Scheme 3 is operative. The product degrades within 1 h at 40°C in $[D_8]$ THF finally leading to the formation of biphenyl. Note that no (η^6 -arene) chromium complexes have been observed during degradation.

Tetraphenylchromate(III) Complexes. According to Hein's protocol to prepare (η^6 -arene)chromium complexes, solid anhydrous CrCl₃ was slowly added in small portions to a Grignard solution of PhMgBr. At the initial stage of this procedure, phenylmagnesium bromide was the excess component with respect to chromium(III) chloride yielding mainly tetraphenylchromate(III) species. Now we intended to study how (η^6 -arene)chromium complexes developed from these tetraphenylchromate(III) compounds. In order to trap intermediates, Lewis bases with increasing donor strength (Et₂O < THF < DME) were applied. Phenylation reagents were diphenylmagnesium and phenyllithium with different phenylation strengths.¹

The reaction of $[{(Et_2O)Li}_3CrPh_6]$ in diethyl ether with *n* equivalents of anhydrous magnesium chloride yielded lithium chloride and phenylmagnesium chloride according to Scheme 6. During this "inverse titration" a reaction mixture gradually

Scheme 6. Reaction of Li₃CrPh₆·3Et₂O with Magnesium Chloride in Diethyl Ether Leading to Phenyl-Poorer Chromates(III)

 Li_3CrPh_6 + n MgCl₂ \longrightarrow $Li_{3-n}CrPh_{6-n}$ + n PhMgCl + n LiCl

formed that offered suitable reaction conditions for the formation of $(\eta^{6}$ -arene)chromium complexes. Experimentally, the value of $n \geq 1.3$ for beginning formation of $(\eta^{6}$ -arene)chromium complexes had been determined which corresponded to the species Li_{1.7}CrPh_{4.7}.³³ This finding verified that hexa- and pentaphenylchromates(III) in diethyl ether were unable to form $(\eta^{6}$ -arene)chromium complexes (this conclusion is in accordance with our investigations discussed above). The reaction yielding π -complexes started with the beginning formation of tetraphenylchromate(III) derivatives.

The red tetraphenylchromates(III) $[Li(dme)_3]$ $[Ph_4Cr(dme)]$ (4-dme) and $[PhMg(dme)_2(thf)]$ $[Ph_4Cr(dme)]$ (4-Mg-dme) were stabilized with bidentate dme ligands and were stable in DME-THF solutions until 60 °C.¹ In order to reduce thermic stability, two procedures seemed feasible: (i) the 1:1 reaction of 3 with halide-free phenyllithium at room temperature in THF and (ii) the reaction of 5-thf-OEt₂ with 1 equiv of HCl-OEt₂ solution at -15 °C.

Route (i) gave a green reaction mixture. Cooling to -50 °C led to a color change to red, and purple crystals of **4-thf** precipitated (Scheme 7). The temperature-dependent color change was reversible. Drying of these crystals in vacuo at -70 °C on a Schlenk frit did not allow complete removal of the adhesive solvent. At the end of this drying procedure, the substance spontaneously converted into a green tenacious

Scheme 7. Synthesis of 4-thf via Phenylation of $Ph_3Cr(thf)_3$ with Phenyllithium in THF at Room Temperature



https://dx.doi.org/10.1021/acs.organomet.0c00602 Organometallics XXXX, XXX, XXX–XXX oil.³⁴ Due to the fact that the red crystals were only stable in contact with mother liquor, no reliable elemental analysis could be performed. Therefore, characterization was only possible by spectroscopic methods or by X-ray structure determination. The molecular structure and atom labeling scheme of solvent-separated $[\text{Li}(\text{thf})_4]$ $[\text{Ph}_4\text{Cr}(\text{thf})_2]$ (4-thf) are depicted in Figure 7.



Figure 7. Molecular structure of $[(thf)_4Li] [cis-(thf)_2CrPh_4]$ ·2THF (4-thf) with selected atom labeling. The two noncoordinating THF molecules per formula unit and the hydrogen atoms are omitted for the sake of clarity. Disordering of phenyl with C1 and thf with O3 is not shown. Selected bond lengths (pm): Cr1–C1 213.5(10), Cr1–C1A 216.5(6), Cr1–C7 216.3(4), Cr1–C13 207.9(5), Cr1–C19 217.4(4), Cr1–O1 226.4(3), Cr1–O2 220.7(3), Li1–O3 191.6(11), Li1–O4 191.3(11), Li1–O5 193.3(10), Li1–O6 192.9(9); bond angles (deg.): C1–Cr1–C7 98.0(3), C1–Cr1–C13 92.8(4), C1–Cr1–C19 89.8(3), C1–Cr1–C19 171.3(17), C7–Cr1–C19 171.35(17), C7–Cr1–O1 85.05(14), C7–Cr1–O2 88.81(14), C13–Cr1–C19 91.29(16), C13–Cr1–O1 94.44(16), C13–Cr1–O2 178.22(15), O1–Cr1–O2 84.13(11), O3–Li1–O4 109.6(5), O3–Li1–O5 115.5(5), O3–Li1–O6 106.7(5), O4–Li1–O5 106.9(5), O4–Li1–O6 110.0(4).

The molecular structure contains the ions $[\text{Li}(\text{thf})_4]^+$ and $[cis-(\text{thf})_2\text{CrPh}_4]^-$ and two noncoordinating THF molecules. The structure of the tetraphenylchromate(III) anion is rather similar to dme adducts **4-dme** and **4-Mg-dme**.¹ The trans effect of the thf ligands leads to a shortening of the Cr–C bond lengths compared to the other Cr–C distances. The O1– Cr1–O2 bond angle (84.13(11)°) is approximately 8.4(1)° larger compared to the adducts with the bidentate dme ligands. This fact enhances the steric pressure in **4-thf** easing elimination of a thf base. However, to date we were unable to isolate pure "LiCrPh₄(thf)_x" with x < 5 that formed above –50 °C; hence, the structure of the green compound remained unsolved. Addition of 1 equiv of HCl–OEt₂ solution and 1,4-dioxane to this green solution gave Ph₃Cr(thf)₃·0.25dx (**3**).

The combination of a suspension of 3 in THF with 2 equiv of $Ph_2Mg(thf)_2$ yielded a clear red solution. At -40 °C, complex 3 crystallized slowly within a few days, suggesting an equilibrium between 3 and tetraphenylchromate(III) species with sparingly soluble derivative 3 crystallizing first. Mixtures of 3 and the stronger phenylating reagent PhLi led to quantitative formation of 4-thf without significant amounts of 3 remaining.

According to Hein and Schmiedeknecht, $M[CrPh_4]$ (M = Li and Na) formed during the 1:2 reaction of $M_3CrPh_6(OEt_2)_3$ with anhydrous $CrCl_3$ (or $CrCl_3(thf)_3$) in a suspension in diethyl ether at -15 °C. The unstable tetraphenylchromate-(III) eliminated biphenyl, and a dark brown dinuclear chromium(II) complex of the type " $[M_2Cr_2Ph_6(L)_3]$ " (L = thf, Et₂O) formed that reacted with the (η^6 -arene)chromium

complexes bis(biphenyl)chromium(0) $\left[(\eta^6 - Ph_2)_2 Cr^0 \right] (\pi - 4)$ and benzene-biphenylchromium(0) $\left[(\eta^6 - C_6 H_6) (\eta^6 - Ph_2) Cr^0 \right]$ $(\pi$ -3).³⁵ It has been recognized that $[M_2Cr_2Ph_6(L)_3]$ was able to initiate polymerization of 1,3-butadiene.³⁶ The fact that this compound was weakly paramagnetic (0.62 $\mu_{\rm B}/{
m Cr}$) suggested a magnetic abnormal chromium(II) compound with a quadruple Cr–Cr bond with two antiferromagnetically coupled electrons residing in chromium-localized orbitals.³ However, we were unable to isolate pure crystalline LiCrPh₃(OEt₂)_{1.5} at -15 °C. Acidolysis of an ethereal suspension of Li₃CrPh₆(OEt₂)₃ with 2 equiv of HCl-OEt₂ solution at -40 °C initially gave a sparingly soluble purple intermediate that converted quickly to the (η^6 -arene) chromium complexes bis(biphenyl)chromium(0) $\left[(\eta^6 - \eta^6 - \eta^6$ $Ph_2)_2Cr^0$ (π -4) and benzene-biphenylchromium(0) [(η^6 - $C_6H_6)(\eta^6-Ph_2)Cr^0]$ (**\pi-3**).

Milder reaction conditions could be maintained during route (ii), reacting **5-thf-OEt**₂ as suspension in diethyl ether with 1 equiv of HCl–OEt₂ at -40 °C. During this procedure, the turquoise substrate converted to purple microcrystalline intermediate which quantitatively gave a dark brown reaction solution. Precipitated lithium chloride was removed at -20 °C. The filtrate was cooled to -40 °C leading to crystallization of dark brown [{(thf)Li}CrPh₃]₂ (**3-Cr**^{II}-**thf**). The molecular structure and atom labeling scheme are depicted in Figure 8.



Figure 8. Molecular structure of $[\{(thf)Li\}CrPh_3]_2$ (**3-Cr^{II}-thf**) with selected atom labeling. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths (pm): Cr1–Cr1A 187.66(8), Cr1–C1 207.4(2), Cr1–C7 208.5(2), Cr1–C13 209.8(2), Cr1–C1 207.4(2), Li1–O1 191.3(5), Li1–C1 241.9(5), Li1–C7A 235.8(5), Li1–C13 229.6(5); nonbonding distances (pm): Cr1···Li1 269.6(4), Cr1···Li2 297.6(5); bond angles (deg): Cr1A–Cr1–C1 91.93(7), Cr1A–Cr1-C7 111.60(7), Cr1A–Cr1–C13 115.64(8), C1–Cr1–C7 101.75(10), C1–Cr1–C13 127.11(1), O1–Li1–C1 119.6(2), O1–Li1–C7A 114.6(2), O1–Li1–C13 128.1(3), C1–Li1–C7A 100.73(18), C1–Li1–C13 84.12(27), C13–Li1–C7A 103.1(2); dihedral angles (deg): C1–Cr1–Cr1A–C1A = C7–Cr1–Cr1A–C1A C7A 180.0(1), C1–Cr1–Cr1A–C7A = C7–Cr1–Cr1A–C1A 76.5(1), C1–Cr1–Cr1A–C13A = C7–Cr1–Cr1A–C1A 24.5(1).

The dinuclear centrosymmetric molecular structure of 3-Cr^{II}-thf contains a short Cr1–Cr1A bond of 187.66(8) pm at the lower range for Cr^{II}–Cr^{II} quadruple bonds for magnetically anormal chromium(II) complexes. It is noteworthy that Cr1 binds only to three phenyl groups leading to the unusual low coordination number of 4. The angle between the planes C1, Cr1, Cr1A, C1A and C7, C13, Cr1, Cr1A, C7A, C13A shows a value of $76.5(1)^{\circ}$. The deviation from the ideal 90° angle is caused by the coordination to the lithium counterions.

The genesis of this product can easily be explained by the weaker coordination strength of diethyl ether compared to THF. Acidolysis of **5-thf-OEt**₂ with HCl–OEt₂ obviously yielded the purple intermediate tetraphenylchromate(III) LiCrPh₄(L)_x (L = OEt₂ and/or thf) which is significantly less stable than pure thf adduct **4-thf**. This enhanced reactivity led to immediate reductive elimination of biphenyl and formation of chromate(II) **3-Cr^{II}-thf** according to Scheme 8. Contrary to these phenyl derivatives, the violet complexes $[Cr(Ar)_4]^{2-}$ (Ar = C₆Cl₅ and o_0o' -F₂C₆H₃) are stable in solution below 0 °C without stabilizing ethereal coligands.³⁸

Scheme 8. Exchange of thf by Diethyl Ether Destabilizes Tetraphenylchromate(III) Initiating Reductive Elimination of Biphenyl and Yielding 3-Cr^{II}-thf which Converts in THF Solution to Solvent-Separated 3-Cr^{II}-thf₄



Dinuclear chromium(II) organometallics were already intensively studied with special interest devoted to the short Cr–Cr quadruple bonds.³⁹ This bond is caused by the interactions of the $3d_{z^2}$ (σ -bond), the $3d_{xz}$ and $3d_{yz}$ (two π bonds), and the $3d_{xy}$ orbitals (δ -bond) between the chromium-(II) atoms.⁴⁰ This bonding type had initially been recognized for K₂[Re₂Cl₈](H₂O)₂ with a very short Re–Re bond and eclipsed orientation of the chloro ligands.⁴¹ The first dinuclear organometallic Cr^{II} complexes of Hein and Tille⁴² as well as of Kurras,⁴³ [{(Et₂O)Li}₂Cr₂(C₆H₄-2-NMe₂)₆] and [Cr₂(C₆H₄-2-OMe)₄] as well as [{(thf)Li}₄Cr₂Me₈], show similar molecular structures (Cr–Cr 183.0(4) pm⁴⁴ as well as 198.0(5) and 196.8(2) pm,⁴⁵ respectively). The analogous nickel complex [{(thf)Li}₂NiMe₄]₂ cannot form a Ni–Ni bond due to electronic reasons and hence, a large Ni–Ni separation of 316.7(1) pm has been observed.⁴⁶

Exchange of the lithium-bound thf molecules in [{(thf)-Li}₄Cr₂Me₈] against the stronger bidentate Lewis base bis(dimethylamino)ethane (tmeda) led to cleavage of the Cr–Cr bond and the mononuclear high-spin complex [{(tmeda)Li}₂CrMe₄].⁴⁷ The paramagnetism of the sodium complex [{(Et₂O)Na}₄Cr₂Me₈] was temperature-dependent,

and in this derivative the largest Cr–Cr quadruple bond length of 326.3(2) pm had been observed.⁴⁸ Another structureinfluencing factor is the bulkiness of the Cr-bound organyl groups. The complex with the butane-1,4-diyl ligand [{(thf)-Li}₄Cr₂{ κ^2 -(CH₂)₄}₄] forms the low-spin compound and with bulkier [(CH₂)₂SiMe₂]^{2–} the mononuclear high-spin species [{(thf)₂Li}₂Cr{ κ^2 -(CH₂)₂SiMe₂]₂].⁴⁹ Most of the magnetic anormal Cr^{II} organometallics have four ligands at each chromium(II) atom with bridging lithium atoms or organyl moieties.⁵⁰ Nevertheless, there are also chromium(II) complexes with only three aliphatic groups per chromium atom with structures similar to 3-Cr^{II}-thf.⁵¹

Recrystallization of $3-Cr^{II}$ -thf from THF solution led to deep red crystals of the solvent-separated ion pair $[(thf)_4Li]_2$ $[Cr_2Ph_6]$ ($3-Cr^{II}$ -thf₄, Figure 9). The molecular structure is



Figure 9. Structural motif of $[(thf)_4Li]_2[(Ph_3Cr)_2]$ (3-Cr^{II}-thf₄). Hydrogen atoms are neglected for clarity reasons. Selected bond length (pm): Cr1–Cr1A 183.7(2).

centrosymmetric with the center of symmetry on the Cr–Cr bond. It is remarkable that this anion is stable without any bridging lithium atoms leading to one of the shortest Cr–Cr quadruple bonds known today. Due to the lack of short contacts between lithium ions and ipso-carbon atoms of the Cr₂Ph₆ subunit are minimized. The steric demand of the phenyl substituents in **3-Cr^{II}-thf** and **3-Cr^{II}-thf**₄ is too large to allow coordination of a fourth phenyl group at each chromium atom. Coordination of a fourth phenyl ligand destabilizes the dinuclear structure and leads to monnuclear high-spin chromate(II) of the type [{(thf)₂Li}₂CrPh₄].^{18a,b}

To the best of our knowledge, $[(tmtaa)Cr]_2$ (tmtaa = tetramethyldibenzotetraaza[14]annulene) is the only other example with a quadruple Cr–Cr bond without bridges between the two halves (however, this complex does not contain Cr–C bonds and, hence, is not a strictly metalorganic derivative).⁵² After 2007, dinuclear chromium complexes have also been prepared with "super-short" multiple Cr^I-Cr^I bonds.⁵³ In these complexes, very short bridging unsaturated NCN and NCCN bridges support the shortening of the Cr–Cr distances. Extremely bulky terphenyl groups also enabled the stabilization of a short quintuple Cr^I-Cr^I bond.¹⁷ The shortest Cr–Cr bond observed until today has a value of 172.93(12) pm.⁵⁴

Comparison of the complexes $[{(thf)Li}CrPh_3]_2$ (3-Cr^{II}thf) and $[(thf)_4Li]_2$ $[Cr_2Ph_6]$ (3-Cr^{II}-thf₄) with derivatives containing quadruple and quintuple Cr–Cr bonds suggests that small coordination numbers are required for the formation of short Cr–Cr bonds. Furthermore, nature of bridging units, stabilizing neutral co-ligands as well as steric and electronic influences of the Cr-bound organic groups influence the Cr– Cr distance. The bond order and the oxidation state +1 or +2 seem to be of slightly smaller importance for the Cr–Cr bond length.

Compound [{(thf)Li}CrPh₃]₂ (**3-Cr**^{II}-thf) could be considered as lithium-containing intermediate on the pathway from tetraphenylchromates(III) to (η^6 -arene)chromium complexes because it reacted in diethyl ether at room temperature to the major product [(η^6 -C₆H₆)(η^6 -Ph₂)Cr⁰] (π -3) and to the side products [(η^6 -Ph₂)₂Cr⁰] (π -4) and [(η^6 -C₆H₆)₂Cr⁰] (π -2). All thermolysis experiments are summarized in Table 1. Heating

Table 1. Summary of Identified Products of DifferentPhenylchromates in Solution after Thermolysis under GivenConditions

	substrate	solv.	Т	time	<i>π</i> - arene	other products
1	6-thf-OEt ₂	Et ₂ O	r.t.	72 h	no	3-Li ₂ O
2	5-thf-OEt ₂	Et_2O	reflux	5 h	no	3-Li ₂ O
3	5-thf-12C4	[D ₈]- THF	40 °C	1 h	no	Ph ₂ 89%, PhH 11%
4a	4-Mg-dme	C_6D_6	r.t.	24 h	no	no reaction
4b	4-Mg-dme	C_6D_6	60 °C	6 h	no	Ph ₂ , PhH
5	LiCrPh ₄ - (OEt ₂) _x	Et ₂ O	−40 °C	2 h	π-3	Ph ₂ 40%, black solid
6	3-Cr ^{II} -thf	Et ₂ O	r.t.	6 h	π-3	Ph ₂ 10%, black solid
7	3 - Cr^{II} -thf ₄	[D ₈]- THF	40 °C	1 h	no	3-Cr ^{II} -thf ₄

of solutions of hexaphenylchromates(III) did not yield (η^{6} arene)chromium complexes regardless of the solvent but ether degradation occurred leading to formation of 3-Li₂O. Thermolysis of pentaphenylchromates(III) yielded biphenyl (89%) and benzene (11%) and a remaining black solid, but again no (η^{6} -arene)chromium complexes were observed. Only lithium salts of tetraphenylchromates(III) thermally degraded with formation of (η^{6} -arene)chromium complexes.

In Table 2, the thermolysis experiments of tetraphenylchromates(III) in dependency of the countercation (Li or Mg) and of the donor strength of the solvent are summarized. From this overview, it is obvious that strong Lewis donor bases (THF and DME) stabilized tetraphenylchromates(III) effectively. The weaker base diethyl ether could dissociate generating free coordination sites. Therefore, subsequent reactions occurred such as reductive elimination of biphenyl and $\sigma-\pi$ rearrangement of phenyl groups. This study verified one of the pathways in Hein's route from phenylchromium(III) compounds to (η^6 -arene)-chromium complexes starting from tetraphenylchromates(III) of lithium with weak Lewis basic ligands authenticating most of the intermediates by X-ray crystal structures.

In Scheme 9, a very likely reaction sequence starting with 3- Cr^{II} -thf is presented which also verifies the product

Scheme 9. Reaction Sequence Finally Yielding (η^{6} -Arene)chromium(0) Complexes π -3 (Major Component) and Side Products π -4 and π -2



distribution of (η^{6} -arene)chromium complexes in the reaction mixture, as found by Hein and Kurras.⁵⁷ Here, tetrahydrofuran acts as a weak Brønsted acid.²⁸

CONCLUSION

In this study we clarified the reaction sequence of Hein's synthesis of (η^6 -arene)chromium complexes starting from pure and isolated halide-free compounds to unambiguously identify intermediates and reaction conditions for the formation of bis(η^6 -arene)chromium(0) complexes. In order to follow Hein's protocol we used weakly coordinating solvents such as diethyl ether and [D₆]benzene. In Table 3, isolated hexa-, penta-, and tetraphenylchromates(III) with lithium counterions are summarized.

Hexa- and pentaphenylchromates(III) are unable to form (η^6 -arene)chromium complexes. Compounds 6-thf-OEt₂ and 5-thf-OEt₂ degrade ether yielding 3-Li₂O. Derivative 5-thf-12C4 shows reductive elimination reactions leading to formation of biphenyl.

Table 2. Lewis Donor Controlled Product Formation of Tetraphenylchromates(III) with Li and Mg Counterions after Thermolysis

Lewis donor	Li complexes	Mg complexes
$\text{DME} \approx \text{THF}^1$	$[Li(dme)_3]$ [Ph ₄ Cr(dme) (4-dme), stable in DME-THF until 60 °C	$[PhMg(dme)_2(thf)]$ $[Ph_4Cr(dme)]$ stable in DME-THF until 60 $^\circ C$
THF	equilibrium in THF, [Li(thf) ₄] [<i>cis</i> -(thf) ₂ CrPh ₄] (4-thf) at $T < -50$ °C, LiCrPh ₄ (thf) _n at $T > -50$ °C	equilibrium between $Ph_3Cr(thf)_3/Ph_2Mg(thf)_2$ and $Mg\{Ph_4Cr(thf)_n\}_2,$ 3 crystallizes in THF at $-40~^\circ C$
$THF \ll Et_2O$	[{(thf)Li}CrPh ₃] ₂ (3-Cr ^{II} -thf) stable below –15 °C and in C ₆ D ₆ or Et ₂ O reaction to π -3 \gg π -4 \approx π -2	(see part III) ⁵⁵
Et ₂ O	($\eta^6\text{-arene})\text{chromium complexes,}^{32}$ in Et_2O below –40 °C mainly formation of $\pi\text{-}3$	reaction at –20 °C to (η^6 -arene)chromium complexes according to Hein and Zeiss ⁵⁶ (major component π -3)

Table 3. Crystallographically Authenticated (Poly)phenylchromium(III) and -Chromium(II) Organometallics and Their Colors

compound	formula	color
6-thf-OEt ₂	$[{(thf)_{2.3}(Et_2O)_{0.7}Li_3}CrPh_6]$	yellow-orange
6-thf ¹	$[Li(thf)_4] [{(thf)Li}_2CrPh_6]$	yellow
5-thf-OEt ₂	$[{(thf)_2(Et_2O)Li_2}CrPh_5]$	turquoise
5-thf	$[{(thf)_2Li}_2CrPh_5]$	green
5-thf-12C4	$[(thf)Li(12C4)]_2 [CrPh_5]$	light green
4-thf	$[Li(thf)_4] [cis-(thf)_2CrPh_4]$	purple
4-dme ¹	[Li(dme) ₃] [(dme)CrPh ₄]	red
4-Mg-dme ¹	[PhMg(dme) ₂ (thf)] [(dme)CrPh ₄]	red
4-Cr ^{II} -thf	$[\{(thf)_2Li\}_2CrPh_4]$	yellow
3 ¹	$[Ph_3Cr(thf)_3] \cdot 0.25 dx$	deep red
3-Li ₂ O	$[\{(Et_2O)Li\}_2Ph_3Cr(\mu-O)]_2$	emerald green
3-Cr ^{II} -thf	$[{(thf)Li}CrPh_3]_2$	red brown
$3-Cr^{II}-thf_4$	$[Li(thf)_4]_2 [Cr_2Ph_6]$	wine red

Tetraphenylchromates(III) with strong Lewis donors L (dme and thf) form stable complexes in DME and THF of the type $[\text{Li}(\text{L})_n]$ [*cis*-(L)_mCrPh₄] (L = dme, m = 1, n = 3 (4-dme) and L = THF, m = 2, n = 4 (4-thf)) as well as [PhMg(dme)₂(thf)] [Ph₄Cr(dme)] (4-Mg-dme). These compounds are unable to form (η^6 -arene)chromium complexes upon heating of the reaction mixtures. Derivative 4-thf is only stable below -50 °C and forms at higher temperatures in THF solution reversibly a dark green product LiCrPh₄(thf)_x of unknown structure.

The *in situ* from a suspension of **5-thf-OEt**₂ in diethyl ether and 1 equiv of HCl–OEt₂ at -40 °C generated purple solution of tetraphenylchromate(III) [Li(L)₄] [Ph₄Cr(L)₂] (L = Et₂O or Et₂O/thf) shows above -20 °C immediate reductive elimination of biphenyl. Furthermore, this approach yields dinuclear chromate(II) complex **3-Cr^{II}-thf** which is stable below -15 °C. This complex reacts in diethyl ether at room temperature to (η^6 -arene)chromium complexes. Recrystallization from THF allows the isolation of pure **3-Cr^{II}-thf**₄ with a very short quadruple Cr–Cr bond (183.7(2) pm) and without stabilizing Li–C bonds to the Cr-bound ipso-carbon atoms.

With this study, the major pathway for the synthesis of $(\eta^{6} - arene)$ chromium complexes in Hein's protocol has been identified, starting from tetraphenylchromates(III) and applying weak donor solvents such as diethyl ether. Intermediately formed chromates(II) have been structurally authenticated.

Our concluding part III of this row of Hein's chromium(III) organometallics will focus on the synthesis of (η^6 -arene) chromium complexes starting from tri-, di-, and monophenylchromium(III) complexes.⁵⁵

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under anaerobic conditions in an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled in an argon atmosphere. Deuterated solvents were dried over sodium, degassed, and saturated with argon. The yields given are not optimized.

¹H and ¹³C NMR spectra and 2D spectra were recorded on a Bruker AC 400 spectrometer. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the solvent.⁵⁸

The chromium contents of the compounds were determined by complexometric titrations against xylenol orange.⁵⁹

Anhydrous chromium(III) chloride, iodobenzene, bromobenzene, and 12-crown-4 were supplied by ABCR GmbH. Diphenylmercury

and *n*-butyllithium solution in hexane (1.6 M) were supplied by Alfa Aesar; phenylmagnesium bromide in THF and diethyl ether were supplied by Sigma-Aldrich.

Lithium sand ($\emptyset \approx 50 \ \mu m$),⁶⁰ mer-CrCl₃(thf)₃,⁶¹ Ph₂Mg(thf)₂,⁶² and Ph₂Mg(dx)_x (with x = 1 and 3)⁶³ were prepared according to literature procedures. The phenyl chromium derivatives [{Li-(OEt₂)}₃CrPh₆]²² and [Li(dme)₃] [Ph₄Cr(dme)] (4-dme), [PhMg-(dme)₂(thf)] [Ph₄Cr(dme)], and [*fac*-Ph₃Cr(thf)₃·0.25dx] (3) were prepared as described earlier.¹ The concentrations of the solutions of phenyllithium and organomagnesium compounds were determined by acidimetric titrations of an aliquot with 10 N hydrochloric acid against phenolphthalein.

Synthesis of [**Li(thf)**]_{2,3}**Li(OEt**₂)_{0,7}**CrPh**₆] (6-thf-OEt₂). Crystalline Ph₃Cr(thf)₃·0.25 dx (3, 5.4 g, 10.35 mmol) was added in small portions to a stirred solution of 46.0 mL of phenyllithium (0.74 M) in diethyl ether (34.0 mmol) at -30 °C. While the red solid dissolved, the color of the solution changed to yellow, and a citron yellow solid precipitated. The reaction mixture was finally stirred for 1 h without cooling. The precipitate was collected on a Schlenk frit (G4), washed with cold diethyl ether and dried in vacuo. Yield: 7.4 g (71% with respect to starting 3) of a yellow powder of 6-thf-OEt₂. Elemental analysis (C₄₈H_{55.4}CrLi₃O₃, M: 753.1): calcd: Cr 6.90. Found: Cr 6.95.

The relative molar ratio of THF and diethyl ether in the product was calculated from the integrals of their resonances in the ¹H NMR spectrum of the hydrolysis product of **6-thf-OEt**₂ (OEt₂/THF = 0.7:2.3, see the Supporting Information). The solid product was stable in the refrigerator at -20 °C. Yellow-orange single crystals of **6-thf-OEt**₂ were obtained by extraction of the yellow powder in boiling diethyl ether and keeping the extract at -10 °C. The molar ratio of THF:OEt₂ in the crystals became smaller with the extended crystallization time. In contact with the mother liquor, the product reacted also at room temperature slowly during 3 days yielding green crystals of [{(Et₂O)Li}₂CrPh₃]₂ (3-Li₂O).

Preparation of the Hydrogen Chloride Solution in Diethyl Ether (HCl-Et₂O). Hydrogen chloride gas was prepared by careful dropwise addition of 21.4 mL (0.4 mol) of concentrated sulfuric acid into a 250 mL three-necked flask containing 5.35 g (0.1 mol) of suspended NH₄Cl and 10 mL of concentrated hydrochloric acid in an argon atmosphere. The two other necks were connected to the argon line and a wash bottle containing concentrated H₂SO₄, respectively. Then the Ar-HCl gas mixture was bubbled into a Schlenk tube containing 50 mL of anhydrous diethyl ether at 78 °C in an argon atmosphere. The gas liberation rate was adapted by the dropping amount of sulfuric acid. The gas flow was regulated easily by the argon quota. The final concentration of hydrogen chloride in the HCl-Et₂O solution was elucidated by titration of an aliquot with M/10 sodium hydroxide solution. Yield: 47 mL (80% with respect to starting NH₄Cl) of HCl-Et₂O solution (1.7 M). The solution can be stored unchanged for weeks at -40 °C.

Determination of the THF/Et₂O Ligand Ratios in the Chromate(III) Complexes 5-thf- OEt_2 and 6-thf- OEt_2 . The complexes (0.2 g) were cooled to -20 °C in a Schlenk tube sealed with a septum. Then 1 mL of carbon tetrachloride and 0.5 mL of ice-cold water was added by a syringe. After an exothermic reaction, the stirred reaction mixture was neutralized with diluted hydrochloric acid. The organic layer was separated and dried with sodium sulfate. A part of the solution was diluted with CDCl₃ and monitored by ¹H NMR spectroscopy. The THF/Et₂O ratio was calculated from the signal intensities of these ethers.

Synthesis of [{(Et₂O)Li}{(thf)₂Li}CrPh₅] (5-thf-OEt₂). Complex 6-thf-OEt₂ (1.27 g, 1.69 mmol) were suspended in 30 mL of diethyl ether, cooled to -30 °C, and stirred. Then 1.0 mL of a HCl–OEt₂ solution (1.7 M, 170 mmol) was added. Then the cooling bath was slowly warmed. At a temperature of -20 °C the solid substance slowly reacted to brown solution. At -10 °C the solution turned green. At the same time a colorless amorphous solid precipitated. Thereafter, stirring was continued for an additional hour until the starting yellow substrate disappeared completely. The precipitate was removed with a frit covered with diatomaceous earth and the filtrate was stored at -20 °C. Overnight turquoise crystals precipitated from the green

mother liquor. These crystals were collected, washed with cold diethyl ether, and briefly dried in vacuo. Yield: 0.76 g (67% with respect to starting **6-thf-OEt**₂) of turquoise crystals of **5-thf-OEt**₂. Elemental analysis ($C_{42}H_{51}$ CrLi₂O₃, M: 669.7): calcd: Cr 7.76. Found: Cr 7.80. The molecular ratio of OEt₂/THF = 1.00:2.05 was determined by ¹H NMR spectroscopy (see Supporting Information).

Improved Synthesis of [{(thf)₂Li]₂CrPh₅] (5-thf) according to Heyn.²⁶ A solution of 0.67 g (1.00 mmol) of turquoise 5-thf-OEt₂ in 5 mL of THF was refluxed for a few minutes. Then the warm flask was cooled immediately down in an ethanol–dry-ice bath to -78 °C. The cold solution was layered with 3 mL of *n*-pentane and stored overnight at -40 °C. Big green crystals of 5-thf grew at the glass wall. In one batch, some yellow crystals of [(thf)₄Li] [{(thf)Li}₂CrPh₆] (6thf) were formed on the bottom of the flask. The green product was collected on a Schlenk frit, washed with *n*-pentane, and dried for a short time in vacuo. Yield: 0.42 g (57% with respect to starting 5-thf-OEt₂) of 5-thf as green crystals. Elemental analysis (C₄₆H₅₇CrLi₂O₄, M:739.8): calcd: Cr 7.03. Found: Cr 7.14. The compound was identical with Heyn's Li₂CrPh₅·3.5THF.

Synthetic Alternatives for $[(12\text{-}crown-4)\text{Li}(thf)]_2[CrPh_5]$ (5-thf-12C4). Synthesis Variant 1. Compound 5-thf-OEt₂ (0.47 g, 0.70 mmol) was dissolved in 10 mL of diethyl ether and at 0 °C, 0.26 g (1.48 mmol) of 12-crown-4 were added with a syringe. During this procedure, a microcrystalline solid precipitated from the green solution which was collected on a Schlenk frit (G4), washed with diethyl ether and dried in vacuo in the dark. Yield: 0.62 g (93% with respect to starting 5-thf-OEt₂) of 5-thf-12C4 as small light green crystals.

Synthesis Variant 2. Compound 6-thf-OEt₂ (0.85 g, 1.13 mmol) was suspended at 0 °C in 20 mL of THF and stirred. Then 0.62 g (3.52 mmol) of 12-crown-4 was added with a syringe. During this handling, the yellow substrate dissolves yielding a green solution. Soon thereafter, a green solid precipitated which was collected on a Schlenk frit, washed with THF, and dried in vacuo in the dark. Yield: 1.05 g (98% with respect to starting 6-thf-OEt₂) of green platelets of 5-thf-12C4. Elemental analysis ($C_{54}H_{73}$ CrLi₂O₁₀, M: 948.0): calcd Cr 5.48. Found: Cr 5.54. The crystals were very sensitive toward light and heat. In contact with [D₈]THF the compound already degraded above 40 °C.

Synthesis of [{(Et₂O)Li}₂OCrPh₃]₂ (3-Li₂O) (by Degradation of 5-thf-OEt₂ in Boiling Diethyl Ether). A solution of 0.75 g (1.12 mmol) of 5-thf-OEt₂ in 10 mL of diethyl ether was refluxed for 5 h. This treatment led to formation of a microcrystalline precipitate in the green solution. Then the reaction solution was stored overnight at -20 °C. The precipitate was collected on a Schlenk frit, washed with cold diethyl ether, and briefly dried in vacuo. Yield: 0.30 g (58% with respect to starting 5-thf-OEt₂) of 3-Li₂O as emerald green crystals. Elemental analysis (C₅₂H₇₀Cr₂Li₄O₆, M: 922.8): calcd: Cr 11.27. Found: Cr 11.46.

Alternative Single-Crystal Preparation of $3-\text{Li}_2O$ (by Degradation of $6-\text{thf-OEt}_2$ in Diethyl Ether at Room Temperature). A suspension of 0.76 g (1.0 mmol) of $6-\text{thf-OEt}_2$ in 20 mL of diethyl ether was kept at room temperature for 3 days. During this time, the majority of the yellow crystals dissolved forming a green solution, and large emerald green crystals of $3-\text{Li}_2O$ grew at the wall of the Schlenk flask, suitable for X-ray crystal structure determination.

Improved Protocol for the Preparation of Salt-Free Phenyl Lithium Solution in Diethyl Ether According to Wittig.⁶⁴ Diphenyl mercury (3.0 g, 10.6 mmol) was slowly added into a stirred slurry of 0.90 g (130 mmol) of lithium sand ($\emptyset \approx 50 \ \mu$ m) in 20 mL of diethyl ether. The solid diphenyl mercury was added in a manner that the reaction mixture kept warm. After the exothermic reaction was finished, the Schlenk tube was put for 5 min in an ultrasound cleaning bath. Then the reaction mixture was filtered by a Schlenk frit. The concentration of phenyl lithium was determined from an acidimetric titration of an aliquot of the filtrate. Yield: 74% (calcd with respect to starting diphenyl mercury).

Crystal Preparation of [Li(thf)₄] [*cis*-(thf)₂Ph₄Cr]·2THF (4-thf) (Modified Protocol According to Schmiedeknecht).³⁴ Ph₃Cr-(thf)₃·0.25dx (3, 0.78 g, 1.50 mmol) was suspended in 6 mL of THF and stirred at 0 °C. Then 2.7 mL (1.51 mmol) of a halide-free phenyllithium solution (0.56 M) in diethyl ether was added dropwise with a syringe. The color of the red solution immediately turned green, and within 5 min the red deposit dissolved completely. The dark green reaction solution is stable for several months at -40 °C. In order to crystallize 4-thf, a part of this solution was transferred into a glass flask which was cooled with liquid nitrogen to -50 °C. During this treatment the green solution turned red and purple crystals precipitated. The crystals were completely covered with oil and mounted on a loop for X-ray diffraction experiments. Attention!If the temperature of the crystals increases above -50 °C, the crystals melt and freeze again giving a purple glassy solid. During drying of crystalline 4-thf on a Schlenk frit at -70 °C, the substance converted to a green oily mass. Therefore, the performance of a reliable elemental analysis was impossible.

Acidolysis of [{(Et₂O)Li}₃CrPh₆] with 2 equiv of HCl–Et₂O. A suspension of 0.758 g (1.0 mmol) of Li₃CrPh₆·3 Et₂O in 10 mL of diethyl ether and 69 μ L (0.5 mmol) of mesitylene as internal standard were cooled and stirred in Schlenk flask covered with a septum. Next, 1.18 mL (2.0 mmol) of HCl–OEt₂ solution (1.7 M) were added with a syringe. During this handling the yellow substrate dissolved and intermediately a sparingly soluble purple solid precipitated which immediately dissolved at -40 °C yielding a dark brown solution which was warmed to room temperature. Diluted sulfuric acid was added. The organic layer was decanted and dried with anhydrous sodium sulfate. Then, 0.2 mL of [D₆]benzene were added to 0.5 mL of this solution and studied by ¹H NMR spectroscopy. In the spectrum the resonances of the (η^6 -arene)chromium complexes (2- π , 3- π (major product), and 4- π) as well as benzene and biphenyl (major product) were observed besides small signals of impurities. ¹H NMR (400.1 MHz, in C₆D₆): 2- π : δ 4.08 (12H, s, η^6 -C₆H₆).⁶⁵

¹H NMR (400.1 MHz, in C₆D₆): **2**- π : δ 4.08 (12H, s, η^{6} -C₆H₆).⁶⁵ **3**- π : δ 4.18 (1H, t, *p*-CH, η^{6} -Ph), 4.25 (2H, t, *m*-CH, η^{6} -Ph), 4.73 (2H, d, *J* = 5.2 Hz, *o*-CH, η^{6} -Ph). The signals of the noncoordinated phenyl group are covered by the signals of biphenyl. The signals of the η^{6} -C₆H₆ ligand are very broad at 297 K. **4**- π : δ 4.26 (*p*-CH, η^{6} -Ph), 4.35 (4H, t, *m*-CH, η^{6} -Ph), 4.85 (4H, d, *J* = 5.2 Hz, *o*-CH, η^{6} -Ph). The signals of the noncoordinated phenyl groups are covered by the signals of biphenyl.

Synthesis of [{(thf)Li}CrPh3]2 (3-Cr^{ll}-thf). A suspension of 3.07 g (4.58 mmol) of 5-thf-OEt, in 50 mL of diethyl ether was suspended at -40 °C and stirred. Then, 2.72 mL (4.62 mmol) of a HCl-OEt₂ solution (1.7 M) were added. During this treatment a microcrystalline purple substance precipitated. Warming to -20 °C led to a complete conversion to a brown solution with a white precipitate. The solids were removed at -20 °C by filtration with a frit covered with diatomaceous earth and stored at -40 °C. At this temperature, a dark red-brown substance crystallized and was collected on a Schlenk frit, washed with very cold diethyl ether, and briefly dried in vacuo. Yield: 0.91 g (55% with respect to starting 5-thf-OEt₂) of dark red-brown crystals of **3-Cr^{II}-thf**. Elemental analysis (C₄₄H₄₆Cr₂Li₂O₂, M: 724.7): calcd: Cr 14.35. Found: Cr 14.15. In solution, this compound already degraded above -15 °C. Stirring at room temperature in diethyl ether yielded a black precipitate (π -3, π -2, and π -4), benzene, and biphenyl, besides small amounts of unknown compounds.

Preparation of [(thf)₄Li]₂ [Cr₂Ph₆] (3-Cr^{II}-thf₄). Compound 3-Cr^{II}-thf (1.22 g, 1.68 mmol) was dissolved at room temperature in 50 mL of THF. The dark red solution was filtered and then stored at -20 °C. Red crystals precipitated and were collected on a Schlenk frit, washed with cold THF, and briefly dried in vacuo. Yield: 1.56 g (80% with respect to starting 3-Cr^{II}-thf) of 3-Cr^{II}-thf₄ as red crystals. Elemental analysis (C₆₈H₉₄Cr₂Li₂O₈, M: 1157.3): calcd: Cr 8.99. Found: Cr 9.13. After stirring of a solution of 3-Cr^{II}-thf₄ in [D₈]THF for 1 h at 40 °C, the solution was cooled to -40 °C. Finally only red crystals of the substrate were obtained.

Reaction of $[(thf)_4Li]_2[Cr_2Ph_6]$ (3-Cr^{II}-thf₄) with Lithiumphenyl. Compound 3-Cr^{II}-thf₄ (2.26 g, 1.95 mmol) was suspended in 50 mL of THF at -40 °C and stirred. Then 6.5 mL of halide-free phenyllithium (3.90 mmol) in diethyl ether (0.6 M) was added dropwise. During this handling, the deposit dissolved leading to a red solution. The volume of this solution was reduced to half of the original volume giving a few yellow crystals. This solution was kept overnight at -40 °C. The crystals were collected on a Schlenk frit, washed with diethyl ether, and dried in vacuo. Yield: 1.34 g (52% with respect to starting **3-Cr^{II}-thf**₄) of yellow crystals of Li₂CrPh₄(thf)₄. This compound is identical with the substance prepared by Seidel et al. via an alternative procedure.^{18a} Elemental analysis (C₄₀H₅₂CrLi₂O₄, M: 662.7): calcd: Cr 7.85. Found: Cr 7.71.

Crystal Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple-scans.⁶⁷⁻⁶⁹ The structures were solved by direct methods (SHELXS)⁷⁰ and refined by full-matrix least-squares techniques against F_0^2 (SHELXL-97⁷ and SHELXL-2014).⁷¹ All hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystals of 5-thf and 4thf were nonmerohedral twins. The twin laws were determined by PLATON⁷² to (-1.000, 0.000, -0.004) (0.000, -1.000, 0.000) (0.000, 0.000, 1.000), and (0.130, 0.000, -0.870) (0.000, -1.000, 0.000) (-1.130, 0.000, -0.130), respectively. The contributions of the main components were refined to 0.727(1) and 0.897(2), respectively. The crystals of 5-thf-12C4 were extremely thin and/or of low quality, resulting in a substandard data set; however, the structure is sufficient to show connectivity and geometry despite the high final R value. We publish only the conformation of the molecule and the crystallographic data. Therefore, the data are not deposited in the Cambridge Crystallographic Data Centre. Crystallographic data as well as structure solution and refinement details are summarized in Table S1 (see Supporting Information). XP⁷³ and POV-Ray⁷⁴ were used for structure representations.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00602.

Crystal parameters and refinement details of the X-ray crystal structures (PDF)

Accession Codes

CCDC 2023347–2023353 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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