1,2-Disubstituted [(η^6-Arene)Cr(CO)$_3$] Complexes by Sequential Nucleophilic Addition/*endo*-Hydride Abstraction

Angelika Fretzen, Alberto Ripa, Ronggang Liu, Gerald Bernardinelli, and E. Peter Kündig*

Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

Abstract: Regioselective addition of organolithium compounds at the *ortho* position in oxazoline, imine, or hydrazone (η^6-arene)tricarbonyl chromium complexes afforded anionic [(η^5-cyclohexadienyl)Cr(CO)$_3$] intermediates. A single-crystal X-ray structure determination of the product of the addition reaction of naphthyllithium with a phenyl oxazoline complex showed structural characteristics of an aza-enolate superimposed on the predominant cyclohexadienyl structure. Reaction of the anionic cyclohexadienyl complex with a trityl salt yielded 1,2-disubstituted [(η^6-arene)Cr(CO)$_3$] complexes. Labeling studies, carried out to provide mechanistic details of the aromatization process, ruled out an isomerization/*exo*-hydride abstraction sequence but were in accord with a process involving *endo*-hydride abstraction.

Keywords: arene complexes · chromium · cyclohexadienyl complexes · hydride abstraction · mechanism

Introduction

Arenes bound to the electrophilic Cr(CO)$_3$ group undergo a variety of regio- and stereoselective transformations that cannot be realized with the free arene.[1,2] The synthetic possibilities thus offered have received considerable attention and, as a result, a substantial amount of effort has been focused on methods that provide efficient access to substituted arene complexes. The three approaches that meet the criteria of selectivity and efficiency are the selective and mild direct complexation of arenes to the Cr(CO)$_3$ fragment,[3–5] the Dötz reaction,[6] and the regioselective transformations of complexed arenes. Of the last, the most widely utilized reaction is the directed lithiation/electrophilic trapping protocol.[2h,m] It makes use of both the directional effects of substituents and the markedly increased acidity of the arene ring hydrogens in the complex.[7] Significant new developments in this field are diastereoselective and enantioselective lithiations.[8,9] Other arene transformation methods involve Pd-mediated reactions of complexed haloarenes[10] or *ipso*- and *tele*-nucleophilic substitution in arenes bearing leaving groups. *Tele*-nucleophilic substitutions are the result of the addition of a nucleophile to the arene, followed by protonation and *anti*-elimination of a leaving group.[11,12] While attractive in concept, competitive decomplexation of the labile cyclohexadiene intermediate seriously limits the usefulness of this procedure. In the absence of a leaving group, rearomatization can be achieved by oxidation, the overall reaction being the formal replacement of a hydride by a C nucleophile. Although the mechanism of this sequence has not yet been established, a reasonable sequence involves metal oxidation followed by intramolecular C(6)-H(*endo*) hydride transfer to the metal, and oxidative cleavage of the metal–arene bond. Attempts to stop this sequence before arene decomplexation, in order to reuse the activating and the regio- and stereodirecting effect of the Cr(CO)$_3$ group, were not successful. Likewise, the addition of electrophiles to effect the abstraction of C(6)-H(*endo*) as a hydride from the (η^5-cyclohexadienyl) intermediate initially failed.[13] Although there is some precedent for *endo*-hydride abstraction in transition metal η^5-cyclohexadienyl complexes,[14,15] it has been reported that anionic cyclohexadienyl chromium complexes lacking an *exo* hydrogen reacted with trityl by abstraction of the *exo* carbanion.[13] Removal of C(6)-H(*endo*) was believed to be unfavorable due to the difficult approach of a bulky electrophile from the same side as the metal.[16]

Aromatization of cyclohexadienyl–metal complexes without decomplexation is facile in complexes with C(6)-H(*exo*). The trityl cation can be conveniently used to effect *exo*-hydride abstraction.[24]

It is now well established that carbanion addition to [(arene)Cr(CO)$_3$] complexes can be readily reversible[2e,j].

[*] E. P. Kündig, A. Fretzen, A. Ripa, R. Liu, G. Bernardinelli
Department of Organic Chemistry, University of Geneva
30, Quai Ernst Ansermet, CH-1211 Geneva 4 (Switzerland)
Fax: Int. code + (41) 22-328-7396
E-mail: peter.kundig@chiorg.unige.ch

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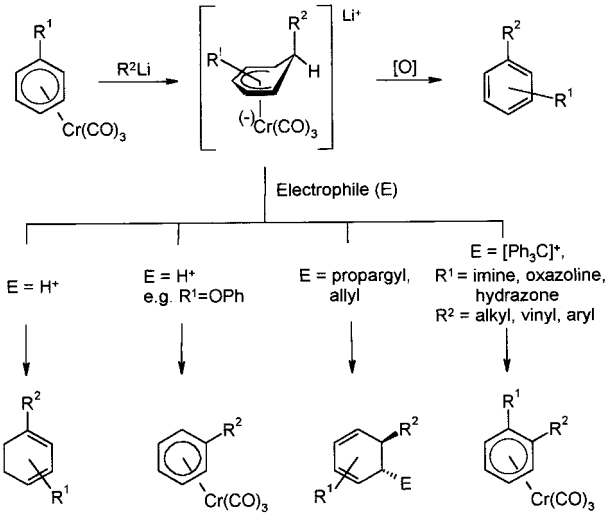
Displacement of this equilibrium by reaction of the carbanion with an electrophile provides a ready explanation for the regeneration of the starting arene complex. We have shown that, under conditions of irreversible nucleophilic addition, small electrophiles (H^+, primary alkyl halides, allyl- and propargyl halides) add to the metal. This sequence has led to a useful procedure for the synthesis of regio- and stereoselectively substituted alicyclic molecules (Scheme 1).[17]



Scheme 1. Reactions of $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes with electrophiles.

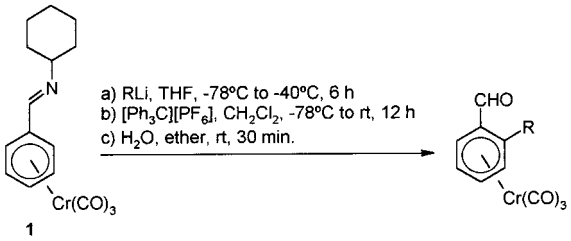
This article reports the results of our reinvestigation of the nucleophilic addition/hydride abstraction sequence[18a]. The reaction of the cyclohexadienyl complexes (analogous to **6**) with the trityl cation results in a new synthesis of *o*-disubstituted arene complexes. We also report on the mechanism of the transformation and on structural details of the key intermediate in the reaction.

Results and Discussion

The nucleophilic addition/hydride abstraction sequence: Following the previously established protocol,[19] addition of the C nucleophiles **a–f** to the $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes **1–4** in THF at $-78\,^\circ C$ to $-40\,^\circ C$ (6 h) afforded the corresponding cyclohexadienyl complexes. In THF, reaction with $[Ph_3C][PF_6]$ gave unidentified mixtures of compounds. A much cleaner reaction was observed in CH_2Cl_2. In a typical procedure, the crude cyclohexadienyl complexes, obtained as orange to brown solids or oils after evaporation of volatiles under vacuum, were taken up in a minimum of dry dichloromethane and, at $-78\,^\circ C$, treated with a saturated solution of $[Ph_3C][PF_6]$ (2.1–2.2 eqiv, 0.4 M). Slow warm-up to room temperature and subsequent work-up yielded the 1,2-disubstituted $[(arene)Cr(CO)_3]$ complexes **2–5** (Schemes 2–4).

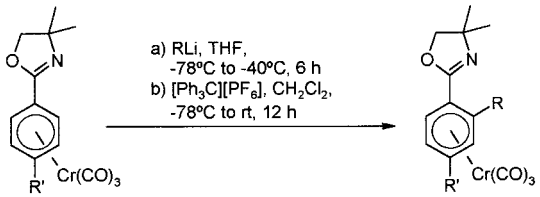
Product yields varied between 49–79%. Reactions with phenyllithium were at the top end of the range, while those with methyllithium were at the bottom end. Based on the observation of color changes during solvent evaporation and the amount of decomposition, we assume this to reflect in part the stability of the intermediate η^5-cyclohexadienyl complex. The ^1H and ^{13}C NMR spectra of complexes **2a–5f** show the usual upfield shift of the aromatic proton and carbon resonances with respect to the corresponding free arenes. *Ortho* substitution is easily recognized by the signal pattern of the aromatic proton resonances. The signals are split up into two doublets and two triplets with couplings between 6 and 7 Hz. Spectra were assigned through a combination of peak multiplicities, chemical shifts, coupling constant analyses, and $^{13}C-^1H$ two-dimensional correlation experiments. Complete data are reported in the experimental section.

Intrigued by the one-pot reaction sequence described above, not only for its synthetic merit but also for the



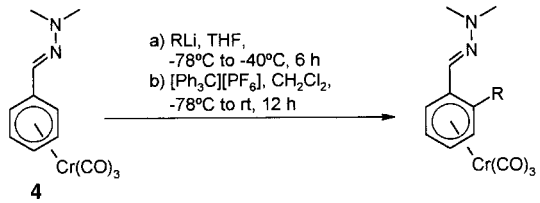
R = methyl (**a**)	64%	**5a**
n-butyl (**b**)	68%	**5b**
vinyl (**c**)	74%	**5c**
phenyl (**d**)	76%	**5d**
thiophenyl (**e**)	52%	**5e**
furanyl (**f**)	60%	**5f**

Scheme 2. Synthesis of 1,2-disubstituted $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes from **1**.



R' = H : **2**	R = methyl (**a**)	51%	**2a**
	n-butyl (**b**)	76%	**2b**
	vinyl (**c**)	52%	**2c**
	phenyl (**d**)	68%	**2d**
	thiophenyl (**e**)	60%	**2e**
R' = OMe : **3**	R = methyl (**a**)	49%	**3a**
	n-butyl (**b**)	66%	**3b**
	vinyl (**c**)	58%	**3c**
	phenyl (**d**)	53%	**3d**

Scheme 3. Synthesis of 1,2-disubstituted $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes from **2** and **3**.



R = methyl (**a**)	50%	**4a**
n-butyl (**b**)	78%	**4b**
vinyl (**c**)	57%	**4c**
phenyl (**d**)	79%	**4d**

Scheme 4. Synthesis of 1,2-disubstituted $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes from **4**.

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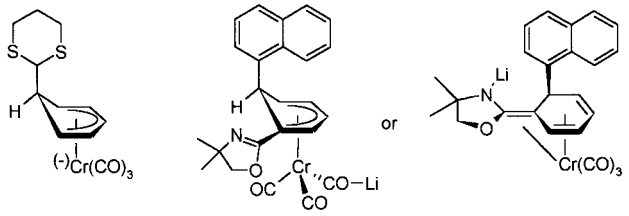
mechanistic questions posed, we pursued this research further by investigating the nature of the intermediates and the mechanism of the aromatization process.

The nature of the intermediates; structure determination of 6: Although the structures of several neutral cylohexadienyl chromium complexes have been published,[11d, 20] there is only one report of a structure determination of an anionic [(η^5-cyclohexadienyl)$Cr(CO)_3$] complex (**7**).[13] The addition of a



7 **6**

nucleophile to the oxazoline complex **2** raises an interesting structural question. Complex **2** contains both a π-bound $[Cr(CO)_3]$ and a σ-bound oxazoline electrophilic group, so the question arises as to which one will dominate the structure of adduct **6**. If the former group dominates the reactivity, we expect a cyclohexadienyl ML_3 complex with the lithium cation coordinated to an oxygen of a CO ligand. If the oxazoline dominates the reactivity, then we expect an aza-enolate with a *N*-bound lithium in a *N*,*O*-ketene-acetal structure. The latter has been proposed as an intermediate in addition reactions of RLi reagents to naphthyl oxazolines.[21] In the complex, this structure may exist with the $Cr(CO)_3$ group bound to both the endocyclic diene system and the exocyclic double bond. There are literature precedents of triene $Cr(CO)_3$ complexes having this bonding characteristic.[22]

Initial attempts to crystallize cyclohexadienyl complexes derived from **2** failed. Though thermally stable, the highly air-sensitive products were obtained as orange oils or powders not suitable for X-ray diffraction. In the event we concentrated on product **6**, obtained by addition of naphthyllithium to complex **2**. The IR spectrum of **6**, as expected for an anionic complex, showed the bands associated with the CO stretching modes ($\tilde{\nu} = 1900$, $1810\ cm^{-1}$) shifted to lower frequencies compared to the neutral starting material.[19] The C=N absorption ($\tilde{\nu} = 1611\ cm^{-1}$) appears at a lower field compared to that in **2** ($\tilde{\nu} = 1651\ cm^{-1}$). Both the ^1H and the ^{13}C NMR spectrum agree with those of other anionic [(η^5-cyclohexadienyl)] complexes.[19, 20] Crystals suitable for X-ray diffraction analysis were obtained by following Semmelhack's procedure of dissolving the (η^5-cyclohexadienyl) complex in dioxane at 40 °C and then permitting crystallization at room temperature.[13] Following a number of unsuccessful attempts, fine yellow needles were finally obtained by leaving the mixture in a Schlenk tube connected to a nitrogen manifold for a period of 10 days. Figures 1 and 2 show ORTEP diagrams of the structure. Details of the structure determination are given in the experimental section. Selected bond lengths and angles are listed in Table 1.

At first glance, intermediate **6** shows the usual structural features of a cyclohexadienyl complex—a three-legged piano-

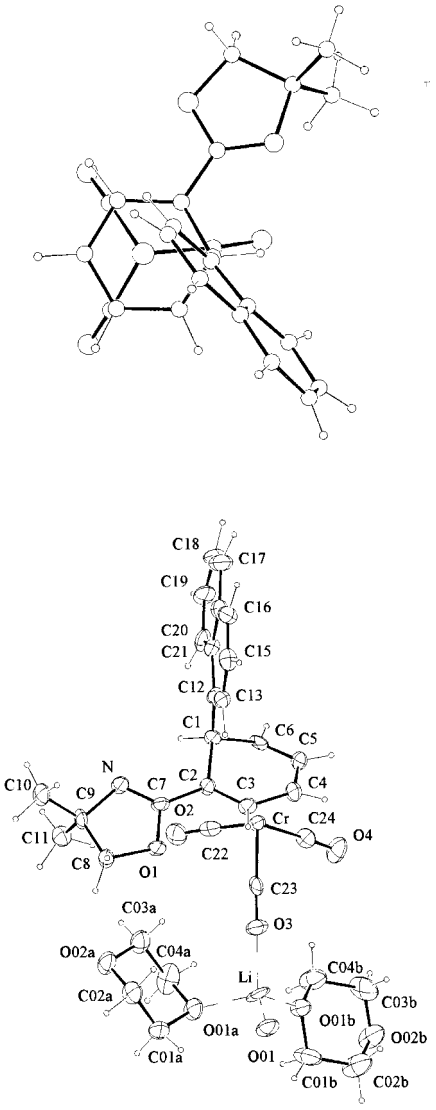


Figure 1. ORTEP plots of **6**. Thermal ellipsoids at the 50% probability level.

stool structure, in which the $Cr(CO)_3$ group adopts an eclipsed conformation with respect to the cyclohexadienyl carbons and the M–CO vector underneath the sp^3-hybridized C1 carbon. The C-Cr-C angles of the $Cr(CO)_3$ group are close to 90° (Table 1). As in other η^5-bonded cyclohexadienyl structures, the five sp^2 carbons are found in a mean plane (with a maximum deviation of 0.03 Å). The interplanar angle between the five cyclohexadienyl carbons and the C1-C2-C6 plane (41.9°) is a little larger than in **7** but it is still within the range of values observed for other [(η^5-cyclohexadienyl)] complexes.[11d,13,20] C–C bond lengths in the dienyl moiety fall into the range of 1.39 to 1.42 Å and do not show a clear alternation of longer and shorter bond lengths. The Cr atom is located at 1.236(2) Å from the dienyl mean plane. On closer inspection of the structure, one notes that the angle between the dienyl and the oxazoline planes is only 23.7(3)°. This is consistent with significant π-overlap between these two groups. This is confirmed by the bond distances: the C2–C7 bond in intermediate **6** is notably shorter (1.42(1) Å) than that in the starting complex **2** (1.470(6) Å). On the other hand, the

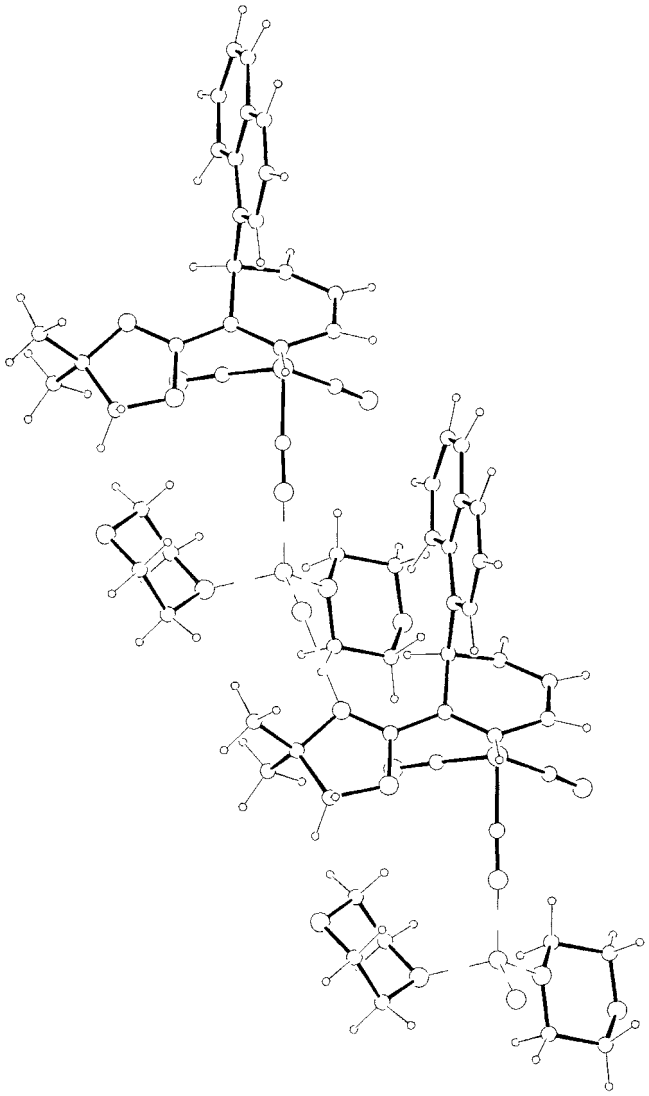


Figure 2. Crystal structure of **6** showing the intermolecular CO···Li···OH_2···N(oxazoline) bridge.

C7–N bond is longer in **6** (1.29(1) Å) than in **2** (1.260(5) Å).[19] These features are in agreement with a partial aza-enolate structure. A cyclohexadienyl structure is expected to have the Li coordinated to a CO ligand oxygen, whereas in an aza-enolate structure, the lithium is expected to be bound to the nitrogen.

The tetrahedrally coordinated lithium cation is bound to one carbonyl oxygen, two oxygens of dioxane and to a water molecule. Small amounts of water, presumably introduced with the solvent or by the rubber tubing connecting the nitrogen manifold to the reaction vessel, were thus crucial for crystallization. However, it should be pointed out here that anionic (cyclohexadienyl)chromium complexes are readily protonated at the metal to form agostic complexes and ultimately cyclohexadienes.[12] The $Li-O_{(H_2O)}$ bond length is 1.88(1) Å in **6** and matches those found in other structures containing Li-coordinated water.[23] Even though the water hydrogen atoms were not observed in the structure, the distance of 2.776(8) Å between the water oxygen and the oxazoline nitrogen of a second cyclohexadienyl chromium complex clearly points to a O–H···N=C hydrogen bridge. The intermolecularly bridging water molecules give rise to the regular chain structure of complex **6** and provides the link between the two limiting structures. Moreover, the water molecule is involved in two hydrogen bonds with two dioxane molecules (O···O = 2.687(8) and 3.098(8) Å). Overall, the structural characteristics of **6** are those of an aza-enolate superimposed on the predominant cyclohexadienyl structure.[24]

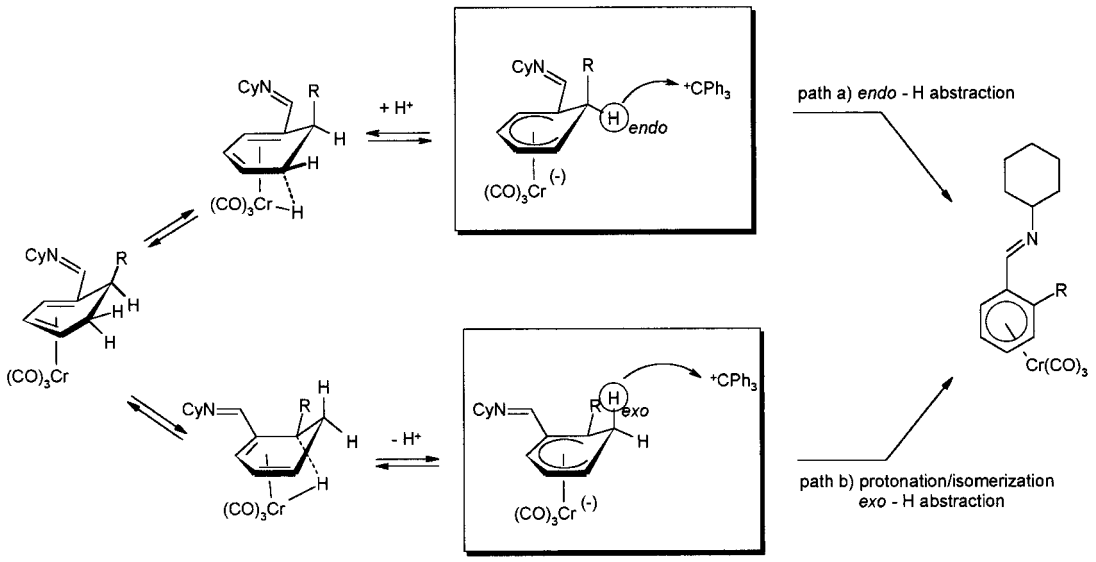
Table 1. Selected bond lengths and angles of **6**.

Cr–C(2)	2.259(7)	C(22)-Cr-C(23)	90.4(4)
Cr–C(3)	2.171(7)	C(22)-Cr-C(24)	96.4(3)
Cr–C(4)	2.180(9)	C(23)-Cr-C(24)	83.3(4)
Cr–C(5)	2.204(9)	C(2)-C(1)-C(6)	102.8(6)
Cr–C(6)	2.278(8)	C(1)-C(2)-C(3)	118.7(8)
C(1)–C(2)	1.55(1)	C(2)-C(3)-C(4)	119.2(7)
C(1)–C(6)	1.52(1)	C(3)-C(4)-C(5)	119.3(8)
C(2)–C(3)	1.42(1)	C(4)-C(5)-C(6)	120.3(8)
C(3)–C(4)	1.41(1)	C(1)-C(6)-C(5)	118.7(6)
C(4)–C(5)	1.41(1)		
C(5)–C(6)	1.39(1)	C(1)-C(2)-C(7)-N	1(1)
C(1)–C(12)	1.53(1)	C(1)-C(2)-C(7)-O(1)	179.3(6)
C(2)–C(7)	1.42(1)	C(7)-C(2)-C(3)-C(4)	170.6(7)
C(7)–N	1.29(1)	C(1)-C(2)-C(3)-C(4)	–24(1)
C(9)–N	1.47(1)	C(2)-C(3)-C(4)-C(5)	4(1)
Cr–C(22)	1.78(1)	C(3)-C(4)-C(5)-C(6)	3(1)
Cr–C(23)	1.803(9)	C(6)-C(1)-C(2)-C(3)	47.4(8)
Cr–C(24)	1.826(8)	C(6)-C(1)-C(2)-C(7)	–146.9(7)
O(2)–C(22)	1.23(1)	C(12)-C(1)-C(2)-C(3)	–74.5(9)
O(3)–C(23)	1.18(1)	C(12)-C(1)-C(2)-C(7)	91.2(9)
O(4)–C(24)	1.17(1)	C(2)-C(1)-C(6)-C(5)	–49(1)
Li–O(3)	1.92(2)	C(12)-C(1)-C(6)-C(5)	76.3(9)
Li–O(01)	1.88(1)		
Li–O(01a)	1.96(2)		
Li–O(01b)	1.91(1)		

Mechanistic considerations: Although we have shown conclusively that hydride abstraction from the intermediates analogous to **6** is feasible, the question of the mechanism of this aromatization remained open. A study of the literature indicated that the trityl cation generally reacts with cyclohexadienyl complexes by *exo*-hydride abstraction. In the absence of *exo*-hydrogens, as is the case here, an isomerization process that interconverts the cyclohexadienyl complex must be considered.[16, 25] A possible pathway, initiated by the presence of a catalytic amount of acid, is shown in Scheme 5 (path B). 1,5-H migrations in neutral protonated (cyclohexadienyl)chromium complexes are very fast processes, even at low temperatures.[12] This pathway would provide a ready explanation for an interconversion to an isomeric cyclohexadienyl complex containing a CH_2 group at the sp^3 center of the cyclohexadienyl ligand. This would then be followed by an *exo*-hydride abstraction by the trityl cation. The proton, which is necessary for the initiation of the isomerization sequence, could come from Ph_3CH or from a number of other sources in the reaction medium.[16b]

The question of *endo*-versus *exo*-hydride abstraction was investigated by using deuterium-labeled complexes and solvents. The requisite labeled benzaldehyde and benzaldehydeimine complexes were prepared using previously established lithiation/electrophile trapping reactions as shown in Scheme 6.[19, 25]

0947-6539/98/0402-0254 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 2

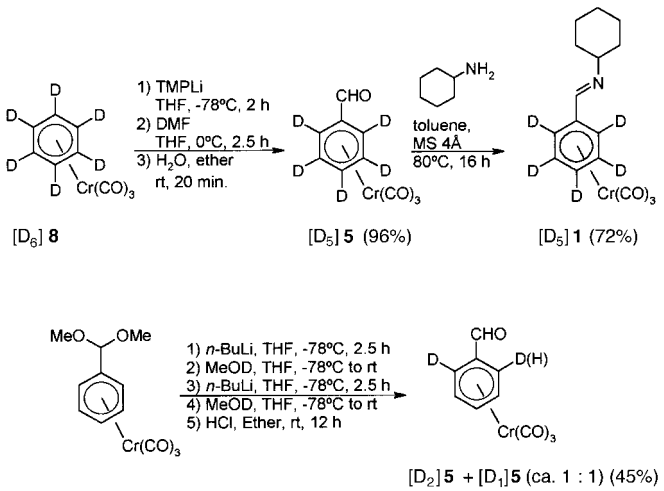


Scheme 5. Possible hydride abstraction mechanisms.

Following the usual reaction protocol, the benzaldehyde imine complex [D_5]**1** was treated sequentially with *n*-butyllithium and [Ph_3C][PF_6] to give [D_4]**5b** in 65% yield. The ^{1}H NMR spectrum of complex [D_4]**5b** exhibited signals associated with the aldehyde function ($\delta = 9.31$) and with the *n*Bu substituent, but no signals in the range for complexed aromatic H. The ^{13}C NMR spectrum clearly displayed four groups of three signals, characteristic for the deuterated aromatic carbons. The only other signal associated with an aromatic C atom is the singlet for the *n*-butyl-substituted carbon atom. Signals which could be assigned to aromatic CH groups were notably absent. The ^{2}H NMR spectrum showed four resonances at $\delta = 5.45$, 4.68, 4.18, and 4.02. This data strongly disagrees with the protonation/isomerization/*exo*-hydride abstraction mechanism shown in Scheme 6, since this mode of action would necessitate a C_{arom}–H bond. Further evidence against this reaction pathway stems from a complementary experiment in which the sequence of nucleophilic addition/hydride abstraction was carried out on the non-deuterated complex **1**, with CD_2Cl_2 as the solvent for the second step. ^{1}H NMR, ^{2}H NMR, ^{13}C NMR, and mass spectroscopy clearly show that complex **1b** was formed without incorporation of deuterium into any of the aromatic positions of the coordinated arene ring.

Finally, the sequence (*n*BuLi addition/reaction with [Ph_3C][PF_6]) was also carried out with the *ortho*-deuterated imine complex (50% [D_2]**1**, 50% [D_1]**1**) to afford **5b** as a mixture of 75% [D_1]**5b** and 25% [D_0]**5b**. NMR and MS analysis also showed the formation of deuterated triphenylmethane in this reaction.

The above experiments rule out the protonation/isomerization/*exo*-hydride mechanism and, while not providing positive evidence for an *endo*-hydride abstraction as shown in Scheme 6 (path a), are fully consistent with this pathway.



Scheme 6. Synthesis of deuterium-labeled complexes for mechanistic investigations.

Conclusion

The sequence described in this paper provides a preparatively useful route to [(*ortho*-substituted arene)$Cr(CO)_3$] complexes. The X-ray structure of **6** gives an unconventional answer to the question of the effect of the two electrophilic activating groups and to the nature of the intermediate cyclohexadienyl complex. The detailed study of the re-aromatization process strongly argues for an *endo*-hydride abstraction pathway. However, the question as to the origin of the high efficiency of this *endo*-H abstraction still remains open. The X-ray structure of **6** does not appear to deviate markedly from other cyclohexadienyl structures. The C(1)-H(*endo*) is not more accessible to the trityl reagent than in similar compounds where this step does not occur. We can therefore contemplate the possible role of the imine, oxazoline, or hydrazone substituent in this process. We have previously argued[19] that the lone pair on nitrogen coordinates the incoming organolithium reagent prior to nucleophilic *ortho* addition. It is tempting to invoke once again the role of the nitrogen lone pair in precoordinating the trityl cation and thus assisting in the hydride removal. This might

not only consist of a proximity effect, but may possibly also change the geometry of the intermediate so that it promotes the abstraction of the *endo*-hydride.

With regard to the use of this sequence in synthesis, we have already demonstrated a diastereoselective reaction with a SAMP hydrazone complex.[18a] These studies have been extended to enantioselective synthesis of planar chiral 1,2-disubstituted [(η^6-arene)Cr(CO)$_3$] complexes by the title reaction sequence, making use of the addition of nucleophiles which are chirally modified in situ.[18b] Details of these reactions and of further applications of planar chiral complexes in organic synthesis will be the subjects of forthcoming publications.

Experimental Section

General: Reactions and manipulations involving organometallic compounds were carried out under an atmosphere of purified nitrogen using an inert gas/vacuum double manifold and standard Schlenk techniques.[27] Flash column chromatography was carried out in air by the method described by Still[28] (silica gel: Merck 60).

All NMR spectra (^{1}H: 200 or 400 MHz; ^{13}C: 50.3 or 100.5 MHz) were recorded at RT on a Varian XL-200 spectrometer or a Bruker 400 MHz spectrometer as indicated. Chemical shifts (δ) are reported relative to tetramethylsilane as the internal standard and referenced to the proton signal for the residual solvent (C_6D_6, $\delta = 7.15$ for ^{1}H, and $\delta = 128.0$ for ^{13}C). Mass spectra were obtained on a Varian CH4 or SM1 spectrometer, relative intensities are given in parentheses. High-resolution mass spectra were measured on a VG analytical 7070E instrument (data system 11250, resolution 7000). IR spectra were recorded in NaCl cells on a Perkin–Elmer 1650 FT-IR spectrometer. Melting points were determined on a Büchi 510 apparatus and are not corrected. Elemental analyses were performed by H. Eder, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

THF and diethylether were dried and distilled from sodium/benzophenone ketyl under N_2 before use. Dichloromethane was freshly distilled from CaH_2 under N_2. Hexane was distilled before use. *n*BuLi (Fluka, 1.7 M), MeLi (Fluka, 1.6 M), and PhLi (Fluka, 1.6 M) were titrated before use.[29] Tetravinyltin (Aldrich) and [Ph_3C][PF_6] (Fluka) were used as received except for the mechanistic studies, for which the trityl salt was recrystallized from acetonitrile prior to use. All other chemicals were purchased from Aldrich or Fluka and were purified following standard literature procedures.[30]

General procedure for the nucleophilic addition/hydride abstraction with complex 1: A solution of RLi (1.2 equiv) was added dropwise by syringe to a solution of the imine complex **1** (0.2 to 0.25 M in THF) at $-78\,^\circ$C. The resulting orange solution was warmed to $-40\,^\circ$C over a period of 2 h, stirred at this temperature for an additional 4 h, and then evaporated to dryness under vacuum. The red-brown oily residue was taken up in a minimum of dry CH_2Cl_2. The solution was cooled to $-78\,^\circ$C and a solution of 2.2 equiv of [Ph_3C][PF_6] (0.4 M in CH_2Cl_2) was quickly added by syringe. The dark red reaction mixture was allowed to warm to room temperature overnight, volatiles were removed under vacuum and the black residue was taken up in ether (10 mL). Deoxygenated water (10 mL) was added and the two-phase system (pH = 2–3) was stirred vigorously at room temperature for 30 min. After separation of the phases and extraction with ether (5 × 10 mL), the combined ether phases were filtered over $MgSO_4$/Celite and the solvent was evaporated. The crude aldehyde complexes were purified by flash column chromatography on silica gel with hexane/ether (9:1 to 4:1) as the eluent. Solids were additionally recrystallized from hexane/ether 1:2.

[(η^6-(2-Methyl)benzaldehyde)Cr(CO)$_3$] (5a): Prepared from the imine complex **1** (323 mg, 1.00 mmol). Yield: 164 mg (64 %), red solid; m.p. 76 °C; IR (toluene): $\tilde{\nu} = 1980$, 1910, 1695 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta =$ 9.79 (s, 1H, CHO), 6.04 (dd, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.2 Hz 1H, arom CH), 5.71 (ddd, ^3J(H,H) = 6.2 Hz, ^3J(H,H) = 6.2 Hz, ^4J(H,H) = 1.2 Hz, 1H, arom CH), 5.21 (dd, ^3J(H,H) = 6.2 Hz, ^3J(H,H) = 6.2 Hz, 1H, arom CH), 5.02 (d, ^3J(H,H) = 6.4 Hz, 1H, arom CH), 2.51 (s, 3H, CH_3); MS (70 eV, EI): *m*/*z* (%): 256 [M^+] (18), 200 [$M^+ - 2$(C≡O)], 52 [Cr^+] (100).

[(η^6-(2-*n*-Butyl)benzaldehyde)Cr(CO)$_3$] (5b): Prepared from the imine complex **1** (323 mg, 1.00 mmol). Yield: 203 mg (68 %), red oil; IR (toluene): $\tilde{\nu} = 1981$, 1912, 1687 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 9.26$ (s, 1H, CHO), 5.43 (dd, ^3J(H,H) = 6.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, arom CH), 4.66 (ddd, ^3J(H,H) = 6.5 Hz, ^3J(H,H) = 6.5 Hz, ^4J(H,H) = 1.1 Hz, 1H, arom CH), 4.15 (dd, ^3J(H,H) = 6.5 Hz, ^3J(H,H) = 6.5 Hz, 1H, arom CH), 3.98 (dd, ^3J(H,H) = 6.5 Hz, ^4J(H,H) = 0.8 Hz, 1H, arom CH), 2.75 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.30 (m, 4H, CH_2), 0.73 (t, ^{3}J(H,H) = 7.0 Hz, 3H, CH_3); MS (70 eV, EI): *m*/*z* (%): 298 [M^+] (2), 214 [$M^+ - 3$(C≡O)] (17), 52 [Cr^+] (100).

[(η^6-(2-Vinyl)benzaldehyde)Cr(CO)$_3$] (5c): Vinyllithium (1.20 mmol) was prepared by adding a solution of MeLi (1.60 M, 2.25 mL, 3.60 mmol) to a solution of tetravinyltin (219 μL, 1.20 mmol) in THF (1.0 mL) at $-78\,^\circ$C. The solution was stirred at this temperature for 1 h before being added to a THF solution (5.0 mL, $-78\,^\circ$C) of the imine complex **1** (323 mg, 1.00 mmol) at $-78\,^\circ$C. Yield: 198 mg (74 %), red solid; m.p. 70 °C; IR (toluene): $\tilde{\nu} =$ 1982, 1918, 1690 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 9.33$ (s, 1H, CHO), 6.59 (dd, ^{3}J(H,H) = 17.3 Hz, ^{3}J(H,H) = 11.1 Hz, 1H, vinyl CH), 5.43 (d, ^{3}J(H,H) = 6.6 Hz, 1H, arom CH), 5.11 (d, ^{3}J(H,H) = 17.3 Hz, 1H, vinyl CH_2), 4.99 (d, ^{3}J(H,H) = 10.6 Hz, 1H, vinyl CH_2), 4.66 (dd, ^{3}J(H,H) = 6.2 Hz, ^{3}J(H,H) = 6.2 Hz, 1H, arom CH), 4.39 (d, ^{3}J(H,H) = 6.6 Hz, 1H, arom CH), 4.19 (d, ^{3}J(H,H) = 6.2 Hz, ^{3}J(H,H) = 6.2 Hz, 1H, arom CH); MS (70 eV, EI): m/z (%): 268 [M^+] (6), 184 [$M^+ - 3$(C≡O)] (91), 52 [Cr^+] (100); HR-MS for $C_{12}H_8O_4Cr$: calcd 267.9827, found 267.9808.

[(η^6-(2-Phenyl)benzaldehyde)Cr(CO)$_3$] (5d): Prepared from the imine complex **1** (323 mg, 1.00 mmol). Yield: 241 mg (76 %), red solid; m.p. 112 °C; IR (toluene): $\tilde{\nu} = 1980$, 1918, 1680 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 9.38$ (s, 1H, CHO), 6.90 (m, 2H), 7.10 (m, 3H), 5.80 (dd, ^3J(H,H) = 6.3 Hz, ^4J(H,H) = 1.0 Hz, 1H, arom CH), 4.62 (ddd, ^3J(H,H) = 6.3 Hz, ^3J(H,H) = 6.3 Hz, ^4J(H,H) = 1.0 Hz, 1H, arom CH), 4.40 (dd, ^3J(H,H) = 6.3 Hz, ^4J(H,H) = 1.0 Hz, 1H, arom CH), 4.23 (dd, ^3J(H,H) = 6.3 Hz, ^3J(H,H) = 6.3 Hz, 1H, arom CH); MS (70 eV, EI): *m*/*z* (%): 318 [M^+] (15), 234 [$M^+ - 3$(C≡O)] (100).

[(η^6-(2-Thiophenyl)benzaldehyde)Cr(CO)$_3$] (5e): 1-Lithium thiophene (1.20 mmol) was prepared by adding freshly distilled thiophene (123 μL, 1.56 mmol) to a solution of *n*BuLi (1.70 M, 705 μL, 1.20 mmol) in THF (1.5 mL) at $-10\,^\circ$C. The solution was stirred at 0–20 °C for 30 min before being added to a THF solution (5.0 mL, $-78\,^\circ$C) of the imine complex **1** (323 mg, 1.00 mmol). Yield: 194 mg (60 %), red solid; m.p. 91 °C; IR (toluene): $\tilde{\nu} = 1983$, 1919, 1687 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 9.52$ (s, 1H, CHO), 6.75 (dd, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.2 Hz, 1H, thioph CH), 6.62 (dd, ^3J(H,H) = 3.6 Hz, ^4J(H,H) = 1.2 Hz, 1H, thioph CH), 6.51 (dd, ^3J(H,H) = 5.1 Hz, ^3J(H,H) = 3.6 Hz, 1H, thioph CH), 5.73 (dd, ^3J(H,H) = 6.5 Hz, ^4J(H,H) = 1.0 Hz, 1H, arom CH), 4.56 (m, 2H, arom CH), 4.17 (m, 1H, arom CH); ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 230.1$ (C≡O), 186.1 (C=O), 135.3, 131.0, 127.6, 127.8, 109.3, 95.8, 93.4, 92.0, 91.3, 89.2; MS (70 eV, EI): *m*/*z* (%): 324 [M^+] (7), 240 [$M^+ - 3$(C≡O)], 52 (100); $C_{14}H_8CrO_4S$ (324.21): calcd C 51.86, H 2.49; found C 54.96, H 2.62.

[(η^6-(2-Furanyl)benzaldehyde)Cr(CO)$_3$] (5f): 1-Lithium furan (1.20 mmol) was prepared by adding freshly distilled furan (113 μL, 1.56 mmol) to *n*BuLi (1.70 M, 705 μL, 1.20 mmol) in THF (1.5 mL) at $-10\,^\circ$C. The solution was stirred at 0–20 °C for 30 min and subsequently added to a THF solution (5.0 mL, $-78\,^\circ$C) of the imine complex **1** (323 mg, 1.00 mmol). Yield: 160 mg (52 %), red solid; m.p. 87 °C; IR (toluene): $\tilde{\nu} =$ 1979, 1918, 1682 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 9.72$ (s, 1H, CHO), 6.88 (dd, ^3J(H,H) = 1.8 Hz, ^4J(H,H) = 0.8 Hz, 1H, furanyl. CH), 6.05 (dd, ^3J(H,H) = 3.5 Hz, ^4J(H,H) = 0.7 Hz, 1H, furanyl. CH), 5.93 (dd, ^3J(H,H) = 3.5 Hz, ^3J(H,H) = 1.9 Hz, 1H, furanyl. CH), 5.81 (dd, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.9 Hz, 1H, arom CH), 4.67 (m, 2H, arom CH), 4.21 (m, 1H, arom CH); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 231.4$ (C≡O), 187.3 (C=O), 147.7, 145.2, 113.4, 112.2, 104.4, 94.6, 94.5, 92.4, 89.0, 88.3; MS 308 [M^+] (5), 224 [$M^+ - 3$(C≡O)], 52 [Cr^+] (100); $C_{14}H_8CrO_5$ (308.21): calcd C 54.56, H 2.62; found C 54.75, H 2.68.

General procedure for the nucleophilic addition/hydride abstraction on complexes 2–4: A solution of RLi (1.2 equiv) was added dropwise by syringe to a solution of complex **2, 3,** or **4** (0.2–0.25 M in THF) at $-78\,^\circ$C. The resulting orange solution was warmed to $-40\,^\circ$C over a period of 2 h

0947-6539/98/0402-0256 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 2

and stirred at this temperature for an additional 4 h, and the reaction mixture evaporated to dryness under vacuum. The red-brown, oily residue was taken up in a minimum of dry CH_2Cl_2. The solution was cooled to $-78\,^{\circ}C$ and a solution of 2.2 equiv $[Ph_3C][PF_6]$ (0.4 M) in CH_2Cl_2 was quickly added by syringe. The dark red reaction mixture was allowed to warm to RT overnight, volatiles were removed under vacuum, and the black residue was taken up in ether (10 mL). A deoxygenated, saturated solution of aq. $NaHCO_3$ (10 mL) was added and the two-phase system was stirred vigorously at room temperature for 10 min. After separation of the phases, and extraction with ether (5×10 mL), the combined etherous phases were filtered over $MgSO_4$/Celite and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel with hexane/ether (9:1 to 2:1) as the eluent. Solids were additionally recrystallized from hexane/ether 1:3.

[(4,4-Dimethyl-2-(η^6-(2-methyl)phenyl)-4,5-dihydro-oxazole)Cr(CO)$_3$] (**2a**): Prepared from the oxazoline complex **2** (311 mg, 1.00 mmol). Yield: 169 mg (51 %), orange solid; m.p. 105 °C; IR (toluene): $\tilde{\nu} = 3020$, 1972, 1902, 1648, 1456, 738, 696 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.86$ (d, $^3J(H,H) = 6.6$ Hz, 1H, arom CH), 4.58 (dd, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 6.2$ Hz, 1H, arom CH), 4.30 (m, 2H, arom CH), 3.59 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.54 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 2.38 (s, 3H, CH_3), 1.10 (s, 6H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 232.6$ (C≡O), 159.8, 110.6, 95.4, 94.3, 92.8, 91.4, 88.3, 78.4 (OCH_2), 68.4, 28.2 (CH_3), 28.0 (CH_3), 21.4 (CH_3); MS (70 eV, EI): *m*/*z* (%): 325 [M^+] (8), 241 [$M^+ - 2$(C≡O)] (16), 52 [Cr^+] (100); HR-MS for $C_{15}H_{15}CrNO_4$: calcd 325.0406, found 325.0413; $C_{15}H_{15}CrNO_4$ (325.04): calcd C 55.72, H 4.63, N 4.14; found C 55.39, H 4.65, N 4.31.

[(4,4-Dimethyl-2-(η^6-(2-*n*-butyl)phenyl)-4,5-dihydro-oxazole)Cr(CO)$_3$] (**2b**): Prepared from the oxazoline complex **2** (311 mg, 1.00 mmol). Yield: 187 mg (51 %), orange oil; IR (toluene): $\tilde{\nu} = 2963$, 1972, 1903, 1648, 1495, 737, 698 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 5.81$ (d, $^3J(H,H) = 6.2$ Hz, 1H, arom CH), 4.60 (dd, $^3J(H,H) = 6.1$ Hz, $^3J(H,H) = 6.1$ Hz, 1H, arom CH), 4.32 (m, 2H, arom CH), 3.46 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.62 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 2.08 (m, 1H, CH_2), 1.60 (m, 1H, CH_2) 1.30 (m, 4H, CH_2), 1.08 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.88 (t, 3H, $^3J(H,H) = 7.1$ Hz, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6,): $\delta = 232.7$ (C≡O), 159.5, 115.1, 95.5, 94.4, 92.3, 91.4 , 88.8, 78.4 (OCH_2), 68.3, 34.1 (CH_2) 28.4 (CH_2), 27.9 (CH_3), 22.8 (CH_2), 13.9 (CH_3); MS (70 eV, EI): *m*/*z* (%): 367 [M^+] (5), 283 [$M^+ - 3$(C≡O)], 52 [Cr^+] (100); HR-MS for $C_{18}H_{21}CrNO_4$: calcd 367.0875, found 367.0890.

[(4,4-Dimethyl-2-(η^6-(2-vinyl)phenyl)-4,5-dihydro-oxazole)Cr(CO)$_3$] (**2c**): Prepared from the oxazoline complex **2** (311 mg, 1.00 mmol). Yield: 169 mg (52 %), orange solid; m.p. 89 °C; IR (toluene): $\tilde{\nu} = 3014$, 2926, 1975, 1907, 1647, 1494, 726 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.76$ (dd, $^3J(H,H) = 17.3$ Hz, $^3J(H,H) = 10.6$ Hz, 1H vinyl CH), 5.80 (d, $^3J(H,H) = 6.6$ Hz, 1H, arom CH), 5.29 (d, $^3J(H,H) = 17.3$ Hz, 1H vinyl CH_2), 5.11 (d, $^3J(H,H) = 11.1$ Hz, 1H, vinyl CH_2), 4.85 (d, $^3J(H,H) = 6.6$ Hz, 1H, arom CH), 4.59 (dd, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 6.2$ Hz, 1H, arom CH), 4.40 (dd, $^3J(H,H) = 6.6$ Hz, $^3J(H,H) = 6.6$ Hz, 1H, arom CH), 3.60 (d, $^2J(H,H) = 8.4$ Hz, 1H, OCH_2), 3.55 (d, $^2J(H,H) = 8.4$ Hz, 1H, OCH_2), 1.11 (s, 6H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 232.3$ (C≡O), 159.8, 134.2, 117.0 (vinyl CH_2), 107.3 (vinyl CH), 94.0, 93.0, 91.1, 89.7, 88.5, 78.5 (OCH_2), 68.4, 28.2 (CH_3), 28.0 (CH_3); MS (70 eV, EI): *m*/*z* (%): 337 [M^+] (8), 253 [$M^+ - 2$(C≡O)] (84), 52 [Cr^+] (100); HR-MS for $C_{16}H_{15}CrNO_4$: calcd 337.0406, found 337.0412; $C_{16}H_{15}CrNO_4$ (325.04): calcd C 56.98, H 4.48, N 4.25; found C 57.20, H 4.54, N 4.07.

[(4,4-Dimethyl-2-(η^6-(2-phenyl)phenyl)-4,5-dihydro-oxazole)Cr(CO)$_3$] (**2d**): Prepared from the oxazoline complex **2** (311 mg, 1.00 mmol). Yield: 225 mg (68 %), orange solid; m.p. 99 °C; IR (toluene): $\tilde{\nu} = 2919$, 1975, 1907, 1644, 1494, 737 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.35$ (m, 2H), 7.10 (m, 3H), 5.75 (d, $^3J(H,H) = 6.2$ Hz, 1H, arom H), 4.71 (d, $^3J(H,H) = 6.2$ Hz, 1H, arom CH), 4.51 (dd, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 6.2$ Hz, 1H, arom CH), 4.43 (d, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 6.2$ Hz, 1H, arom CH), 3.49 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.41 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 1.06 (s, 6H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 232.5$ (C≡O), 160.9, 137.5, 129.1, 128.6, 128.0, 113.8, 94.4, 94.3, 93.6, 91.6, 90.5, 79.5 (OCH_2) 67.8, 27.8 (CH_3), 27.7 (CH_3); MS (70 eV, EI): *m*/*z* (%): 387 [M^+] (1), 331 [$M^+ - 2$(C≡O)] (10), 303 [$M^+ - 3$(C≡O)] (100); HR-MS for $C_{18}H_{17}CrNO_2$ [$M^+ - 2$(C≡O)]: calcd 331.0664, found 331.0624; $C_{20}H_{17}CrNO_4$ (325.04): calcd C 62.02, H 4.42, N 3.61; found C 61.96, H 4.36, N 3.53.

[(4,4-Dimethyl-2-(η^6-(2-thiophenyl)phenyl)-4,5-dihydro-oxazole)Cr(CO)$_3$] (**2e**): Prepared from the oxazoline complex **2** (311 mg, 1.00 mmol). Yield: 235 mg (60 %), red solid; m.p. 108 °C; IR (toluene): $\tilde{\nu} = 3014$, 1976, 1909, 726 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 7.08$ (dd, $^3J(H,H) = 3.5$ Hz, $^4J(H,H) = 1.3$ Hz, 1H, thioph CH), 6.83 (dd, $^3J(H,H) = 4.9$ Hz, $^4J(H,H) = 0.9$ Hz, 1H, thioph CH), 6.67 (dd, $^3J(H,H) = 4.9$ Hz), $^3J(H,H) = 3.5$ Hz, 1H, thioph CH), 5.62 (dd, $^3J(H,H) = 6.6$ Hz, $^4J(H,H) = 1.32$ Hz, 1H, arom CH), 4.84 (dd, $^3J(H,H) = 6.2$ Hz, $^4J(H,H) = 0.9$ Hz, arom CH), 4.41 (ddd, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 6.2$ Hz, $^4J(H,H) = 0.9$ Hz, 1H, arom CH), 4.35 (ddd, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 6.2$ Hz, $^4J(H,H) = 0.9$ Hz, 1H, arom CH), 3.58 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.46 (d, 1H, $^2J(H,H) = 8.0$ Hz, OCH_2), 1.11 (s, 6H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): $\delta = 232.2$ (C≡O), 160.6, 139.2, 129.8, 128.9, 126.7, 104.9, 95.5, 94.4, 93.3, 91.0, 90.5, 79.7 (OCH_2), 68.0, 28.1 (CH_3), 27.7 (CH_3); MS (70 eV, EI): *m*/*z* (%): 393 [M^+] (1), 309 [$M^+ - 2$(C≡O)] (100); HR-MS for $C_{16}H_{15}CrNO_2S$ [$M^+ - 2$(C≡O)]: calcd 337.0228, found 337.0215.

[(4,4-Dimethyl-2-(η^6-(2-methyl-4-methoxy)phenyl)-4,5-dihydro-oxazole)-Cr(CO)$_3$] (**3a**): Prepared from the *para*-anisyloxazoline complex **3** (342 mg, 1.00 mmol). Yield: 191 mg (64 %), yellow oil; IR (toluene): $\tilde{\nu} = 3020$, 1969, 1896, 1493, 738 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 6.08$ (d, $^3J(H,H) = 7.1$ Hz, 1H, arom CH), 4.55 (d, $^3J(H,H) = 1.8$ Hz, 1H, arom CH), 4.32 (dd, $^3J(H,H) = 7.1$ Hz, $^4J(H,H) = 2.0$ Hz, 1H, arom CH), 3.59 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.54 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 2.97 (s, 3H, CH_3), 2.49 (s, 3H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 232.7$ (C≡O), 159.4, 143.5, 111.2, 95.9, 86.3, 81.0, 78.3 (OCH_2), 75.0, 68.3, 55.1 (OCH_3), 28.1 (CH_3), 27.9 (CH_3), 21.7 (CH_3); MS (70 eV, EI): *m*/*z* (%): 355 [M^+] (2), 299 [$M^+ - 2$(C≡O)] (20), 271 [$M^+ - 3$(C≡O)] (98), 52 [Cr^+] (100); HR-MS for $C_{14}H_{17}CrNO_3$ [$M^+ - 2$(C≡O)]: calcd 299.0613, found 299.0611.

[(4,4-Dimethyl-2-(η^6-(2-*n*-butyl-4-methoxy)phenyl)-4,5-dihydro-oxazole)-Cr(CO)$_3$] (**3b**): Prepared from the *para*-anisyloxazoline complex **3** (342 mg, 1.00 mmol). Yield: 262 mg (66 %), yellow oil; IR (toluene): $\tilde{\nu} = 3022$, 1968, 1896, 1495, 737 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 6.08$ (d, $^3J(H,H) = 7.1$ Hz, 1H, arom CH), 4.70 (d, $^4J(H,H) = 2.2$ Hz, 1H, arom CH), 4.35 (dd, $^3J(H,H) = 7.1$ Hz, $^4J(H,H) = 2.2$ Hz, 1H, arom CH), 3.74 (m, 1H, CH_2), 3.59 (d, 1H, $^2J(H,H) = 8.0$ Hz, OCH_2), 3.54 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.02 (s, 3H, OCH_3), 2.14 (m, 1H, CH_2), 1.71 (m, 1H, CH_2), 1.39 (m, 3H, CH_2), 1.09 (s, 6H,CH_3), 0.93 (m, 3H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): $\delta = 232.7$ (C≡O), 159.1, 143.3, 115.8, 96.2, 85.9, 80.3, 78.3 (OCH_2), 74.9, 68.2, 55.1 (OCH_3), 34.4 (CH_2), 34.2 (CH_2), 28.1 (CH_3), 27.8 (CH_3), 22.9 (CH_2), 14.1 CH_3); MS (70 eV, EI): *m*/*z* (%): 397 [M^+] (1), 341 [$M^+ - 2$(C≡O)] (12), 313 [$M^+ - 3$(C≡O)] (100); HR-MS for $C_{19}H_{23}CrNO_5$: calcd 397.0981, found 397.0970.

[(4,4-Dimethyl-2-(η^6-(2-vinyl-4-methoxy)phenyl)-4,5-dihydro-oxazole)Cr(CO)$_3$] (**3c**): Prepared from the *para*-anisyloxazoline complex **3** (342 mg, 1.00 mmol). Yield: 212 mg (58 %), orange solid; m.p. 86 °C; IR (toluene): $\tilde{\nu} = 1970$, 1901, 1647, 1538, 1279, 1014, 661 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.90$ (d, $^3J(H,H) = 10.9$ Hz, 1H, vinyl CH), 6.08 (d, $^3J(H,H) = 7.2$ Hz, 1H, arom CH), 5.30 (d, $^3J(H,H) = 17.3$ Hz, 1H, vinyl CH_2), 5.14 (d, $^3J(H,H) = 11.2$ Hz, 1H, vinyl CH_2), 5.03 (d, $^4J(H,H) = 2.3$ Hz, arom CH), 4.35 (dd, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 2.3$ Hz, 1H, arom CH), 3.57 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.51 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 2.04 (s, 3H, OCH_3), 1.08 (s, 3H, CH3), 1.07 (s, 3H, CH_3); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 232.7$ (C≡O), 159.4, 143.6, 134.5 (vinyl CH), 117.7 (vinyl CH_2), 108.6, 95.7, 85.5, 78.5 (OCH_2), 76.1, 75.0, 68.5, 55.2 (OCH_3), 28.1 (CH3), 28.02 (CH_3); MS (70 eV, EI): *m*/*z* (%): 367 [M^+] (1), 311 (12), 283 [$M^+ - 3$(C≡O)] (90), 52 [Cr^+] (100); HR-MS for $C_{15}H_{17}CrNO_3$ [$M^+ - 2$(C≡O)]: calcd 311.0613, found 311.0632.

[(4,4-Dimethyl-2-(η^6-(4-methoxy-2-phenyl)phenyl)-4,5-dihydro-oxazole)-Cr(CO)$_3$] (**3d**): Prepared from the *para*-anisyloxazoline complex **3** (342 mg, 1.00 mmol). Yield: 266 mg (64 %), yellow oil; IR (toluene): $\tilde{\nu} = 3019$, 1974, 1906, 1496, 726, 690 cm^{-1}; H NMR (200 MHz, C_6D_6): $\delta = 7.46$ (m, 2H), 7.13 (m, 3H), 6.08 (d, $^3J(H,H) = 7.0$ Hz, 1H, arom CH), 4.90 (d, $^4J(H,H) = 2.2$ Hz, 1H, arom CH), 4.37 (dd, $^3J(H,H) = 6.9$ Hz, $^4J(H,H) = 2.2$ Hz, 1H, arom CH), 3.48 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 3.24 (d, $^2J(H,H) = 8.0$ Hz, 1H, OCH_2), 2.94 (s, 3H, OCH_3), 1.09 (s, 3H, CH_3), 1.07 (s, 3H, CH_3); ^{3}C NMR (100.5 MHz, C_6D_6): $\delta = 232.7$ (C≡O), 160.6, 142.5, 137.4, 129.8, 129.7, 128.6, 115.1, 95.8, 87.8, 81.2, 79.4(OCH_2), 75.9, 67.8, 55.2 (OCH_3), 27.8 (CH_3), 27.2 (CH_3); MS (70 eV, EI): *m*/*z* (%): 417 [M^+] (1), 361 [$M^+ - 2$(C≡O)] (7), 333 [$M^+ - 3$(C≡O)] (100); HR-MS for $C_{20}H_{129}CrNO_4$ [$M^+ - $(C≡O)]: calcd 389.0719, found 389.0715.

[(*N*,*N*-Dimethyl-*N*′-(η^6-(2-methyl)-benzylidene)-hydrazone)Cr(CO)$_3$] (**4a**): Prepared from the hydrazone complex **4** (284 mg, 1.00 mmol). Yield: 149 mg (50%), yellow solid; m.p. 76 °C; IR (toluene): $\tilde{\nu}$ = 3025, 2910, 1962, 1889, 1494, 727, 700 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 6.52 (s, 1H, CHN), 6.04 (dd, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.3 Hz, 1H, arom CH), 4.93 (d, ^3J(H,H) = 5.75 Hz, 1H, arom CH), 4.55 (m, 1H, arom CH), 4.53 (d, ^3J(H,H) = 5.75 Hz, 1H, arom CH), 2.48 (s, 6H, CH_3), 1.82 (s, 3H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): δ = 234.3 (C≡O), 123.2 (C=N), 105.1, 94.4, 91.9, 91.0, 90.5, 89.3, 42.0 (CH_3), 18.4 (CH_3); MS (70 eV, EI): *m*/*z* (%): 298 [M^+] (10), 242 [$M^+ - 2$(C≡O)] (6), 52 [Cr^+] (100); HR-MS for $C_{13}H_{14}CrN_2O_3$: calcd 298.0409, found 298.0378.

[(*N*,*N*-Dimethyl-*N*′-(η^6-(2-butyl)-benzylidene)-hydrazone)Cr(CO)$_3$] (**4b**): Prepared from the hydrazone complex **4** (284 mg, 1.00 mmol). Yield: 265 mg (78%), orange oil; IR (toluene): $\tilde{\nu}$ = 3026, 2913, 1961, 1890, 1494, 727, 700 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 6.03 (d, ^3J(H,H) = 6.63 Hz, 1H, arom CH), 4.62 (m, 3H, arom CH), 2.58 (m, 1H, CH_2), 2.54 (s, 3H, CH_3), 2.09 (m, 1H, CH2), 1.30 (m, 2H, CH2), 1.27 (m, 2H, CH_2), 0.80 (t, ^3J(H,H) = 7.5 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): δ = 234.3 (C≡O), 123.4 (C=N), 109.8, 105.1, 93.9, 91.9, 91.6, 90.4, 42.0 (CH_3), 33.2 (CH_2), 32.3 (CH_2), 22.6 (CH_2), 13.9 (CH_3); MS (70 eV, EI): m/z (%): 340 [M^+] (17), 284 [$M^+ - 2$(C≡O)] (6), 256 [$M^+ - 2$(C≡O)] (20), 52 [Cr^+] (100); HR-MS for $C_{16}H_{20}CrN_2O_3$: calcd 340.0879, found 340.0894.

[(*N*,*N*-Dimethyl-*N*′-(η^6-(2-vinyl)-benzylidene)-hydrazone)Cr(CO)$_3$] (**4c**): Prepared from the hydrazone complex **4** (284 mg, 1.00 mmol). Yield: 176 mg (57%), orange solid; m.p. 125 °C; IR (toluene): $\tilde{\nu}$ = 3024, 1964, 1894, 1494, 730 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): δ = 6.63 (s, 1H, CHN), 6.47 (dd, ^3J(H,H) = 17.3 Hz, ^3J(H,H) = 10.5 Hz, 1H, vinyl CH), 5.94 (dd, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.1 Hz, 1H, arom CH), 5.31 (dd, ^3J(H,H) = 17.3 Hz, ^2J(H,H) = 0.8 Hz, 1H, vinyl CH_2), 5.05 (dd, 1H, ^3J(H,H) = 10.2 Hz, ^2J(H,H) = 0.8 Hz, vinyl CH_2), 4.93 (dd, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.1 Hz, 1H, arom CH), 4.66 (m, 1H, arom CH), 4.49 (m, 1H, arom CH), 2.44 (s, 6H, CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): δ = 233.8 (C≡O), 131.6 (C=N), 122.8 (vinyl CH_2), 117.9 (vinyl CH_2), 105.3, 103.2, 92.4, 90.9, 90.4, 88.9, 42.0 (CH_3); MS (70 eV, EI): m/z (%): 310 [M^+] (17), 226 [$M^+ - 3$(C≡O)] (23), 52 [Cr^+] (100); HR-MS for $C_{14}H_{14}CrN_2O_3$: calcd 310.0410, found 310.0420.

[(*N*,*N*-Dimethyl-*N*′-(η^6-(2-phenyl)-benzylidene)-hydrazone)Cr(CO)$_3$] (**4d**): Prepared from the hydrazone complex **4** (284 mg, 1.00 mmol). Yield: 284 mg (79%), red solid; m.p. 122 °C; IR (toluene): $\tilde{\nu}$ = 2919, 1964, 1893, 1563, 1496, 727, 699 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): δ = 7.39 (m, 2H), 7.06 (m, 3H), 6.61 (s, 1H, CHN), 6.02 (dd, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.3 Hz, 1H, arom CH), 4.93 (dd, ^3J(H,H) = 6.4 Hz, ^4J(H,H) = 1.1 Hz, 1H, arom CH), 4.78 (m, 1H, arom CH), 4.40 (dd, 1H, ^3J(H,H) = 6.2 Hz, ^4J(H,H) = 1.2 Hz, arom CH), 2.35 (s, 6H, (CH_3); ^{13}C NMR (100.5 MHz, C_6D_6): δ = 233.9 (C≡O), 131.0 (C=N), 129.8, 128.6, 128.3, 124.6, 110.6 , 107.2, 96.8, 94.2, 88.8, 87.0, 41.9 (CH_3); MS (70 eV, EI): *m*/*z* (%): 360 [M^+] (1), 276 [$M^+ - 3$(C≡O)] (19), 52 [Cr^+] (100); HR-MS for $C_{18}H_{16}CrN_2O_3$: calcd 360.0566, found 360.0544.

Preparation of the anionic cyclohexadienyl complex 6: α-Bromonaphthalene (528 mL, 2.50 mmol) was added dropwise at −78 °C to a solution of *n*BuLi (2.00 M, 1.38 mL, 2.77 mmol) in THF (2 mL). The light yellow suspension was stirred at −50 °C for an additional 15 min, diluted with THF (8 mL) and a solution of oxazoline complex **2** (622 mg, 2.00 mmol) in THF (6 mL) was added slowly by syringe at −78 °C. The reaction mixture was allowed to warm to −40 °C over 2 h, was stirred at this temperature for a further 4 h before it was taken to dyness in vacuo. Towards the end of the evaporation, the cooling bath was replaced by a water bath at 40 °C. The orange-brown solid was washed with small portions of ether and dried under vacuum. The yellow solid thus obtained was taken up in dioxane at 40 °C and filtered over Celite. The orange to brown solution was left in a Schlenk tube connected to a nitrogen manifold. After 10 days at room temperature, complex **6** crystallized in the form of fine yellow needles which were separated and analyzed by X-ray diffraction. IR (DMSO): $\tilde{\nu}$ = 1900, 1810, 1777, 1611 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 8.13 (d, ^3J(H,H) = 8.4 Hz, 1H, naphth. CH), 7.81 (d, ^3J(H,H) = 7.6 Hz, naphth. CH), 7.56 (d, ^3J(H,H) = 8.0 Hz, 1H, naphth. CH), 7.50 (t, ^3J(H,H) = 7.2 Hz, naphth.CH), 7.44 (t, ^3J(H,H) = 7.2 Hz, 1H, naphthyl. CH), 7.27 (t, 1H, ^3J(H,H) = 7.6 Hz, naphthyl. CH), 6.84 (d, 1H, ^3J(H,H) = 7.2 Hz, naphth. CH), 5.64 (d, ^3J(H,H) = 5.6 Hz, 1H, HC-3), 4.99 (t, ^3J(H,H) = 6.0 Hz, 1H, HC-4), 4.76 (d, ^3J(H,H) = 5.6 Hz, HC-6), 4.41 (t, ^3J(H,H) = 5.0 Hz, 1H, HC-5), 3.58 (d, ^3J(H,H) = 8.0 Hz, 1H, OCH_2) 3.74 (d, ^3J(H,H) = 8.0 Hz, 1H, OCH_2), 3.37 (m, 1H, CH), 1.07 (s, 6H, CH_3).

Crystal structure of 6: $[Cr(C_{24}H_{20}NO_4)]^-Li^+ \cdot 4.5\,(C_4H_8O_2) \cdot (H_2O)$; M_r = 859.9; μ = 2.758 mm^{-1}, $F(000)$ = 1824 , ρ_{calcd} = 1.33 g cm^{-3}, monoclinic, $P2_1/c$, Z = 4, a = 20.830(6), b = 10.578(1), c = 20.422(4) Å, β = 107.78(1)°, V = 4285(1) Å^3, from 20 reflections (40° < 2θ < 59°), yellow prism 0.10 × 0.20 × 0.50 mm mounted on a quartz fiber with RS3000 oil. Cell dimensions and intensities were measured at 180 K on a Nonius CAD4 diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation (λ = 1.5418 Å), $\omega - 2\theta$ scans, scan width 1.2°+0.25 tgθ, and scan speed 0.14° s^{-1}. Two reference reflections measured every 45 min showed variation less than 3.5 σ (I). $-22 < h < 22$; $0 < k < 11$; $0 < l < 21$; 6486 measured reflections, 5369 unique reflections of which 3794 were observed [$|F_o| > 4\sigma(F_o)$]; R_{int} for equivalent reflections: 0.046. Data were corrected for Lorentz and polarization effects and for absorption[31] (A^* min, max = 1.334, 3.158). The structure was solved by direct methods using MULTAN87,[32] all other calculations used the XTAL[33] system and ORTEP[34] programs. Atomic scattering factors and anomalous dispersion terms were taken from ref. [35]. Full-matrix least-squares refinement based on $|F|$ and a weight of 1 gave final values R = ωR = 0.077, and S = 2.75 for 700 variables and 3794 contributing reflections. The maximum shift/error on the last cycle was 0.105. Hydrogen atoms were refined with restraints on bond lengths and angles. The final difference electron density map showed a maximum of +1.05 (near the Cr atom) and a minimum of −0.70 e Å^{-3}. Four dioxane molecules are located in general positions and one in special position (2a) about a center of inversion.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100564. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code + (44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Synthesis of [(η^6-[D_5]benzaldehyde)Cr(CO)$_3$] ([D_5]**5**): A solution of *n*BuLi (1.56 M, 5.64 mL, 8.80 mmol) was added at −78 °C to a solution of of 2,2,6,6-tetramethylpiperidine (1.36 mL, 8.80 mmol) in THF (40 mL). After 30 min at this temperature, a solution of (η^6-[D_6]benzene)chromium-tricarbonyl ([D_6]**8**, 1.76 g, 8.00 mmol) in THF (10 mL) was added slowly. The yellow reaction mixture was stirred at −78 °C for an additional 3 h. A yellow suspension was obtained. DMF (3.00 mL, 24.0 mmol) was added and the resulting yellow solution was stirred at 0 °C for 2 h. The solvent was evaporated, the residue was dissolved in ether (20 mL), and hydrolysis was carried out by stirring vigorously with H_2O (20 mL). Aqueous and ethereal layer were separated, the aqueous phase was extracted with ether (3 × 10 mL), and the combined organic phases were dried over $MgSO_4$ and filtered. After evaporation of the solvent [D_5]**5** (1.89 g) was obtained as a red powder in 96% yield. IR (toluene): $\tilde{\nu}$ = 1981, 1926, 1692 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 8.74 (s, 1H, CHO); ^{2}H NMR (400 MHz, C_6H_6): δ = 5.04 (s, 2H), 4.48 (s, 1H), 4.08 (s, 2H).

Synthesis of [(η^6-[D_5]phenylmethylene)cyclohexanamine)Cr(CO)$_3$] ([D_5]**1**): [(η^6-[D_5]Benzaldehyde)Cr(CO)$_3$] ([D_5]**5**, 1.80 g, 7.30 mmol), cyclohexylamine (912 μL, 8.03 mmol), and molecular sieves (3.65 g, 4 Å) in toluene (15 mL) were heated to 85 °C for 18 h (the course of the reaction was followed by IR spectroscopy). After filtration over Celite and evaporation of the solvent, the product was purified by recrystallization from hexane/ether (1:1). Imine complex [D_5]**1** (1.72 g) was obtained as fine, orange needles in 72% yield. IR (toluene): $\tilde{\nu}$ = 2922, 1973, 1903, 1719 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.24 (s, 1H, CHN), 2.97 (m, 1H), 1.58, 1.33 – 1.21 (m, 10H); ^{2}H NMR (400 MHz, C_6H_6): δ = 5.31 (s, 2H), 4.44 (s, 3H); ^{13}C NMR (100.5 MHz, C_6D_6): δ = 232.6 (C≡O), 154.2(C=N), 101.0, {92.6, 92.3, 92.0}, {92.5, 92.2, 92.0}, {91.2, 90.9, 90.7}, 69.4 (CH), 34.7 (CH_2), 25.9 (CH_2), 24.7 (CH_2); MS (70 eV, EI): *m*/*z* (%): 328 [M^+] (2), 272 [$M^+ - 2$(C≡O)] (10), 52 (100); HR-MS for $C_{16}H_{12}CrD_5O_3N$: calcd 328.0937, found 328.0927.

[(η^6-(*n*-butyl)[D_4]benzaldehyde)Cr(CO)$_3$] ([D_4]**5b**): Imine complex [D_5]**1** (131 mg, 0.40 mmol) was treated with *n*BuLi (1.75 M, 285 μL, 0.5 mmol) following the general reaction procedure for nucleophilic addition/hydride abstraction. After purification by flash column chromatography, aldehyde complex [D_4]**5b** (78.5 mg) was isolated in 65% yield. ^{1}H NMR (400 MHz, C_6D_6): δ = 9.31 (s, 1H, CHO), 2.77 (m, 1H, CH_2), 1.87 (m, 1H, (CH_2), 1.22 – 1.06 (m, 4H, CH_2), 0.76 (t, 3H, ^3J(H,H) = 7.2 Hz, CH_3); ^{2}H NMR (400 MHz, C_6H_6): δ = 5.45, 4.69, 4.18, 4.02; ^{13}C NMR (100.5 MHz, C_6D_6): δ = 231.2 (C≡O), 186.7(C=N), 116.4, {95.3, 95.1, 94.8}, {95.0, 94.7, 94.5}, 93.9,

0947-6539/98/0402-0258 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 2

{90.6, 90.3, 90.0}, {87.9, 87.6, 87.4}, 34.5 (CH_2), 31.6 (CH_2), 22.5 (CH_2), 13.8 (CH_3); MS (70 eV, EI): *m*/*z* (%): 302 [M^+] (14), 246 [$M^+ - 2(C{\equiv}O)$] (4), 218 [$M^+ - 3(C{\equiv}O)$] (88), 52(100); HR-MS for $C_{14}H_{10}CrD_4O_4$: calcd 302.0548, found 302.0544.

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