

New Chromium Enolates

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Dedicated to *Duilio Arigoni* on the occasion of his 75th birthday

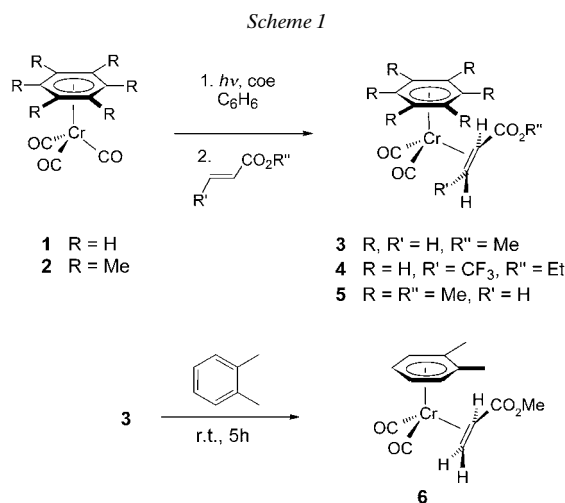
Three new (η^2 -acrylate)(η^6 -arene)dicarbonylchromium complexes are reported. They were obtained either by CO/acrylate exchange in $[\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3]$ (**1**) via the photolytically generated η^2 -cyclooctene intermediate or by arene exchange in $[\text{Cr}(\eta^2\text{-methyl acrylate})(\eta^6\text{-benzene})(\text{CO})_2]$ (**3**) (Scheme 1). On crystallization, $[\text{Cr}(\eta^2\text{-methyl acrylate})(\eta^6\text{-}o\text{-xylene})(\text{CO})_2]$ (**5**) underwent partial resolution. The degree of this resolution was analyzed via X-ray crystal-structure determination (Fig. 1) and was correlated to the CD spectra in solution (Fig. 6), thus allowing the assignment of the absolute configuration. The reaction of $[\text{Cr}(\eta^2\text{-acrylate})(\eta^6\text{-benzene})(\text{CO})_2]$ complexes with cyclopentad-1,3-diene or 1*H*-indene afforded new (η^6 -cyclopent-2,4-dien-1-yl)- or (η^6 -1*H*-inden-1-yl)(η^3 -oxaallyl)chromium complexes (Scheme 2). A mechanism is proposed that involves arene-ligand substitution by the diene ligand, initiated by haptotropic rearrangement of the acrylate from a η^2 - to a η^4 -coordination mode, followed by hydride migration from the diene to the acrylate (Scheme 3). An X-ray crystal-structure determination of $[\text{Cr}(\text{CO})_2(\eta^5\text{-1*H*-inden-1-yl})\{\eta^3\text{-CH}(\text{CH}_2\text{CF}_3)\text{-C}(\text{O})\text{OEt}\}]$ (**8**) reveals a metal enolate that is best described as η^3 -oxaallyl species (Fig. 2). A shorter, more-efficient route to the $[\text{Cr}(\eta^5\text{-1*H*-inden-1-yl})(\eta^3\text{-oxaallyl})]$ complexes was devised via the reaction of $[\text{Cr}(\text{CO})_2(\eta^2\text{-cyclooctene})(\eta^6\text{-1*H*-indene})]$ with methyl acrylate (Scheme 4).

Introduction. – The arene–chromium bond in $[\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3]$ (**1**) is inert, and substitution of the arene by other ligands requires temperatures in excess of 100°. Three examples to the point are the arene displacement in $[\text{Cr}(\text{arene})(\text{CO})_3]$ complexes in refluxing pyridine to yield $[\text{Cr}(\text{CO})_3(\text{py})_3]$ [1], arene exchange in a sealed reactor in THF at 140° [2], and the generation of the diene-hydrogenation catalyst ‘ $[\text{Cr}(\text{CO})_3]$ ’ from **1** in a coordinating solvent upon heating to 160° [3]. Thanks to the robust metal–arene bond, $[\text{Cr}(\text{arene})(\text{CO})_3]$ complexes are easily handled, and the metal–arene bond can be conserved under a large variety of reaction conditions. This has been used extensively in organic synthesis, where the electrophilic $[\text{Cr}(\text{CO})_3]$ group is an activating and stereodirecting element in the transformation of arenes (for reviews, see [4a]; for recent examples, see [4b]). The drawback of an inert metal–arene bond is equally obvious. The absence of a low-energy pathway for bond cleavage translates into harsh conditions for arene exchange and precludes the catalytic use of the $[\text{Cr}(\text{CO})_3]$ fragment in arene-transformation reactions under mild conditions [5]. The forcing conditions required to cleave the metal–arene bond are intricately linked to the first step of the arene displacement, the slippage of the arene from a η^6 - to a η^4 -coordination mode. Arene substituents that facilitate this step render the metal–arene bond more labile. Arene exchange becomes facile with condensed aromatics [6] or upon two-electron reduction [7]. While the goal of catalytic arene transformations via temporary activation of the arene to a transition-metal Lewis acid has not yet been realized, first successful results towards labilizing the metal–benzene bond in a

$[\text{Cr}(\text{CO})_3]$ complex analogue have been obtained. In our group, we have shown that haptotropic arene slippage can be induced by a ligand modification where a bifunctional electrophilic coligand labilizes the arene–metal bond. This has led to the surprising finding that, in $[\text{Cr}(\eta^6\text{-benzene})(\text{CO})_2(\eta^2\text{-methyl acrylate})]$ (**3**), the metal–benzene bond is more labile than the metal–alkene bond [8]. *Semmelhack* and co-workers showed that arene exchange can also be induced by other ligands that emulate the bonding characteristics of CO and possess a functional group that can temporarily bind to the metal and thereby induce arene dissociation [9].

We here report the application of this principle to the synthesis of new cyclopentadienyl- and indenylchromium enolates from arene precursor complexes. Because of the key role that metal enolates play in the aldol reaction, structural insight and routes of access to new metal enolates are of manifest interest.

Results and Discussion. – The acrylate complexes **4** and **5** were prepared *via* photolytic CO substitution for cyclooctene (coe) in the corresponding $[\text{Cr}(\text{arene})(\text{CO})_3]$ complex [10] followed by alkene exchange as described previously for **3** [8]. The *o*-xylene complex **6** was obtained *via* an arene-exchange reaction of **3**. Both, the trifluoromethyl complex **4** and the methylbenzene complexes **5** and **6** are less reactive and, thus, easier to handle than the parent complex **3** (*Scheme 1*).



Spectral characteristics identify **3–6** as η^2 -alkene complexes. Both, the alkene ^1H and ^{13}C -NMR resonances are shifted upfield compared to the uncoordinated ligand (*e.g.* for **6** by 3 and 90 ppm, resp.). A much smaller shift (10 ppm for **6**) is found for the C=O resonance of the acrylate ligand. The IR spectrum of **6** shows an absorption at 1698 cm^{-1} . Based on the above data, we conclude that the ester function is not interacting directly with the metal center as spectral characteristics for η^4 -coordinated acrylates are different (see [11a] for initial report) [11b][12].

Crystals suitable for X-ray analysis were obtained by crystallization of **5** from toluene/hexane at -10° and of **6** from *o*-xylene/hexane at -10° . An ORTEP

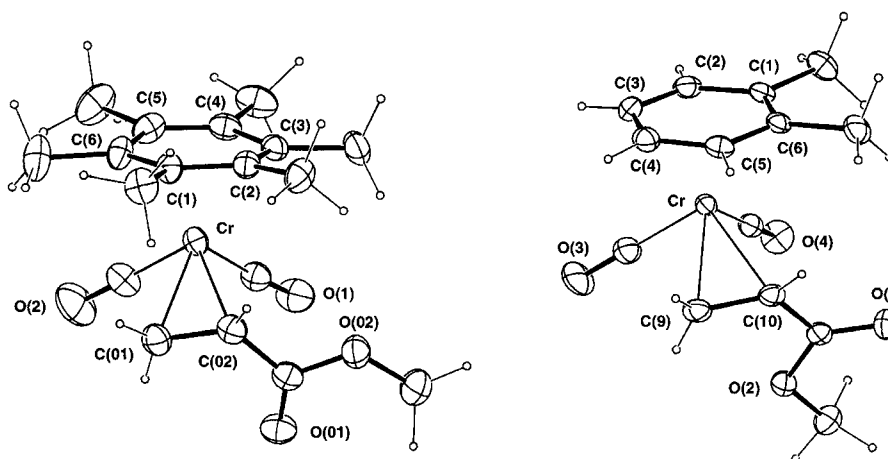


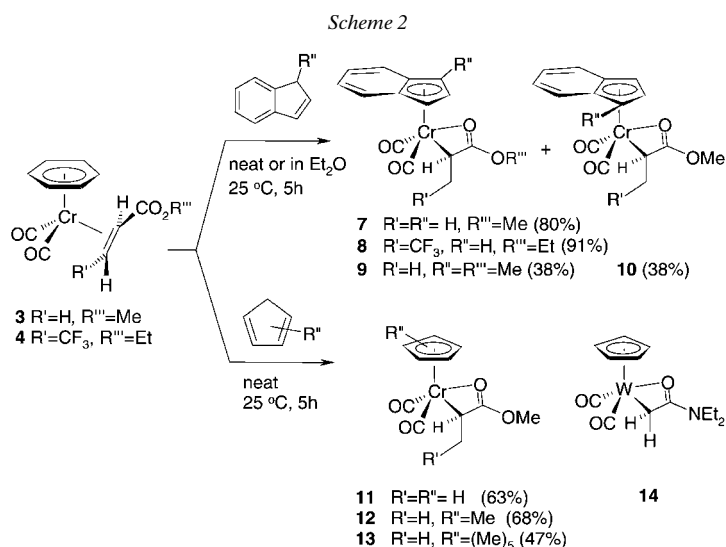
Fig. 1. ORTEP Views of the $[\text{Cr}(\eta^6\text{-hexamethylbenzene})(\text{CO})_2(\text{exo}'\text{-}\eta^2\text{-methyl acrylate})]$ (**5**) and $[\text{Cr}(\eta^6\text{-o-xylene})(\text{CO})_2(\text{exo}'\text{-}\eta^2\text{-methyl acrylate})]$ (**6**) complexes. Ellipsoids are represented with 40% probability level. Arbitrary numbering. Selected bond distances [Å] for **5**: Cr–C(1) 2.311(6), Cr–C(2) 2.320(6), Cr–C(3) 2.247(5), Cr–C(4) 2.261(5), Cr–C(5) 2.274(6), Cr–C(6) 2.243(6), Cr–C(01) 2.193(7), and Cr–C(02) 2.178(6). Selected bond distances [Å] for **6**: Cr–C(1) 2.266(3), Cr–C(2) 2.289(3), Cr–C(3) 2.237(3), Cr–C(4) 2.247(3), Cr–C(5) 2.228(3), Cr–C(6) 2.212(3), Cr–C(9) 2.207(3), and Cr–C(10) 2.213(3).

representation of the structures is shown in Fig. 1. The η^2 -binding mode of the acrylate in **5** and in **6** is corroborated in the crystal structures.

In our hands, (reaction of $[\text{Cr}(\eta^6\text{-benzene})(\text{CO})_2(\text{coe})]$ with other α,β -unsaturated carbonyl compounds (methyl vinyl ketone, *N,N*-dimethylacrylamide, methyl crotonate, methyl methacrylate) or with acrylonitrile failed to give isolable complexes [13].

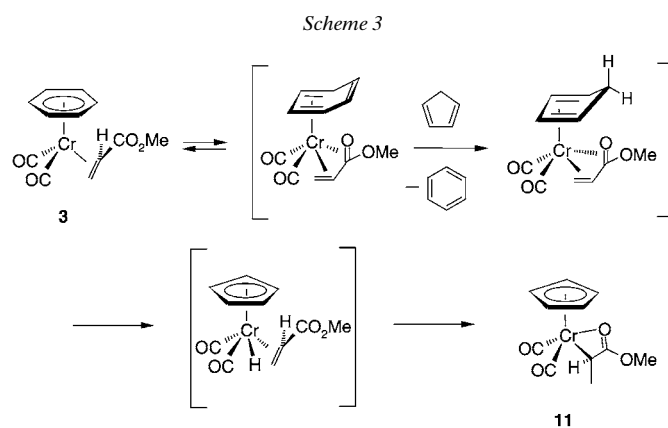
As reported previously, the red-orange η^2 -acrylate complex **3** readily undergoes arene exchange at 25° [8]. Arene-exchange reactions are feasible also with **4** but they are slower than with **3**. In contrast, the hexamethylbenzene complex **5** is inert under these conditions. The reaction of **4** with 1*H*-indene is different in that it does not afford the corresponding $[\text{Cr}(\eta^2\text{-methyl acrylate})(\eta^6\text{-1*H*-indene})(\text{CO})_3]$ complex but a new, deep violet complex. Spectral characteristics and a crystal-structure determination (see below) identify this complex as the ($\eta^5\text{-1*H*-inden-1-yl}$)chromium enolate **8**. The results of reactions of **3** and **4** with 1*H*-indene, 1-methyl-1*H*-indene, and cyclopentadienes are shown in Scheme 2.

The 1-methyl-1*H*-indene afforded a 1:1 mixture of the diastereoisomeric complexes **9** and **10**. The lower yields of isolated cyclopentadienyl complexes **11–13** compared to those of the indenyl complexes **7–10** reflect the high reactivity of the former and the resulting difficulty in their isolation. A reasonable reaction sequence for the formation of cyclopentadienylchromium and indenylchromium enolate complexes involves $\eta^6 \rightarrow \eta^4$ slippage of the arene induced by a haptotropic rearrangement ($\eta^2 \rightarrow \eta^4$) of the acrylate ligand. Substitution of the η^4 -arene by cyclopenta-1,3-diene (or 1*H*-indene) is followed by H-migration from the cyclopenta-1,3-diene (or 1*H*-indene) to the terminal C-atom of the acrylate to give the enolate complex (Scheme 3). Presumably, this H-migration involves first an oxidative addition of the metal into



the endo C–H bond of the coordinated cyclopentadiene followed by an insertion of the acrylate into the Cr–H bond. The metal thus passes from Cr⁰ to Cr^{II} in this process. The coordination of the carbonyl function to the metal in **7–13** results in a stable 18e[−] configuration at the metal.

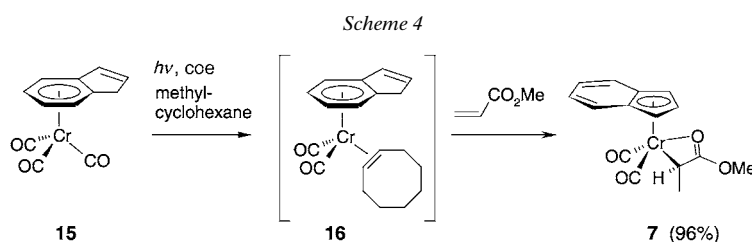
There is much literature precedent for intramolecular H-transfer in organometallic chemistry (for examples, see [14]), including examples involving coordinated acrylates [15]. Intermolecular nucleophilic addition to Fe-coordinated acrylates has also been reported [16]. Arene substitution in [Mo(toluene)(CO)₃] by cyclopenta-1,3-diene to give [Mo(Cp)H(CO)₃] occurs under mild conditions [17], but the much more-robust arene–metal bond in [Cr(benzene)(CO)₃] (**1**) prevents this exchange. The hydrido-



chromium complex $[\text{Cr}(\text{Cp})\text{H}(\text{CO})_3]$ is, however, readily formed on treating the labile complex $[\text{Cr}(\text{naphthalene})(\text{CO})_3]$ with cyclopenta-1,3-diene [18].

The closest literature analog to **7–13** is the W complex **14**. It was reported by *Bergman and Heathcock* and was obtained *via* a different route [19]. The Cr analog was not investigated in their study because it was deemed to be too unstable to isolate. In the $^1\text{H-NMR}$ spectrum, the η^3 -oxaallyl complex **7** exhibits a q at $\delta -0.49$ for the proton at the C-atom bound to the metal center. Similar shifts are reported for complex **14**. This region of the NMR spectrum is normally associated with sp^3 metal-bound C-atoms, *e.g.*, $[\text{Cr}(\text{Cp})(\text{CH}_2\text{CO}_2\text{Me})(\text{CO})_3]$ shows a δ of 1.75 for the methylene protons [20]. The related iron and chromium complexes $[\text{Fe}(\text{Cp})(\text{CH}_3)(\text{CO})_2]$ and $[\text{Cr}(\text{Cp})(\text{CH}_3)(\text{CO})_3]$ show a δ of 0.33 [21] and 0.68 [22], respectively. In the $^{13}\text{C-NMR}$ spectrum of **7**, the carbonyl resonance is shifted by 25 ppm (δ 152.2) in comparison with the parent acrylate complex (δ 177.2). For the tungsten analogue **14**, a δ of 163.2 is reported, and the carbonyl function is clearly coordinated to the metal center [19]. A parallel can also be drawn to Li enolates, where similar NMR shifts for the carbonyl C-atom in the case of lithium cycloalkancarboxylates are found [23]. The $\bar{\nu}$ (CO) IR bands reported for **7** (1960, 1892 cm^{-1}) are higher in energy than for **14** (1926, 1826 cm^{-1}). We attribute this to the difference in electron-donating properties of the amide *vs.* the ester function. While a metallacycle has also been initially invoked for **14**, the bonding mode of the crystal structure agrees with a formulation as a η^3 -oxaallyl complex, and for **7–13** we follow this nomenclature.

The reaction sequence leading to complexes **7–10** as described above required the isolation of the labile methyl acrylate complexes **3** and **4**. A shorter route of access was sought and found *via* haptotropic rearrangement in the $1H$ -indene complex **15**. Intramolecular η^6/η^5 rearrangements [24] in $1H$ -indene complexes has been extensively investigated by the groups of *Nesmeyanov* [25], *Ustynyuk* [26], *Ceccon* [27], and *McGlinchey* [28]. Taking the cue from their findings, a solution of the cyclooctene complex **16** was prepared by photolysis of $[\text{Cr}(\eta^6-1H\text{-indene})(\text{CO})_3]$ (**15**) in methylcyclohexane/cyclooctene [10a]. Progress was monitored by IR-spectral analysis of samples taken during the reaction. They show the disappearance of the carbonyl bands of **15** at 1972 and 1904 cm^{-1} and the concomitant growth of bands at 1908 and 1859 cm^{-1} assigned to **16**. Addition of methyl acrylate then afforded **7** in high yield in a sequence of reactions involving alkene exchange, acrylate-induced haptotropic rearrangement, and H-shift from $1H$ -indene to the terminal C-atom of the methyl acrylate ligand (*Scheme 4*). Again, other α,β -unsaturated carbonyl compounds (methyl vinyl ketone, *N,N*-dimethylacrylamide, methyl crotonate, methyl methacrylate) failed to give isolable complexes.



Suitable crystals for X-ray analysis of complex **8** were obtained from toluene/hexane at -40° (Fig. 2). For a discussion of the structural features of **8**, a comparison with reported structures was undertaken. Examples of Cr, Mo, and W complexes were selected (see **14** (Scheme 2) and **17–20**) and different parameters compared to find general trends in this family of compounds. The ring slippage was analyzed taking different parameters as reference. Several methods have been suggested for describing the ring slippage in π -arene complexes [20a][29][30]. *Faller*, *Crabtree*, and *Habib* used parameters to describe the distortions arising in 1*H*-inden-1-yl complexes, and we adopted the same definitions of S , Δ , σ , Ω , and ψ (Fig. 3) [31a]. All compounds show

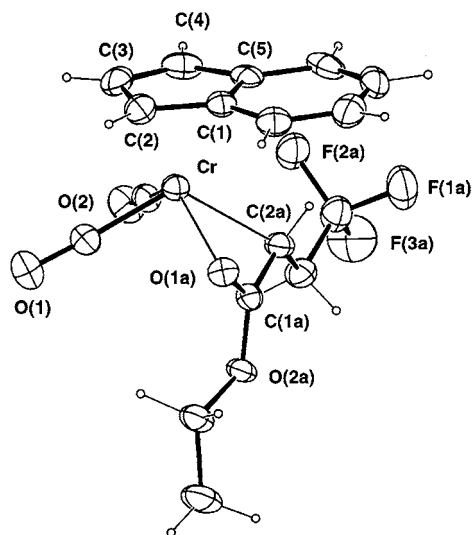


Fig. 2. ORTEP View of the $[Cr(\eta^5\text{-}1H\text{-inden-}1\text{-yl})\{\text{endo}'\text{-}\{3,3,3\text{-trifluoro-}1\text{-[ethoxy(carbonyl-}\kappa\text{O})\text{]propyl-}\kappa\text{C}}\}(CO)_2]$ complex (**8**). Ellipsoids are represented with 40% probability level. Arbitrary numbering. Selected bond distances [Å]: Cr–C(1) 2.336(6), Cr–C(2) 2.177(6), Cr–C(3) 2.156(5), Cr–C(4) 2.186(6), Cr–C(5) 2.347(6), Cr–C(1a) 2.316(4), Cr–C(2a) 2.236(5), and Cr–O(1a) 2.111(3).

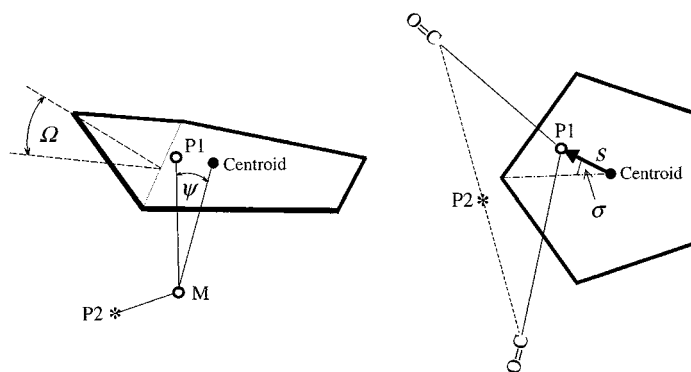
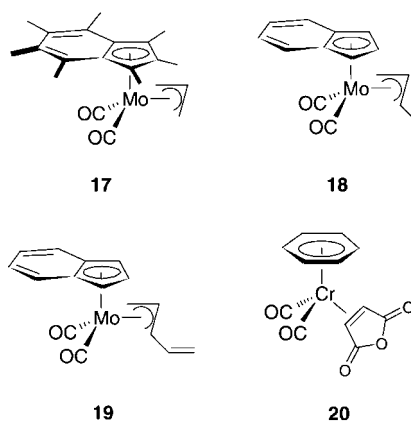


Fig. 3. Deformation and slip parameters in π -arene complexes

slip vectors \mathbf{S} (of length Δ) in the opposite direction of the allyl (or oxaallyl) ligand and more or less bisecting the OC–M–CO angle. For our purpose, it seems advantageous to describe a new descriptor τ as the torsional angle P1–centroid–M–P2 (where P1 is the end-point of the \mathbf{S} vector and P2 the mid-point between the C-atoms of the two M-bound CO ligands). This parameter is more appropriate than the σ angle to describe the difference in the slippage of these complexes, and it allows us to quantify the amplitude and the direction (through the sign of the torsional angle) of the distortion relative to an ideal situation where $\tau = 0$. Deformation and slip parameters are shown in *Table 1*.

The [Mo(η -1*H*-inden-1-yl)(π -allyl)(CO)₂] complexes **17**–**19** and analogous compounds presented in *Table 1* all show a slip distortion of the metal atom away from the allyl ligand. The degree of ring slippage depends on the nature of the ligand and follows the order: 1*H*-inden-1-yl > Cp > aryl. The values of τ range *ca.* from -7 to $+15^\circ$, with the exception of **6** where $\tau = 43.7^\circ$. This distortion can be attributed to the presence of the two vicinal Me substituents of the *o*-xylene and has also been observed in [Cr(η^6 -*o*-xylene)(CO)₃] [32]. The symmetrically substituted arene complexes **5**, **17**, and **20** exhibit much smaller distortions.



Another influence on the deviation of τ from its ideal value (0°) is the location of the side extension of the allyl (or oxaallyl) or alkene ligands. In other words, the intramolecular crowding due to the allyl or alkene substitution leads to a rotation of the \mathbf{S} vector in the opposite direction. This tendency is clearly illustrated in *Figs. 4* and *5* for **5** and **8** where τ is positive whereas τ is negative for **18** and **19**.

The relative orientations between the arene and the allyl ligands are clearly differentiated between the η^3 -allyls ($\phi \approx 30^\circ$), η^2 -acrylates ($\phi \approx 70^\circ$), and η^3 -oxaallyls ($\phi \approx 90^\circ$). The major variation can be attributed to the different binding mode of these ligands.

The 1*H*-inden-1-yl complexes like **8** show a ‘*trans*’ conformation of the carbonyls to the six-membered ring, as do also all [Mo(allyl)(1*H*-inden-1-yl)(CO)₂] complexes.

Table 1. Deformation and Slip Parameters for 1H-Inden-1-yl, Cyclopenta-2,4-dien-1-yl, and Arene Complexes of Allyl and Oxaallyl Derivatives

	M	M–arene[Å]	M–allyl[Å]	ϕ [°] ^{a)}	Δ [Å] ^{b)}	σ [°]	ψ [°]	τ [°]	Ω [°]	Ref.
[Cr(η^6 -hexamethylbenzene)(CO) ₂ (<i>exo</i> '- η^2 -methyl acrylate)] (5)	Cr	1.776(1)	1.991(7)	67.5(6)	0.044	–	1.4	6.1	–	^{c)}
[Cr(η^6 - <i>o</i> -xylene)(CO) ₂ (<i>exo</i> '- η^2 -methyl acrylate)] (6) ^{c)}	Cr	1.751(1)	2.010(3)	70.3(3)	0.038	–	1.3	43.7	–	^{c)}
[Cr(η^6 -mesitylene)(CO) ₂ (<i>exo</i> '- η^2 -maleic anhydride)] (20) ^{c)}	Cr	1.778	1.957	71.1	0.050	–	1.6	11.1	–	[42]
[W(η^5 -cyclopenta-2,4-dien-1-yl)- { <i>endo</i> '-[2-(diethylamino)-2-(oxo- κ O)ethyl- κ C]}(CO) ₂] (14)	W	2.005	1.449	84.8	0.148	15.2	4.2	14.4	2.0	[19]
[Cr(η^5 -1 <i>H</i> -inden-1-yl){ <i>endo</i> '-[3,3,3-trifluoro-1-[ethoxy(carbonyl- κ O)]propyl- κ C]}(CO) ₂] (8) ^{d)}	Cr	1.879(1)	1.423(11)	90.0(5)	0.207	5.5	6.3	14.3	5.8(5)	^{c)}
[Mo(η^5 -heptamethyl-1 <i>H</i> -inden-1-yl)(<i>exo</i> '- η^3 -allyl)(CO) ₂] (17)	Mo	2.027	1.931	30.3	0.129	3.9	3.7	1.4	3.0	[43]
[Mo(η^5 -1 <i>H</i> -inden-1-yl)(<i>exo</i> '- η^3 -crotyl)(CO) ₂] (18)	Mo	2.046	2.004	32.9	0.145	6.3	4.0	–6.7	3.0	[32a]
[Mo(η^5 -1 <i>H</i> -inden-1-yl)(<i>exo</i> '- η^3 -penta-2,4-dienyl)(CO) ₃] (19)	Mo	2.037	2.001	33.6	0.143	14.8	4.0	–6.1	3.6	[44]

^{a)} Dihedral angle between the mean planes of the arene and the allyl moieties. ^{b)} $\Delta = |\mathcal{S}|$. ^{c)} This work. ^{d)} The arene ring shows a folding of 5.7[°] (away from the Cr-atom) between the mean planes passing through C(6), C(1), C(2), C(3) and C(3), C(4), C(5), C(6) (see Fig. 1 for numbering). ^{e)} Not deposited at the CCDC; the atomic coordinate of the O(4) atom reported in [37] was erroneous and has been recalculated.

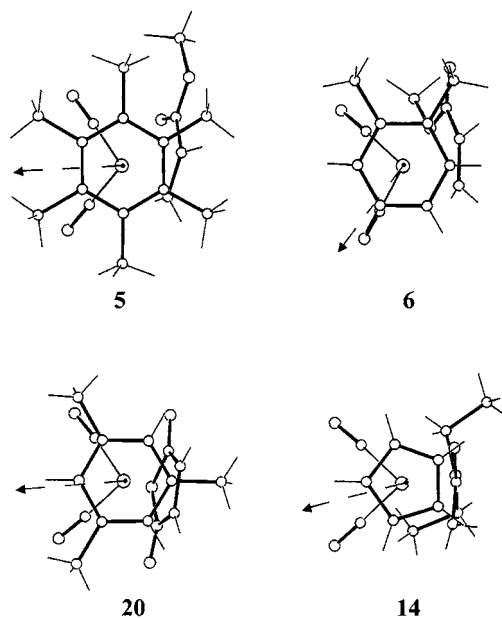


Fig. 4. Perspective views along the normal to the plane of the five- or six-membered rings for the $[M(\eta\text{-allyl})(\eta\text{-arene})(CO)_2]$ reported in Table 1 showing the centroid (black dot ●) and the direction (dotted arrow) of the slip vector **S**

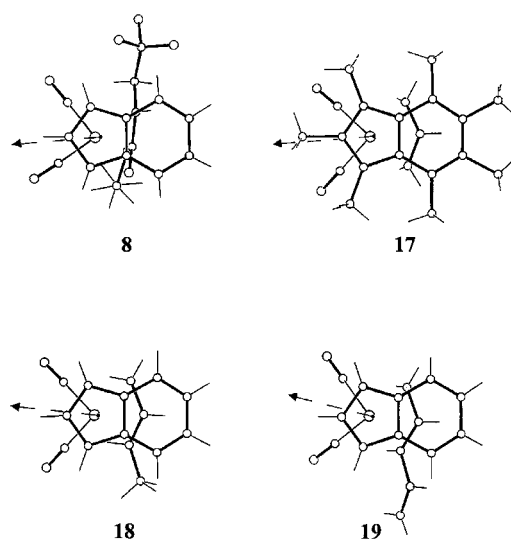


Fig. 5. Perspective views along the normal to the plane of the five-membered rings for the $[M(\eta^5\text{-1H-inden-1-yl})(\eta\text{-allyl})(CO)_2]$ reported in Table 1 showing the centroid (black dot ●) and the direction (dotted arrow) of the slip vector **S**

Complex **8** exhibits some $\eta^5 \rightarrow \eta^3$ ring slippage with $\Delta = 0.207 \text{ \AA}$ and $\Omega = 5.8^\circ$. However, complexes are considered η^5 as long as $\Delta < 0.25 \text{ \AA}$ and $\Omega < 10^\circ$ [32]. Complexes that are considered to be η^3 show Δ in the range of 0.69 to 0.80 \AA and Ω between 20° to 30° [33]. Complex **8** has to be considered η^5 with a Δ value close to the upper limit. A possible explanation for the difference observed between allyl and oxaallyl is based on the σ -donor and π -acceptor properties of the ligands. The good σ -donor oxaallyl, is believed to favor the η^3 -coordination by its ability to increase electron density at the metal center. On the other hand, a good π -acceptor ligand should favor the η^5 -coordination mode [34]. Finally the slippage of the 1*H*-inden-1-yl ligand is still present in solution and can be evaluated by comparison of the chemical shift in the ^{13}C -NMR spectrum of C(1) and C(5) in the complex (see *Fig. 2* for numbering) and in the (1*H*-inden-1-yl)sodium salt. The differences of the chemical-shift values for complex **8** are -16.5 and -13.5 ppm, respectively, with a δ 130.7 for the corresponding C-atoms of (1*H*-inden-1-yl)sodium. Values between -10 and -20 ppm are representative of an 1*H*-inden-1-yl with a partial slippage. A difference of $+5$ to $+30$ ppm would be needed to assign a η^3 -coordination to the indenyl ligand [35] (for a detailed analysis of the indenyl effect, see [36]).

Finally, all crystal structures where the H-atoms of the alkene, allyl, or oxaallyl moieties have been observed (**14** and **17**) or refined (**5**, **6**, and **8**) show important out-of-plane deviations of the H-atoms, away from the metal. On coordination to a metal center, the C-atoms of these ligands are expected to have pyramidalization due to some sp^3 character.

X-Ray Crystal Structures. – A summary of crystal data, intensity measurement, and structure refinement for **5**, **6**, and **8** is reported in *Table 2*¹⁾.

Cell dimension and intensities were measured at 200 K. Data were corrected for *Lorentz* and polarization effects and for absorption. The crystal structures were solved by direct methods using *Sir-97* [37]. All calculations were performed with *XTAL* system [38] and *ORTEP* [39] programs. All H-atoms were observed and refined with a fixed value of their isotropic displacement parameters. For complex **6**, H-atoms of the Me groups were refined with restraints on bond lengths and bond angles and blocked in the last cycles.

Depending on the conditions of crystallization, the racemic complex **5** underwent spontaneous resolution leading to crystals with a chiral crystal structure in space group $P2_12_12_1$. Moreover, all crystals were twinned by a rotation of *ca.* 4.5° around the [011] direction. A preliminary data collection on a twinned crystal allowed us to separate and integrate the diffracted intensities for both components of the twin [40]. After resolution and refinement of the structure, the *Flack* parameter [41] clearly showed that both components of the twin were of the same chirality. Circular-dichroism measurements with four distinct twinned crystals chosen at random showed classical spectra for (arene)chromium complexes, two of them displayed, however, opposite *Cotton* effects from the others. The final data collection was carried out on a previously oriented and

¹⁾ CCDC-220686, -220687, and -220688 contain supplementary crystallographic data for **5**, **6**, and **8**, respectively. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)).

Table 2. Crystal Data, Intensity Measurement, and Structure Refinement for **5**, **6**, and **8**

	5	6	8
Formula	C ₁₈ H ₂₄ CrO ₄	C ₁₄ H ₁₆ CrO ₄	C ₁₇ H ₁₅ CrF ₃ O ₄
<i>M_r</i>	356.4	300.3	392.3
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	8.8789(4)	12.7036(11)	9.8210(8)
<i>b</i> [Å]	12.9626(8)	7.2159(4)	9.9971(9)
<i>c</i> [Å]	14.7439(7)	15.1360(13)	10.3915(9)
α [°]	90	90	115.157(4)
β [°]	90	105.235(10)	97.760(5)
γ [°]	90	90	108.120(5)
<i>V</i> [Å ³]	1696.9(2)	1338.7(2)	834.3(1)
<i>Z</i>	4	4	2
<i>D_{calc}</i> [g · cm ⁻³]	1.395	1.490	1.562
Crystal size [mm]	0.05 × 0.14 × 0.25	0.06 × 0.10 × 0.30	0.18 × 0.33 × 0.50
Crystal color	red	red	dark violet
Radiation	Mo <i>K</i> α	Mo <i>K</i> α	Cu <i>K</i> α
μ [mm ⁻¹]	0.69	0.86	6.13
<i>T_{min}</i> , <i>T_{max}</i>	0.8598, 0.9671	0.8072, 0.9519	0.1698, 0.3872
((sin θ)/ λ) _{max} [Å ⁻¹]	0.616	0.616	0.531
Diffractionmeter	<i>Stoe-IPDS</i>	<i>Stoe-IPDS</i>	<i>Stoe-STADI4</i>
Scan type	ϕ	ϕ	$\omega/2\theta$
No. measured refl.	21402	13443	2170
No. independent refl.	3323	2605	2029
No. observed refl.	2361	1824	1833
Criterion for observed $ F_o > 4\sigma(F_o)$	$ F_o > 4\sigma(F_o)$	$ F_o > 4\sigma(F_o)$	
Refinement (on <i>F</i>)	full-matrix	full-matrix	full-matrix
No. parameters	218	193	272
Max. and $\Delta\rho$ [e · Å ⁻³]	0.28, -0.37	0.42, -0.26	0.46, -0.68
Flack parameter [41]	-0.02(3)	-	-
<i>R</i> , ωR	0.034, 0.035	0.029, 0.030	0.043, 0.046

cut crystal to obtain a mono-domain (non-twinned) sample for the diffraction measurement.

It should be noted that another crystallization batch from the same solvent mixture showed that crystals exhibited pairs of domain structures twinned by inversion in different ratios (one enantiomer predominant over the other). Thus, data collections from two different crystals and subsequent refinements showed *Flack* parameters of 0.36(4) (e.e. 28(8)%) and 0.90(3) (e.e. -80(6)%). The CD spectra, normalized to equal crystal volume, of solutions from the two crystals used for the X-ray-diffraction analysis are reported in *Fig. 6*. These indeed show that the spectra of the solution from the first crystal is weaker and in form of the mirror image of that from the second crystal. The agreement between the ratio of the e.e. from X-ray diffraction (-0.35(10)) and the ratio of the normalized peak height at 350 nm of the CD spectra (-0.42) could be considered as very good. Thus, the positive and negative *Cotton* effects at 350 nm are attributed to the (*S*)- and (*R*)-absolute configuration, respectively.

Conclusions. – When coordinated as η^2 -alkene, methyl acrylate labilizes coligands by temporary rearrangement to a η^4 -coordination mode. Arene displacement by

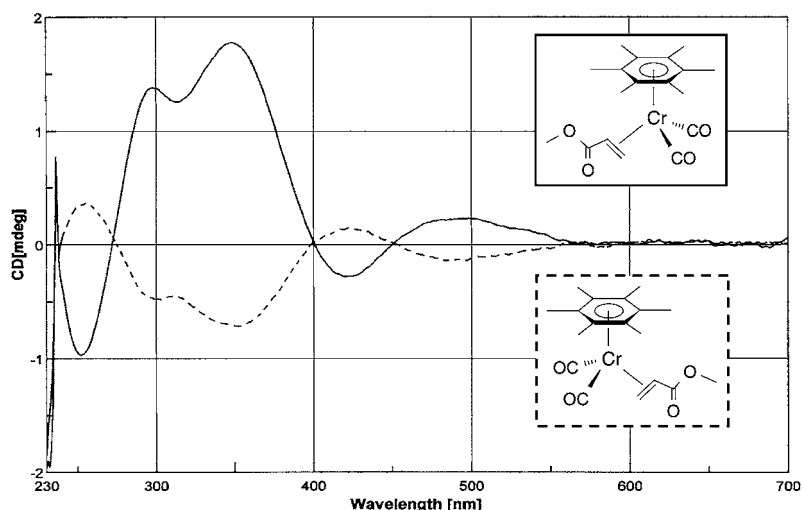


Fig. 6. CD Spectra of solutions from the two crystals of **5** exhibiting pairs of domain structures twinned by inversion in different ratios (see text). The solid-line spectrum corresponds to a solution of the crystal determined to be of 80% e.e. ((*S*)-configuration); (*S*) refers to the absolute configuration of C(α) of the acrylate ligand. The dotted line corresponds to a solution of a crystal determined to be of 36% e.e. ((*R*)-configuration, see also Fig. 1).

cyclopenta-1,3-diene or 1*H*-indene is followed by H-migration to the acrylate. With 1*H*-indene, this can also be achieved in an intramolecular reaction. Spectroscopic and structural data on the new enolate complexes were obtained and compared to analogous known complexes. We note that both the acrylate intermediate and the enolate complexes are chiral, and it is of interest to note that partial resolution of racemic **5** occurred on crystallization and that the combination of X-ray analysis and CD spectra of the measured crystals allow the assignment of the absolute configuration. Studies aimed at the synthesis of nonracemic complexes and the delineation of the reactivity of the enolate complexes are in progress.

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Experimental Part

General. THF and Et₂O were dried and distilled from Na/benzophenone ketyl (diphenylmethanone radical ion(1-)) under N₂ before use. CH₂Cl₂ and hexane were freshly distilled from CaH₂ under N₂. All chemicals were purchased from Aldrich or Fluka. Reactions and manipulations involving organometallic compounds were carried out under purified N₂ by using an inert gas/vacuum double manifold and standard Schlenk techniques. M.p.: Büchi 510 apparatus; not corrected. CD Spectra: Jasco J-700; quartz cell. IR Spectra: NaCl cells; Perkin-Elmer 1650-FT-IR spectrometer. NMR Spectra: ¹H at 200, 300, or 400 MHz; ¹³C at 50.3, 75.5, or 100.5 MHz; at r.t.; Varian XL-200, Bruker 300-MHz, or Bruker 400-MHz spectrometers; chemical shifts δ rel. to SiMe₄; *J* in Hz. MS: Varian CH4 or SMI spectrometers; in *m/z* (%). High-resolution (HR) MS: anal. VG 7070E instrument (data system 11250, resolution 7000). Elemental analyses: H. Eder, Section de Pharmacie, Université de Genève. Many compounds lacked stability for elemental analysis, while errors of others were above the admitted limits of accuracy, a common occurrence with F-containing compounds.

(η^6 -Benzene)dicarbonyl[η^2 -ethyl (2E)-4,4,4-trifluorobut-2-enoate]chromium (**4**). A soln. of [Cr(η^6 -benzene)(η^2 -cis-cyclooctene)(CO)₂] was prepared by photolysis (Philips, HPK 125) of [Cr(benzene)(CO)₃] (**1**; 0.642 g, 3 mmol) in benzene (200 ml) and cyclooctene (16 ml) [10b]. After completion of the irradiation, the soln. was transferred under N₂ from the photoreactor into a Schlenk tube, and ethyl (2E)-4,4,4-trifluorobut-2-enoate (0.504 g, 0.450 ml, 3 mmol) was added dropwise. After 16 h stirring at r.t., the mixture was filtered through *Celite*, and the filtrate was evaporated. The residue was taken up in hexane/benzene 20:1 and recrystallized at –40°: 0.783 g (83%) of **4**. Red-orange crystals. M.p. 77–78° (dec.). IR (hexane): 1967, 1919, 1702. ¹H-NMR (C₆D₆, 200 MHz): 4.51 (s, 6 H); 4.05 (m, 2 H); 3.65 (m, 1 H); 2.79 (d, *J* = 10.1, 1 H); 1.07 (t, *J* = 7.2, 3 H). ¹³C-NMR (C₆D₆, 50 MHz): 244.6; 241.1; 176.3; 130.5 (*q*, *J* = 265, CF₃); 98.9; 60.3; 48.8 (*q*, *J* = 34); 39.9; 14.6. ¹⁹F-NMR (376 MHz, C₆D₆): 107.57 (d, *J* = 7.2). MS: 298 (2, [M – 2CO]⁺), 220(3), 158(2), 130(11), 123(50), 78(100), 52(26). Anal. calc. for C₁₄H₁₃CrF₃O₄ (354.24): C 47.47, H 3.70; found: C 47.29, H 3.74.

Dicarbonyl(η^6 -hexamethylbenzene)(η^2 -methyl prop-2-enoate)chromium (**5**). As described for **4**, with [Cr(hexamethylbenzene)(CO)₃] (**2**; 1.068 g, 3.6 mmol) and, after formation of [Cr(η^6 -hexamethylbenzene)(η^2 -cis-cyclooctene)(CO)₂], with methyl prop-2-enoate (0.310 g, 3.6 mmol): 0.942 g (74%) of **5**. Red-orange solid. M.p. 162–164° (dec.). IR (hexane): 1918, 1965, 1703. ¹H-NMR (200 MHz, C₆D₆): 3.64 (s, 3 H); 2.63 (dd, *J*_{trans} = 10.9, *J*_{gem} = 2.2, 1 H); 2.08 (dd, *J*_{trans} = 10.9, *J*_{cis} = 8.2, 1 H); 1.64 (s, 3 H); 1.57 (dd, *J*_{cis} = 8.2, *J*_{gem} = 2.2, 1 H). ¹³C-NMR (50 MHz, C₆D₆): 247.3; 177.8; 107.7; 50.3; 43.9; 43.4; 16.1. MS: 356 (1, M⁺), 300(2), 270(0.5), 242(3), 217(19), 162(88), 52(11). HR-MS: 356.1035 (M⁺, C₁₈H₂₃CrO₄; calc. 356.1080).

Dicarbonyl(η^6 -1,2-dimethylbenzene)(η^2 -methyl prop-2-enoate)chromium (**6**). A soln. of **3** (0.109 g, 0.40 mmol) in 1,2-dimethylbenzene (2 ml, 17 mmol) was stirred for 5 h, then filtered over *Celite*, concentrated to 0.5 ml, and treated with hexane (5 ml). Cooling to –30° afforded 0.86 g (72%) of **6**. Red-orange solid. M.p. 61–62°. IR (benzene): 1925, 1869, 1698. ¹H-NMR (C₆D₆, 200 MHz): 4.39 (m, 3 H); 4.28 (m, 1 H); 3.60 (s, 3 H); 2.82 (dd, *J*_{trans} = 11.1, *J*_{cis} = 7.6, 1 H); 2.69 (d, *J*_{trans} = 11.1, 1 H); 2.25 (d, *J*_{cis} = 7.6, 1 H); 1.60 (s, 3 H); 1.58 (s, 3 H). ¹³C-NMR (50 MHz, C₆D₆): 246.4; 245.7; 177.4; 108.4; 98.7; 97.8; 96.5; 96.4; 50.7; 41.7; 39.1; 18.2; 18.1. MS: 300 (0.4, M⁺), 244(1), 214(0.5), 186(1), 158(9), 106(68), 52(18).

Dicarbonyl[(1,2,3,3a,7a- η)-1H-inden-1-yl][2-methoxy-1-methyl-2-(oxo- κ O)ethyl- κ C]chromium (**7**). From **3**: An orange soln. of [Cr(η^6 -benzene)(η^2 -methyl acrylate) (CO)₂] (**3**; 0.327 g, 1.2 mmol) and freshly distilled 1H-indene (0.278 g, 2.4 mmol) in Et₂O (20 ml) was stirred at r.t. for 5 h under N₂. The mixture was evaporated and the crude product recrystallized from hexane at –78°. The product was kept under N₂ at –30°: 0.298 g (80%) of **7**. Violet crystals.

From **15**: A soln. of [Cr(1H-indene)(CO)₃] [45] (**15**; 276 mg, 1.090 mmol) in methylcyclohexane (150 ml) and cyclooctene (20 ml) in a Pyrex photoreactor was irradiated for 30 min with a high-pressure Hg arc (150 W). Agitation and CO removal was realized by passing a slow stream of N₂ through the soln. After filtration over *Celite* under N₂, the soln. was cooled to 0°, and methyl prop-2-enoate (2.5 equiv.) was added to the soln. of the cyclooctene complex at 0°. The mixture was warmed to r.t. overnight, filtered through *Celite*, and the filtrate evaporated. Recrystallization from hexane at –78° afforded 338 mg (96%) of **7**. Violet solid. M.p. 132° (dec.). IR (hexane): 1960s, 1892s. ¹H-NMR (C₆D₆, 200 MHz): 7.10–6.84 (m, 1 H); 6.80–6.74 (m, 1 H); 6.72–6.60 (m, 3 H); 4.52–4.40 (m, 2 H); 2.97 (s, 3 H); 2.13 (d, *J* = 5.6, 3 H); –0.49 (*q*, *J* = 5.6, 1 H). ¹³C-NMR (C₆D₆, 100 MHz): 260.1; 259.1; 152.2; 127.5; 127.3; 125.7; 124.8; 117.5; 113.3; 91.3; 84.2; 76.2; 53.9; 50.6; 13.5. MS: 282(3), 230(8), 167(8), 142(6), 115(100), 89(15), 63(15), 52(40).

Dicarbonyl[(1,2,3,3a,7a- η)-1H-inden-1-yl][3,3,3-trifluoro-1-[ethoxy(carbonyl- κ O)]propyl- κ C]chromium (**8**). As described for **7** from **3**, with [Cr(η^6 -benzene)(η^2 -ethyl (2E)-4,4,4-trifluorobut-2-enoate (CO)₂] (**4**; 0.106 g, 0.300 mmol) and 1H-indene (0.070 g, 0.600 mmol, 0.070 ml): 0.107 g (91%) of **8**. Violet crystals. M.p. 65° (dec.). IR (hexane): 1964s, 1898s. ¹H-NMR (C₆D₆, 200 MHz): 6.95–6.88 (m, 1 H); 6.79–6.72 (m, 1 H); 6.70–6.63 (m, 3 H); 4.50–4.60 (m, 1 H); 4.27–4.19 (m, 1 H); 3.72–3.57 (m, 1 H); 3.15–3.40 (m, 3 H); 0.66 (t, *J* = 7.1, 3 H); –0.56 (t, *J* = 6.4, 1 H). ¹³C-NMR (C₆D₆, 50 MHz): 260.4; 259.8; 153.1; 127.5 (*q*, *J* = 276, CF₃); 125.9; 117.2; 114.2; 90.9; 84.1; 77.0; 60.5; 47.6; 33.7; 14.1. ¹⁹F-NMR (C₆D₆, 376 MHz): 97.88 (t, *J* = 10.9). MS: 336(3), 212 (24), 168(20), 125(97), 124(38), 116(100), 115(98), 55(33), 52(14), 45(27). Anal. calc. for C₁₇H₁₅CrF₃O₄: C 52.05, H 3.85; found: C 51.60, H 3.89.

Dicarbonyl(η^5 -cyclopenta-2,4-dien-1-yl)[2-methoxy-1-methyl-2-(oxo- κ O)ethyl- κ C]chromium (**11**). A soln. of **3** (0.109 g, 0.4 mmol) in freshly distilled cyclopenta-1,3-diene (2 ml, 24 mmol) was stirred at r.t. for 5 h under N₂. The mixture was evaporated and the crude product recrystallized from hexane at –78°. The product was kept under N₂ at –30°: 0.065 g (63%) of **11**. Violet-red crystals. M.p. 100° (dec.). IR (hexane): 1964s, 1894s. ¹H-NMR (C₆D₆, 200 MHz): 4.44 (s, 5 H); 3.31 (*q*, *J* = 5.9, 1 H); 3.10 (s, 3 H); 2.18 (d, *J* = 5.9, 3 H). ¹³C-NMR (C₆D₆, 100 MHz): 261.6; 258.5; 151.4; 93.5; 50.6; 39.9; 14.3. MS: 260(1), 232(2), 204(12), 182(45), 148(75), 117(51), 88(30), 57(100), 52(83). HR-MS: 260.0171 (M⁺, C₁₁H₁₂CrO₄; calc. 260.0141).

Dicarbonyl[2-methoxy-1-methyl-2-(oxo-κO)ethyl-κC](η⁵-1-methylcyclopenta-2,4-dien-1-yl)chromium (12). A soln. of **3** (0.109 g, 0.4 mmol) in freshly distilled MeCp (2 ml, 18 mmol) was submitted to two freeze-pump-thaw cycles. The orange soln. was stirred at r.t. for 5 h under N₂. The mixture was evaporated and the red crude product recrystallized from hexane at –78°. The product was kept under N₂ at –30°: 0.077 g (68%) of **12**. Red crystals. IR (hexane): 1966s, 1890s. ¹H-NMR (C₆D₆, 200 MHz): 5.00–4.90 (*m*, 1 H); 4.30–4.23 (*m*, 2 H); 3.95–3.85 (*m*, 1 H); 3.15 (*s*, 3 H); 3.02 (*q*, *J* = 6.4, 1 H); 2.17 (*d*, *J* = 6.4, 3 H); 1.41 (*s*, 3 H). ¹³C-NMR (C₆D₆, 50 MHz): 151.8; 115.8; 92.4; 92.3; 88.5; 88.1; 50.1; 39.8; 14.2; 1.5.

Dicarbonyl[2-methoxy-1-methyl-2-(oxo-κO)ethyl-κC]((1,2,3,3a,7a-η)-1-methyl-1H-inden-1-yl)chromium (9/10). A soln. of **3** (0.109 g, 0.4 mmol) in freshly distilled 1-methyl-1H-indene (2 ml, 15 mmol) was submitted to two freeze-pump-thaw cycles. The orange soln. was then stirred at r.t. for 5 h under N₂. The mixture was evaporated and the crude product recrystallized from hexane at –78°. The product was stored at –30° under N₂: 0.098 g (76%) of **9/10** 1:1 (by ¹H-NMR). Violet crystals. IR (hexane): 1956s, 1887s. ¹H-NMR (C₆D₆, 200 MHz): 7.10–6.90 (*m*, 1 H); 6.90–6.83 (*m*, 1 H); 6.80–6.55 (*m*, 3 H); 4.85–4.70 (*m*, 1 H); 4.40–4.30 (*m*, 1 H); 4.30–4.20 (*m*, 2 H); 2.98 (*s*, 3 H); 2.11 (*d*, 3 H); 2.07 (*d*, 3 H); –0.42 (*q*, 1 H); –0.79 (*q*, 1 H). ¹³C-NMR (C₆D₆, 75.5 MHz): 216.7; 152.8; 152.1; 128.9; 127.6; 127.2; 127.1; 126.6; 126.4; 125.3; 125.0; 119.4; 118.7; 118.1; 117.0; 114.6; 112.5; 93.9; 92.9; 92.5; 92.2; 54.2; 52.9; 50.8; 42.7; 30.9; 30.7; 13.7; 13.2.

Dicarbonyl[2-methoxy-1-methyl-2-(oxo-κO)ethyl-κC](η⁵-pentamethylcyclopenta-2,4-dien-1-yl)chromium (13). An orange soln. of **3** (0.109 g, 0.4 mmol) and 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (0.108 g, 0.4 mmol, 0.13 ml) in Et₂O (20 ml) was stirred at r.t. for 5 h under N₂. The mixture was evaporated and the crude product recrystallized from hexane at –78°. The product was kept under an N₂ at –30°: 0.062 g (47%) of **13**. Violet solid. M.p. 78–80°. IR (hexane): 1944s, 1874s. ¹H-NMR (C₆D₆, 200 MHz): 3.20 (*s*, 3 H); 2.16 (*d*, *J* = 6.3, 3 H); 1.50 (*s*, 15 H). ¹³C-NMR (C₆D₆, 100 MHz): 262.4; 260.4; 152.2; 103.7; 50.6; 46.4; 13.9; 9.7. MS: 330(1), 274(9), 218(100), 186(24), 134(7), 119(11), 88(4), 57(17), 52(14). HR-MS: 330.0934 (*M*⁺, C₁₆H₂₂CrO₄⁺; calc. 330.0923).

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