General Synthesis of Cyclopentadienylchromium(II) η^3-Allyl Dicarbonyl Complexes

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Thermally stable chromium(II) dicarbonyl complexes bearing substituted η^3-allyl and η^5-cyclopentadienyl ligands have been prepared via oxidative addition of the allyl bromide to tris(acetonitrile)tricarbonylchromium at −30 °C in acetonitrile, followed by in situ addition of the ancillary cyclopentadienyl ligand anion at low temperature. Spectroscopic data for allyl complexes **1**, **2**, and **4**−**7** indicate that the solution configuration of the allyl ligand is preferentially exo, while the data for the 2-methylallyl derivative **3** suggest the formation of a 65:35 mixture of endo and exo isomers. The cyclohexenyl and indenyl complexes **5** and **7**, respectively, exhibit interesting spectroscopic and structural characteristics. While most complexes were prepared in good yield, the addition of sterically larger ancillary ligands was problematic: the addition of indenyllithium led to low yields of the allylchromium complex, while treatment with (pentamethylcyclopentadienyl)lithium led to the isolation of only organic products. These diminished returns are attributed to attack of the ancillary ligand anion directly on the coordinated allyl ligand of the intermediate formed by oxidative addition. Solid-state structures of the η^3-allyl, crotyl, and cyclohexenyl complexes, all in the exo configuration, have been determined by X-ray crystallography.

Permethyltitanocene(III) η^3-allyl and substituted bis(indenyl)titanium(III) η^3-allyl complexes undergo regioselective central carbon alkylation upon treatment with organic free radicals.[1,2] The resulting titanacyclobutane complexes can be converted inter alia to cyclic organic compounds via carbonylation[2b,c] and isonitrile insertion,[2e] providing a basis for developing applications of this reactivity pattern in organic synthesis. To extend this methodology to other transition-metal systems, we have initiated investigations of the corresponding chromium η^3-allyl complexes. The literature, however, reveals that many chromium η^3-allyl complexes are thermally unstable and existing synthetic strategies are not particularly attractive for development in an explicitly organic context.[3−12] Thus, we turned to developing general synthetic methodology for preparing low-valent allylchromium complexes.

Although the corresponding cyclopentadienylmolybdenum dicarbonyl η^3-allyl complexes can be prepared directly from the reaction of $Na[CpMo(CO)_3]$ with allyl bromide[13] or by oxidative addition of allyl bromide to $(CH_3CN)_3Mo(CO)_3$ followed by treatment with LiCp,[14] neither method can be extended directly to the preparation of the chromium analogues. The oxidative addition of allyl bromide to $(CH_3CN)_3Cr(CO)_3$, for example, reportedly returns only chromous halide complexes, providing no evidence for the formation of even transient allyl intermediates.[14] Here we report that conditions for the latter process can be modified to provide a general new synthesis of substituted cyclopentadienylchromium dicarbonyl η^3-allyl complexes.[15]

Initially, modification of the anionic alkylation procedure was investigated. When allyl tosylate is substituted for allyl halide and trimethylamine *N*-oxide is introduced to induce decarbonylation at low temperature, $Na[CpCr(CO)_3]$ can indeed be converted to the η^3-allyl complex **1**, albeit in unacceptably low yields (eq

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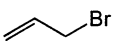
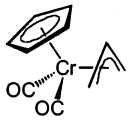
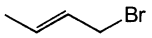
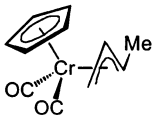
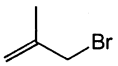
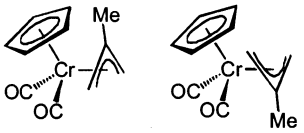
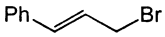
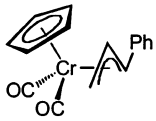
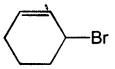
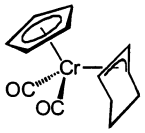
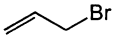
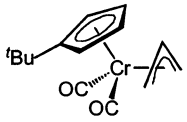
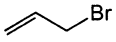
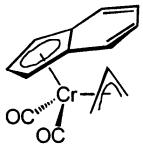
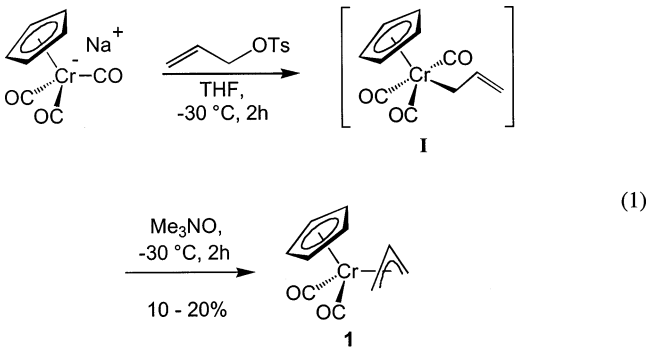
Table 1. Synthesis of η^3-Allyl Complexes 1−7 from $(CH_3CN)_3Cr(CO)_3$ (Eq 2)

Entry	Substrate	Reaction Time (h)[a]	$MCpR'_n$	Product		ν_{CO}[b]	% Yield
1		1	C_5H_4Na		**1**	1939, 1869	75
2		1	C_5H_4Na		**2**	1932, 1863	73
3		6	C_5H_4Na	 **3** *exo* **3** *endo*		1943, 1938, 1880, 1870	71
4		2	C_5H_4Na		**4**	1936, 1869	61
5		12	C_5H_4Na		**5**	1923, 1860	12
6		1	$^tBuC_5H_4Li$		**6**	1931, 1863	69
7		1	C_9H_7Li		**7**	1938, 1871	25

[a] The time refers to the period allowed for the oxidative addition of allyl substrate to $(CH_3CN)_3Cr(CO)_3$. [b] Infrared spectra recorded in THF solution, in units of cm^{-1}.

1). The modest success of this reaction is presumably

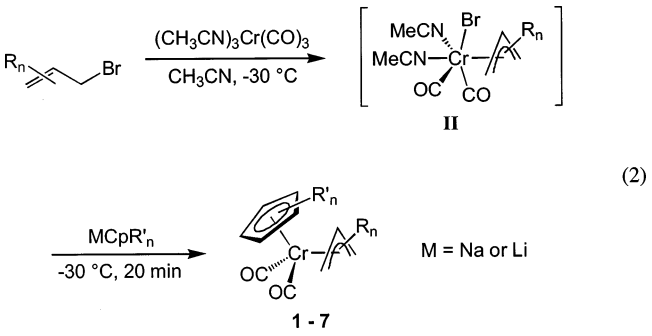


(1)

dependent on stabilizing the proposed seven-coordinate σ-allyl intermediate **I** to avoid chromium−carbon bond homolysis.[16] Consistent with this hypothesis, warming the solution to room temperature prior to addition of trimethylamine *N*-oxide provides only intractable decomposition products.

Fortunately, modification of the oxidative addition procedure was more successful, providing the desired chromium(II) allyl complexes in much higher yields (eq 2, Table 1). Treatment of $(CH_3CN)_3Cr(CO)_3$ with allyl bromide in acetonitrile at −30 °C, for example, results in a rapid color change from yellow to red, attributed to the formation of the thermally unstable intermediate **II** (eq 2). Subsequent addition of NaCp in acetonitrile to intermediate **II** at low temperature yields allyl complex **1** (entry 1) in good yield after chromatography

(15) Only two members of this compound class have been previously reported. (a) CpCr(η^3-cyclopentenyl)dicarbonyl, prepared in <5% yield by treatment of chromocene with CO and H_2 at high pressure: Fischer, E. O.; Ulm, K. *Chem. Ber.* **1961**, *94*, 2413. (b) CpCr(η^3-crotyl)dicarbonyl, isolated in 12% yield by photolysis of $[CpCr(CO)_3]_2$ in the presence of 1,3-butadiene. This complex was not completely characterized: Fischer, E. O.; Kögler, H. P.; Kuzel, P. *Chem. Ber.* **1960**, *93*, 3006. Fritz, H. P.; Keller, H.; Fischer, E. O. *Naturwissenschaften* **1961**, *48*, 518.



(2)

on neutral alumina(I). Warming of the reaction mixture prior to the addition of NaCp results in the formation of an uncharacterizable paramagnetic green material. Importantly, substituting allyl chloride in this procedure results in little or no reaction with $(CH_3CN)_3Cr(CO)_3$.

The ^{1}H NMR and infrared spectra of complex **1** indicate that only a single configurational isomer of the molecule is present in solution, identified in the solid state as exo by X-ray crystallography (Figure 1).[17] Interestingly, this contrasts with the case for the molybdenum analogue $CpMo(\eta^3\text{-}C_3H_5)(CO)_2$, which exists in solution as an approximate 1:1 mixture of endo and exo isomers.[18] Spectroscopic data for the crotyl (**2**) and cinnamyl (**4**) complexes (entries 2 and 4, respectively) suggest that both species also exist exclusively in the exo configuration, while the ^{1}H NMR spectrum of the 2-methylallyl complex **3** (entry 3) reveals that the product is formed as an approximately 65:35 mixture of isomers favoring the endo configuration.[19] The minor exo isomer selectively crystallizes from pentane, as established by X-ray crystallography (Figure 2).[20]

One limiting factor in this methodology is the persistent formation of $(CO)_5Cr(CH_3CN)$[21] as a minor side product. The formation of this complex is minimized by using a vigorous nitrogen purge throughout the reaction; this relatively polar impurity is readily removed by chromatography on neutral alumina. A second limitation arises from the decreasing rate of oxidative addition as a function of the steric size and substitution of the allyl substrate. Thus, in the reaction of 3-bromocyclohexene with $(CH_3CN)_3Cr(CO)_3$, only a very slow (~12 h) color change to red is observed. Subsequent addition of NaCp provides the expected cyclohexenyl complex **5**, but in only 12% isolated yield (entry 5).

Despite the low yield, cyclohexenyl complex **5** revealed several intriguing spectroscopic and structural features. While ^{1}H NMR spectroscopy shows typical signals for the terminal allyl, central allyl, and adjacent methylene protons at δ 4.02 (t, 1H), 3.47 (m, 2H), and δ 1.79 (m, 4H), respectively, the two remaining aliphatic proton resonances appear at unique positions. Thus, two upfield multiplets are observed, at δ 0.77 (m, 1H) and 0.38 (dtt, 1H), corresponding to the equatorial and axial protons, respectively, of the distal methylene group. The unusual shielding of this group is ascribed to a chairlike conformation of the cyclohexenyl ring, which places

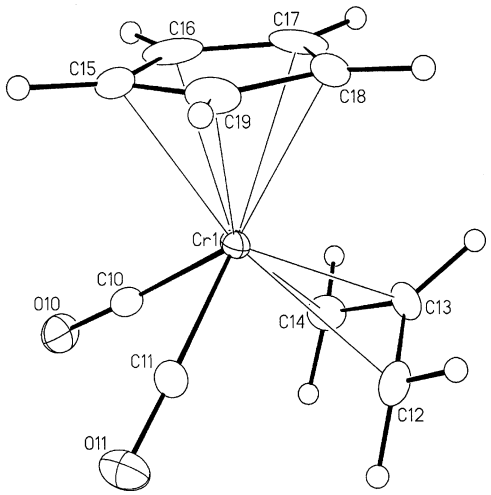


Figure 1. Solid-state molecular structure of complex **1**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr−C(10) = 1.814(6), Cr−C(11) = 1.817(5), Cr−C(12) = 2.231(5), Cr−C(13) = 2.108(4), Cr−C(14) = 2.239(5), Cr−C(15) = 2.164(5), Cr−C(16) = 2.178(6), Cr−C(17) = 2.315(5), Cr−C(18) = 2.215(5), Cr−C(19) = 2.190(5), O(10)−C(10) = 1.168(6), O(11)−C(11) = 1.155(6), C(12)−C(13) = 1.393(8), C(13)−C(14) = 1.397(8); C(10)−Cr−C(15)= 95.3(2), C(10)−Cr−C(11) = 83.4(2), C(10)−Cr−C(13) = 107.4(2), C(12)−Cr−C(14) = 65.0(2), C(11)−Cr−C(13) = 107.9(2), C(13)−Cr−C(18) = 88.8(2), C(12)−C(13)−C(14) = 118.8(5).

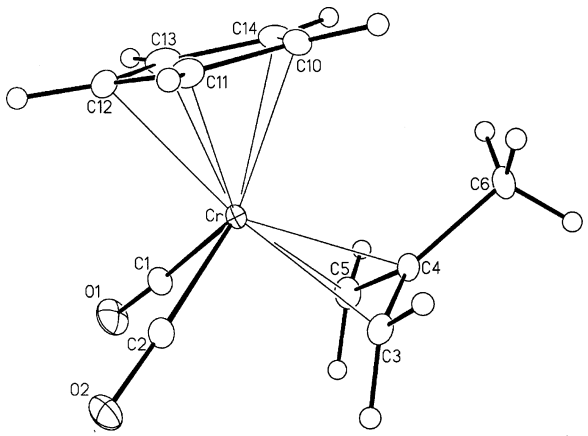


Figure 2. Solid-state molecular structure of complex **3** (exo isomer). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.813(18), Cr−C(2) = 1.821(19), Cr−C(3) = 2.234(17), Cr−C(4) = 2.149(16), Cr−C(5) = 2.233(18), Cr−C(10) = 2.233(17), Cr−C(11) = 2.196(18), Cr−C(12) = 2.169(18), Cr−C(13) = 2.196(2), Cr−C(14) = 2.233(2), O(1)−C(1) = 1.163(2), O(2)−C(2) = 1.153(2), C(3)−C(4) = 1.403(3), C(4)−C(5) = 1.405(3), C(4)−C(6) = 1.514(2); C(1)−Cr−C(12) = 95.5(8), C(1)−Cr−C(2) = 82.1(8), C(1)−Cr−C(4) = 107.0(8), C(3)−Cr−C(5) = 64.8(7), C(2)−Cr−C(4) = 107.6(7), C(4)−Cr−C(10) = 89.7(7), C(3)−C(4)−C(5) = 116.9(16).

(16) MacConnachie, C. A.; Nelson, J. M.; Baird, M. C. *Organometallics* **1992**, *11*, 2521.

(17) Crystal data for complex **1** ($C_{10}H_{10}CrO_2$, −80 °C): monoclinic, $P2_1/c$ (No. 14), a = 12.2466(11) Å, b = 13.0523(12) Å, c = 12.3583(12) Å, β = 110.815(2)°, V = 1846.5(3) Å^3, Z = 8, ρ_{calcd} = 1.541 g cm^{-3}, μ = 1.198 mm^{-1}, R1 = 0.0605, wR2 = 0.1271 ($F_o^2 \geq -3\sigma(F_o^2)$).

(18) King, R. B. *Inorg. Chem.* **1966**, *5*, 2242. Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840.

(19) We tentatively assign the minor constituent in solution as exo on the basis of ^{1}H NMR spectroscopy, which gave δ and J values very similar to those observed for complex **1**.

(20) Crystal data for complex **3** ($C_{11}H_{12}CrO_2$, −80 °C): monoclinic, $P2_1/c$ (No. 14), a = 7.5642(6) Å, b = 9.1655(7) Å, c = 14.7183(11) Å, β = 92.9750(10)°, V = 1019.04(14) Å^3, Z = 4, ρ_{calcd} = 1.487 g cm^{-3}, μ = 1.091 mm^{-1}, R1 = 0.0312, wR2 = 0.0915 ($F_o^2 \geq -3\sigma(F_o^2)$).

(21) Bachman, R. E.; Whitmire, K. H. *Inorg. Chem.* **1995**, *34*, 1542.

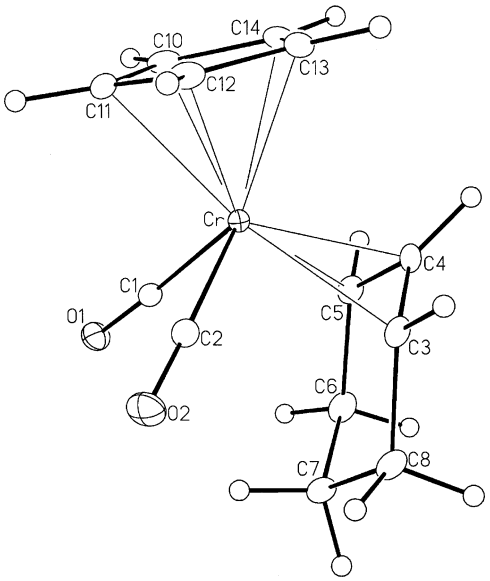


Figure 3. Molecular structure of complex **5**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.825(15), Cr−C(2) = 1.821(15), Cr−C(3) = 2.275(15), Cr−C(4) = 2.091(14), Cr−C(5) = 2.276(15), Cr−C(10) = 2.206(15), Cr−C(11) = 2.185(15), Cr−C(12) = 2.205(15), Cr−C(13) = 2.225(15), Cr−C(14) = 2.231(15), O(1)−C(1) = 1.155(18), O(2)−C(2) = 1.158(19), C(3)−C(4) = 1.407(2), C(4)−C(5) = 1.411(8), C(5)−C(6) = 1.512(2), C(6)−C(7) = 1.531(2), C(7)−C(8) = 1.523(2); C(1)−Cr−C(11) = 93.3(6), C(1)−Cr−C(2) = 85.0(7), C(1)−Cr−C(4) = 109.3(6), C(3)−Cr−C(5) = 63.4(5), C(2)−Cr−C(4) = 107.4(6), C(4)−Cr−C(13) = 88.6(6), C(3)−C(4)−C(5) = 116.2(14), C(5)−C(6)−C(7) = 113.3(13), C(6)−C(7)−C(8) = 113.3(14), C(3)−C(8)−C(7) = 113.4(13).

these protons underneath the metal, physically near the π-system of the carbonyl ligands. This conformation is indeed confirmed in the solid-state structure by X-ray crystallography (Figure 3).[22]

The introduction of other cyclopentadienyl-type ligands was also investigated. Thus, substituting (*tert*-butylcyclopentadienyl)lithium for NaCp after oxidative addition of allyl bromide affords the corresponding allyl complex **6** (entry 6) in good yield. The use of indenyllithium, however, provides only a low yield of the sterically more crowded complex **7** (entry 7). This is attributed to competitive addition of the indenyl anion to the allyl ligand rather than the metal center, producing a mixture of allylindene isomers as the major reaction product, identified by spectroscopic comparison to authentic material.[23] The addition of (pentamethylcyclopentadienyl)lithium unsurprisingly results in exclusive formation of allylpentamethylcyclopentadiene, again determined by spectroscopic comparison to authentic material.[24] Larger anions are clearly too sterically encumbered to access the metal center, instead preferentially alkylating the allyl ligand.

Careful inspection of the ^{1}H NMR spectrum of indenyl complex **7** suggests the presence of two stereoisomers in solution, one formed in only trace amounts. In the major isomer, the severe upfield shift (−0.11 ppm) of the central allyl proton strongly suggests the allyl ligand is in the exo configuration, positioned directly beneath the indenyl aromatic ring, as drawn. This configuration has been confirmed in the solid state by a crude structure determination on a poorly diffracting crystal, which provided both atom connectivity and ligand orientation, but not high-resolution structural data.

A reasonably general procedure for the synthesis of novel chromium(II) dicarbonyl complexes bearing substituted η^5-cyclopentadienyl and η^3-allyl ligands has thus been developed. Further investigation into the optimization of yields and the general reactivity of this class of compounds is in progress. Preliminary results suggest that the stability of intermediate **II** can be significantly enhanced by ionization/precipitation of the bromide ligand using potassium hexafluorophosphate. This strategy may provide higher yields and greater steric latitude in the subsequent formation of cyclopentadienyl derivatives. Finally, it appears that the strongly bound carbonyl ligands can be weakened considerably by oxidizing the metal center to chromium(III), providing a potential pathway into a broad range of potentially valuable allylchromium systems.

Experimental Section

General Procedures. Air-sensitive manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. All reagents were purchased from commercial suppliers or prepared according to reported procedures. Solvents were purified by distillation from sodium or potassium benzophenone ketyl. Infrared (IR) spectra were obtained on solutions in KBr cells and are reported in wavenumbers (cm^{-1}) calibrated to the 1601 cm^{-1} absorption of polystyrene. Chemical shifts are referenced to residual protiated solvent. The abbreviation fwhm denotes the full width at half-maximum of complex multiplet signals. *J* values are reported as observed to ±0.1 Hz, despite the inherently lower resolution of the data set. Accurate integration of the ^{1}H NMR cyclopentadienyl signals was difficult, even with a pulse delay of 7 s. High-resolution mass spectra (HRMS) were obtained in electron impact mode operating at 40 eV. Combustion analyses were performed by the University of Alberta Microanalysis Laboratory. Due to the high volatility of the samples or problematic combustion, several compounds failed to afford consistent elemental analysis.

Synthesis of (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylchromium (1). Method A. In a Schlenk flask under an inert atmosphere, sodium tricarbonyl(η^5-cyclopentadienyl)-chromate[25] (100 mg, 0.446 mmol) was dissolved in 20 mL of THF and cooled to −30 °C. Allyl tosylate (104 mg, 0.49 mmol) was added dropwise, and the solution was stirred at −30 °C for 30 min. Trimethylamine *N*-oxide (165 mg, 2.23 mmol) in methanol (5 mL) was then added, and the solution was warmed to room temperature. After 30 min the solvent was removed under reduced pressure from the dark orange solution, yielding an orange-green residue. The residue was extracted into pentane, and the orange solution was filtered through a sintered-glass funnel layered with a short plug of Celite. The extracts were combined, and the solvent was removed under reduced pressure to give complex **1** as a light orange powder (19.1 mg, 20%).

(22) Crystal data for complex **5** ($C_{13}H_{14}CrO_2$, −80 °C): monoclinic, $P2_1/c$ (No. 14), a = 13.2121(4) Å, b = 7.3278(2) Å, c = 12.0989(4) Å, β = 108.0060(10)°, V = 1113.99(6) Å^3, Z = 4, ρ_{calcd} = 1.516 g cm^{-3}, μ = 1.007 mm^{-1}, R1 = 0.0239, wR2 = 0.0686 ($F_o^2 \geq -3\sigma(F_o^2)$).

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Method B. In a Schlenk flask under an inert atmosphere, tris(acetonitrile)tricarbonylchromium[26] (100 mg, 0.386 mmol) was dissolved in 20 mL of acetonitrile and cooled to −30 °C. Allyl bromide (33.4 μL, 0.386 mmol) was added dropwise, and an immediate color change to red was observed. The solution was stirred at −30 °C for 1 h. Sodium cyclopentadienide (34.0 mg, 0.386 mmol) in acetonitrile (10 mL) was then added dropwise, and the solution was warmed to room temperature over a period of 15 min. The solvent was removed under reduced pressure to yield a dark orange residue. The residue was extracted several times with pentane, and the orange solution was filtered through a sintered-glass funnel layered with a short plug of Celite. The extracts were combined and passed through a 1 × 10 cm neutral alumina(I) column and eluted with hexane. The first five 20 mL fractions were combined, and the solvent was removed under reduced pressure to give complex **1** as a light orange powder (62 mg, 75%). IR (ν_{CO}, cm^{-1}, THF): 1939 (s), 1869 (s). ^{1}H NMR (500 MHz, C_6D_6): δ 3.97 (s, 5H), 3.73 (tt, J = 11.1, 7.0 Hz, 1H), 2.67 (dt, J = 7.0, 1.1 Hz, 2H), 0.48 (dt, J = 10.9, 1.1 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 247.1, 87.9, 71.0, 47.0. HRMS calcd for $C_{10}H_{10}CrO_2$: m/z 214.0083, found 214.008 87. Anal. Calcd for $C_{10}H_{10}CrO_2$: C, 56.08; H, 4.71. Found (sample recrystallized from pentane): C, 55.83; H, 4.82. Crystals suitable for X-ray diffraction studies were grown from a concentrated solution of **1** in methylcyclohexane at −34 °C.

Synthesis of (η^3-3-Methylallyl)(η^5-cyclopentadienyl)-dicarbonylchromium (2). This compound was obtained by using method B, except crotyl bromide (35.2 μL, 0.386 mmol) was used as the substrate. Yield: 64.3 mg (73%) of a bright yellow powder. IR (ν_{CO}, cm^{-1}, THF): 1932 (s), 1863 (s). ^{1}H NMR (500 MHz, C_6D_6): δ 4.04 (s, 5H), 3.65 (dtq, J = 10.5, 7.0, 0.5 Hz, 1H), 2.51 (ddd, J = 7.0, 2.0, 0.5 Hz, 1H), 1.52 (d, J = 6.5 Hz, 3H), 1.03 (br dq, J = 10.0, 6.5 Hz, 1H), 0.36 (ddd, J = 10.0, 2.0, 0.5 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 249.9, 246.6, 88.1, 72.8, 68.9, 41.6, 19.5. HRMS calcd for $C_{11}H_{12}CrO_2$: m/z 228.024 25, found 228.024 53. Anal. Calcd for $C_{11}H_{12}CrO_2$: C, 57.89; H, 5.30. Found (sample recrystallized from pentane): C, 57.73; H, 5.02.

Synthesis of (η^3-2-Methylallyl)(η^5-cyclopentadienyl)-dicarbonylchromium (3). This compound was obtained by using method B, except 2-methyl-3-bromopropene (38.9 μL, 0.386 mmol) was used as the substrate and the time allowed for oxidative addition was 6 h. Yield: 62.5 mg (71%) of a dark orange powder. IR (ν_{CO}, cm^{-1}, THF): 1943 (s), 1938 (s), 1880 (s), 1870 (s). ^{1}H NMR (500 MHz, C_6D_6): *endo* isomer, δ 4.08 (s, 5H), 2.88 (s, 2H), 1.72 (s, 2H), 1.46 (s, 3H); *exo* isomer (assignments based on similarities of chemical shift and J values to that of complex **1**), δ 4.06 (s, 5H), 2.59 (s, 2H), 1.46 (s, 3H), 0.54 (s, 2H). ^{13}C NMR (125 MHz, C_6D_6): *endo* isomer, δ 252.8, 104.6, 87.8, 47.8, 23.5; *exo* isomer, δ 247.8, 115.0, 88.4, 48.4, 25.8. HRMS calcd for $C_{11}H_{12}CrO_2$: m/z 228.024 25, found 228.024 23. Anal. Calcd for $C_{11}H_{12}CrO_2$: C, 57.89; H, 5.30. Found (sample recrystallized from pentane): C, 56.99; H, 5.21. Crystals suitable for X-ray diffraction studies were grown of the exo isomer from a concentrated solution of **3** in methylcyclohexane at −34 °C.

Synthesis of (η^3-3-Phenylallyl)(η^5-cyclopentadienyl)-dicarbonylchromium (4). This compound was obtained by using method B, except cinnamyl bromide (571 μL, 3.86 mmol), tris(acetonitrile)tricarbonylchromium (1.00 g, 3.86 mmol), and sodium cyclopentadienide (0.408 g, 4.63 mmol) were used. Yield: 683 mg (61%) of a dark orange powder. IR (ν_{CO}, cm^{-1}, THF): 1936, 1869. ^{1}H NMR (500 MHz, C_6D_6): δ 7.18 (m 2H, H), 7.09 (m, 2H, H), 7.0 (tt, J = 7.0, 2.5 Hz, 1H, H), 4.55 (dt, J = 10.5, 7.0 Hz, 1H), 3.94 (s, 5H), 2.72 (dd, J = 7.0, 2.0 Hz, 1H, H), 1.90 (d, J = 11.0 Hz, 1H, H), 0.60 (ddd, J = 10.5, 2.0, 0.5 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 250.6, 246.9, 128.7, 128.5, 126.7, 125.9, 89.2, 69.9, 69.2, 42.4. HRMS calcd for $C_{16}H_{14}CrO_2$: m/z 290.039 89, found 290.040 22. Anal. Calcd for $C_{16}H_{14}CrO_2$: C, 66.20; H, 4.86. Found (sample recrystallized from pentane): C, 65.54; H, 4.72.

Synthesis of (η^3-Cyclohexenyl)(η^5-cyclopentadienyl)-dicarbonylchromium (5). This compound was obtained by using method B, except 3-bromocyclohexene (44.4 μL, 0.386 mmol) was used as the substrate and the time allowed for oxidative addition was 12 h. Yield: 12.0 mg (12%) of a light orange powder. IR (ν_{CO}, cm^{-1}, THF): 1923 (s), 1860 (s). ^{1}H NMR (500 MHz, C_6D_6): δ 4.09 (s, 5H), 4.02 (t, J = 7.5 Hz, 1H), 3.47 (complex m, fwhm = 14.2 Hz, 2H), 1.79 (complex m, fwhm = 19.4 Hz, 4H), 0.77 (complex m, fwhm = 26.0 Hz, 1H), 0.38 (ddddd, by appearances nearly a dtt, J = 14.1, 10.8, 10.6, 7.4, 7.3 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 246.0, 88.8, 63.4, 61.4, 22.3, 18.7. HRMS calcd for $C_{13}H_{14}CrO_2$: m/z 254.039 89, found 254.039 87. Anal. Calcd for $C_{13}H_{14}CrO_2$: C, 61.41; H, 5.55. Found (sample recrystallized from pentane): C, 61.07; H, 5.55. Crystals suitable for X-ray diffraction studies were grown from a concentrated solution of **5** in pentane at −34 °C.

Synthesis of (η^3-Allyl)(η^5-*tert*-butylcyclopentadienyl)-dicarbonylchromium (6). This compound was obtained by using method B, except lithium *tert*-butylcyclopentadienide (49.5 mg, 0.386 mmol) was used as the ancillary ligand source. Yield: 72.0 mg (69%) of a light orange powder. IR (ν_{CO}, cm^{-1}, THF): 1931 (s), 1863 (s). ^{1}H NMR (500 MHz, C_6D_6): δ 4.15 (t, J = 2.0 Hz, 2H), 3.83 (tt, J = 11.0, 7.0 Hz, 1H), 3.65 (t, J = 2.5 Hz, 2H), 2.77 (br d, J = 7.0 Hz, 2H), 1.14 (s, 9H), 0.52 (br d, J = 11.0 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 247.6, 120.0, 88.9, 84.8, 71.4, 47.7, 31.5, 31.4. HRMS calcd for $C_{14}H_{18}CrO_2$: m/z 270.071 20, found 270.071 71. Anal. Calcd for $C_{14}H_{18}CrO_2$: C, 62.21; H, 6.71. Found (sample recrystallized from pentane): C, 61.75; H, 6.63.

Synthesis of (η^3-Allyl)(η^5-indenyl)dicarbonylchromium (7). This compound was obtained by using method B, except indenyllithium (47.0 mg, 0.386 mmol) was used as the ancillary ligand source. Yield: 25.5 mg (25%) of a bright red powder. IR (ν_{CO}, cm^{-1}, THF): 1938 (s), 1871 (s). ^{1}H NMR (500 MHz, C_6D_6): *exo* isomer, δ 6.44 (m, second order, 4H), 5.12 (d, J = 2.5 Hz, 2H), 4.64 (t, J = 2.5 Hz, 1H), 2.50 (dt, J = 7.0, 1.0 Hz, 2H), 0.58 (dt, J = 11.5, 1.0 Hz, 2H), −0.11 (tt, J = 11.7 Hz, 7.5 Hz, 1H); *endo* isomer (partial data only), δ 3.59 (d, J = 7.0 Hz, 2H), −0.63 (d, J = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6): *exo* isomer, δ 248.6, 125.7, 124.7, 106.8, 86.2, 84.1, 79.1, 55.8. HRMS calcd for $C_{14}H_{12}CrO_2$: m/z 264.024 23, found 264.024 39. Anal. Calcd for $C_{14}H_{12}CrO_2$: C, 63.64; H, 4.58. Found (sample recrystallized from pentane): C, 62.83; H, 3.99.

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Supporting Information Available: Text giving detailed assignments of ^{1}H and ^{13}C NMR spectra for all new compounds and text and tables giving details of the X-ray structure determinations for complexes **1**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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