π-Arene Complexes. 8.[1] Early/Late Heterobimetallic Complexes of Chromium with σ,π-Bridged Arene Ligands

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New heterobimetallic and trimetallic complexes of titanium, $[Ti(\eta^5\text{-}C_5H_5)_2(Cl)(\mu\text{-}\eta^1{:}\eta^6\text{-}RC_6H_4)Cr(CO)_3]$ (R = H (**1**), *o*-F (**2**), *p*-CH_3 (**3**), *m*-CH_3 (**4**), $[Ti(\eta^5\text{-}C_5H_5)_2(Cl)(\mu\text{-}\eta^1{:}\eta^6\text{-}C_6Me_5CH_2)Cr(CO)_3]$ (**5**), and $[(\mu\text{-}\{Ti(\eta^5\text{-}C_5H_5)_2\})\{(\eta^1{:}\eta^6\text{-}RC_6H_4)Cr(CO)_3\}_2]$ (R = H (**6**), *p*-CH_3 (**7**)), and gold, $[Au(PPh_3)(\mu\text{-}\eta^1{:}\eta^6\text{-}RC_6H_4)Cr(CO)_3]$ (R = H (**9**), *o*-F (**10**)), were prepared by the addition of the transition-metal halide $Ti(\eta^5\text{-}C_5H_5)_2(Cl)_2$ or $Au\{PPh_3\}Cl$ to a tetrahydrofuran solution of the appropriate lithiated (π-arene)tricarbonylchromium(0) substrate. The characterization of the bi- and trinuclear products by analytical and NMR, IR, and mass spectral data is supported by X-ray studies of the fluorobenzene (**2**) and toluene (**3**) derivatives, which confirm that the phenyl ligand is π-coordinated to the chromium tricarbonyl group, as well as σ-bonded to the bent metallocene. Crystals of **2** were monoclinic, $P2_1/n$, with a = 10.431 (4) Å, b = 12.506 (13) Å, c = 13.905 (3) Å, β = 106.38 (2)°, and Z = 4. Crystals of **3** were orthorhombic, *Pbca*, with a = 14.138 (2) Å, b = 13.625 (2) Å, c = 19.229 (6) Å, and Z = 8.

Introduction

Attention has recently shifted to the synthesis of compounds with simple ligands linking two disparate metal centers, whereby enhanced or alternative reactivity patterns are expected.[2]

The role of metal–carbon σ-bonds in ligand activation has been the topic of many studies in transition-metal chemistry.[3] The syntheses of the first examples of bi- and trimetallic complexes with σ-bonds linking "early" (Ti(IV)) and "late" (Au(I)) transition-metal fragments to π-bonded arenes of $(arene)Cr(CO)_3$ substrates have been attempted and are reported in this paper. In contrast with the Cr^0–L–Mn^I complexes (both d^6 species), reported earlier,[1] this proposed arrangement could lead to a system in which the interactions of two dissimilar metal fragments, e.g. Cr^0–L–Ti^{IV} (d^6–d^0) and Cr^0–L–Au^I (d^6–d^{10}), could be explored in terms of their activating effect on the bridging benzene ligand.

Although several lithiated arene compounds have been reacted with Cp_2TiCl_2[4] and $Au(PPh_3)Cl$,[5] the lithium derivatives of organometallic moieties have thus far been limited to cyclopentadienyl complexes.[6] Lithiated arene ligands of chromium are known to be strong nucleophiles.[1,7]

Because of the absence of a metal–metal bond in these systems, the influence of the two metals differs from the phenomenon of "strong metal–support interactions" (SMSI) observed for catalysts in which a late transition metal is deposited on an early-transition-metal support.[8]

Experimental Section

Materials and Methods. All reactions and subsequent manipulations were performed with use of conventional techniques for the handling of air-sensitive compounds.[9] All other solvents were purified, degassed, and dried according to standard methods.[10] Unless otherwise specified, reagent grade chemicals were used without further purification. Column packings for liquid column chromatography consisted of SiO_2 (0.063–0.200 mm) cooled by recycling cold (−20 °C) methanol through column jackets. Prior to use, dichloromethane and acetone were distilled from P_2O_5; hexane, benzene, and pentane were distilled from sodium wire, while ether and tetrahydrofuran were freshly distilled from sodium–benzophenone ketyl under an inert atmosphere. The chromium derivatives $(\eta^6\text{-}RC_6H_5)Cr(CO)_3$ (R = H, F, CH_3) and $(\eta^6\text{-}C_6Me_6)Cr(CO)_3$ were prepared according to published procedures[11] and were lithiated according to the methods described by Card and Trahanovsky[12] and Yaouanc and co-workers.[13]

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-300 spectrometer with reference to the deuterium signal of the solvent employed. ^1H NMR and ^{13}C NMR spectra were measured at 300.135 and 75.469 MHz, respectively, unless specified otherwise. The ^1H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) with residual resonances as internal standards for determining chemical shifts. NMR solvents were degassed by several freeze–pump–thaw cycles, and NMR sample tubes were sealed under nitrogen. Infrared spectra were recorded as liquid solutions on a Bomem Michelson-100 FT spectrophotometer, and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Mass spectra were recorded on a

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Perkin-Elmer RMU-6H instrument operating at 70 eV. Elemental analyses were obtained from the Analytical Division (PCMT) of the Council for Scientific and Industrial Research, Pretoria, South Africa. Melting points were recorded in capillaries on a Gallenkamp hot-stage apparatus and are uncorrected.

Synthesis. Preparation of [η^6-{Chlorobis(cyclopentadienyl)titanio(IV)}benzene]tricarbonylchromium(0) (1). A cooled (−78 °C) solution of 0.64 g (3 mmol) of (η^6-benzene)tricarbonylchromium(0) in 30 mL of THF was treated dropwise with 2.1 mL of a 1.6 mol/dm^3 solution of butyllithium (3.3 mmol). The mixture was stirred for 20 min while the temperature was raised to −30 °C. This freshly prepared (η^6-lithiobenzene)tricarbonylchromium(0) solution was cooled to −50 °C and added to an equimolar solution of Cp_2TiCl_2 (0.78 g, 3 mmol) in THF (30 mL) at −78 °C. After it was stirred for 30 min, the reaction mixture was warmed to room temperature and stirring was continued for 1 h. Removal of the solvent under reduced pressure gave a blue-green solid, which was subjected to column chromatography on silica gel. Elution with a dichloromethane–hexane (1:1) mixture yielded a yellow fraction identified as unreacted chromium starting material, followed by a blue-purple zone containing $[Ti(Cp)_2Cl(\mu\text{-}\eta^1{:}\eta^6\text{-}C_6H_5)Cr(CO)_3]$ (1). In addition, a number of other bands observed in low yield were not collected and identified. After the solvent was removed, the residue was dissolved in a minimum amount of dichloromethane and filtered through a plug of Celite, whereafter an equal volume of hexane was carefully layered on top of the dichloromethane. The Schlenk tube was left undisturbed at −4 °C for several days and placed in a dry-ice box for 6 h, after which the mother liquor was decanted and the remaining blue-black crystals of 1 were dried under high vacuum; yield 69% (0.44 g). Anal. Calcd for $C_{19}H_{15}O_3ClCrTi$: C, 53.48; H, 3.54. Found: C, 53.00; H, 3.63.

Preparation of [η^6-{Chlorobis(cyclopentadienyl)titanio(IV)}-*o*-fluorobenzene]tricarbonylchromium(0) (2). The same general procedure used for the synthesis of 1 was followed for the preparation of 2, now using (π-fluorobenzene)tricarbonylchromium(0) (0.696 g, 3 mmol). Analytically pure blue-black crystals of $[Ti(Cp)_2Cl(\mu\text{-}\eta^1{:}\eta^6\text{-}o\text{-}C_6H_4F)Cr(CO)_3]$ (2) were obtained after recrystallization from a dichloromethane–hexane mixture at −4 °C: yield 52% (0.36 g); mp 192 °C. Anal. Calcd for $C_{19}H_{14}O_3FClTiCr$: C, 51.32; H, 3.17. Found: C, 51.43; H, 3.16.

In addition, an orange-red solid was isolated and identified as $[\{Cr(CO)_3\}_2(\mu\text{-}\eta^1{:}\eta^6\text{-}o\text{-}C_6H_4(F)C_6H_5)]$ (8): yield 11% (0.079 g); mp 175 °C. Anal. Calcd for $C_{18}H_9O_6FCr_2$: C, 48.66; H, 2.04. Found: C, 48.27; H, 2.11.

Preparation of [η^6-{Chlorobis(cyclopentadienyl)titanio(IV)}-*p*-toluene]tricarbonylchromium(0) (3). A procedure analogous to that of 1 was followed, using (η^6-toluene)tricarbonylchromium(0) (0.68 g, 3 mmol) instead of the π-benzene precursor. Careful layering of hexane over a concentrated solution of the complex in dichloromethane yielded blue-black crystals of a mixture of $[Ti(Cp)_2Cl(\mu\text{-}\eta^1{:}\eta^6\text{-}p\text{-}C_6H_4Me)Cr(CO)_3]$ (3) and $[Ti(Cp)_2Cl(\mu\text{-}\eta^1{:}\eta^6\text{-}m\text{-}C_6H_4Me)Cr(CO)_3]$ (4). Recrystallization of the mixture afforded an analytically pure sample of 3: yield 61% (0.42 g); mp 183° dec. Anal. Calcd for $C_{20}H_{17}O_3ClCrTi$: C, 54.49; H, 3.89. Found: C, 54.10; H, 3.76. Complex 4 was characterized spectroscopically (see text).

Preparation of [η^6-{(Chlorobis(cyclopentadienyl)titanio(IV))methyl}pentamethylbenzene]tricarbonylchromium(0) (5). The same procedure used for the synthesis of 1 was followed, the π-benzene derivative being replaced with (η^6-hexamethylbenzene)tricarbonylchromium(0) (0.89 g, 3 mmol). The second yellow zone from column chromatography yielded $[Ti(Cp)_2(Cl)(\mu\text{-}\eta^1{:}\eta^6\text{-}C_6Me_5CH_2)Cr(CO)_3]$ (5) upon crystallization from dichloromethane–hexane at −4 °C. The complex was stored cold under an inert atmosphere but nevertheless decomposed over a period of 3 weeks: yield 40% (0.36 g); orange crystals; mp 103 °C dec. Anal. Calcd for $C_{25}H_{27}O_3ClCrTi$: C, 58.77; H, 5.33. Found: C, 58.00; H, 4.97.

Preparation of [μ-{Bis(cyclopentadienyl)titanio(IV)}bis(η^6-benzene)]bis{tricarbonylchromium(0)} (6). A procedure similar to that of 1 was followed for the preparation of the title compound, except that 2 equiv of $(\eta^6\text{-}LiC_6H_5)Cr(CO)_3$ (6 mmol) was used. Blue crystals of $[(\mu\text{-}\{Ti(Cp)_2\})\{(\eta^1{:}\eta^6\text{-}C_6H_5)Cr(CO)_3\}_2]$ (6) were obtained from dichloromethane–pentane at −20 °C. The complex decomposes with time to a brick red solid: yield 37% (0.47 g); mp 202 °C dec. Anal. Calcd for $C_{28}H_{20}O_6TiCr_2$: C, 55.63; H, 3.34. Found: C, 55.74; H, 3.42.

Table I. Crystallographic Data for 2 and 3

	2	3
mol formula	$C_{19}H_{14}ClFO_3CrTi$	$C_{20}H_{17}ClO_3CrTi$
mol wt	444.7	440.7
cell dimens		
a, Å	10.431 (4)	14.138 (2)
b, Å	12.506 (13)	13.625 (2)
c, Å	13.905 (3)	19.229 (6)
β, deg	106.38 (2)	
V, Å^3	1740 (2)	3704 (1)
space group (No.)	$P2_1/n$ (14)	*Pbca* (61)
ρ(calc), g cm^{-3}	1.697	1.570
cryst size, mm	0.13 × 0.13 × 0.14	0.13 × 0.25 × 0.41
Z	4	8
F(000)	896	1788
μ(Mo Kα), cm^{-1}	11.8	11.0
scan ratio, $\omega{:}2\theta$	1:1	1:1
scan range, θ, deg	$3 \le \theta \le 25$	$3 \le \theta \le 30$
zone collected		
h min, max	0, 12	0, 19
k min, max	0, 14	0, 19
l min, max	−16, 16	0, 27
scan width, deg	$0.50 + 0.34 \tan\theta$	$0.61 + 0.34 \tan\theta$
no. of data measd	3383	6093
no. of rflns used	$1936 > 2\sigma(I)$	$2255 > 4\sigma(I)$
no. of params refined	236	239
max shift/esd	0.02	0.21
residual electron density, e Å^{-3}	0.57	0.66
R	0.065	0.058
R_w	0.043	0.037

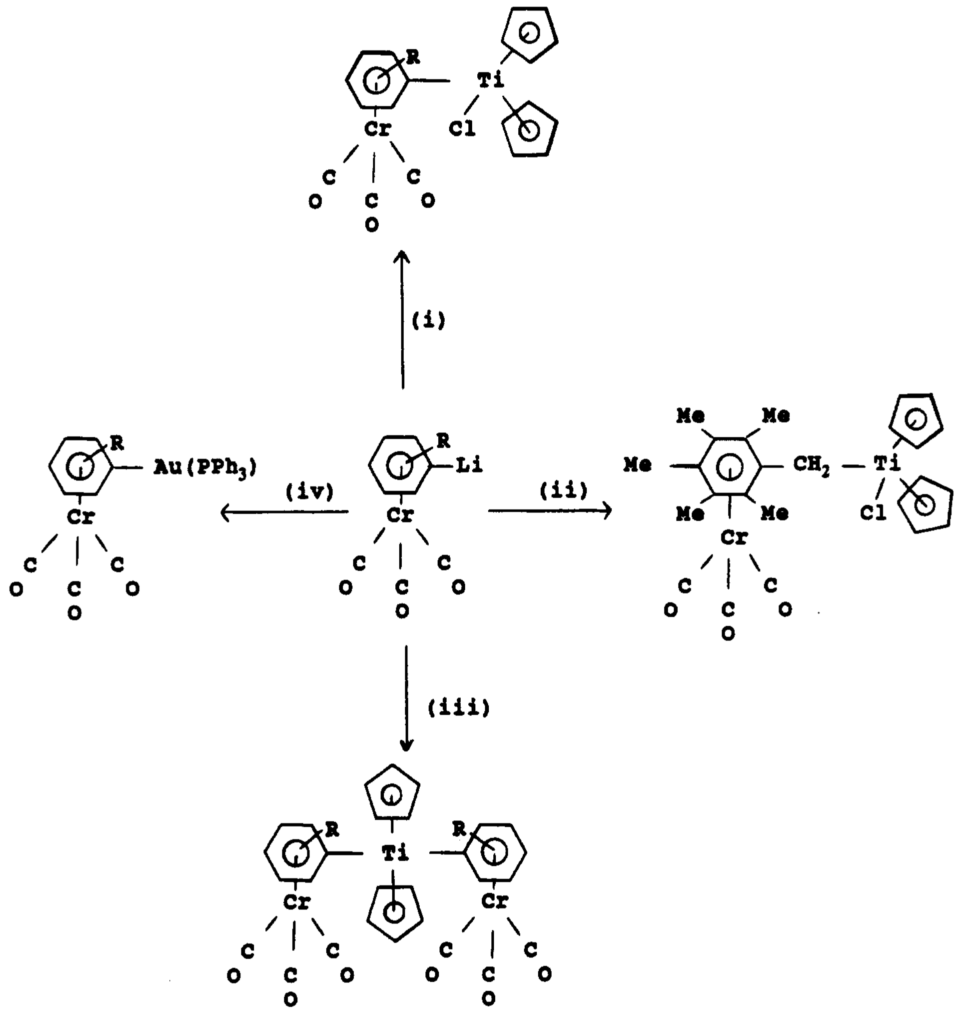
Preparation of [μ-{Bis(cyclopentadienyl)titanio(IV)}bis(η^6-*p*-toluene)]bis{tricarbonylchromium(0)} (7). The same procedure used for 1 was again employed with the exception that 2 equiv of $(\eta^6\text{-}LiC_6H_4Me)Cr(CO)_3$ (6 mmol) was used. A low yield of 0.39 g (29% yield) of purple-blue crystals of $[(\mu\text{-}\{Ti(Cp)_2\})\{(\eta^1{:}\eta^6\text{-}p\text{-}C_6H_4Me)Cr(CO)_3\}_2]$ (7) was obtained after crystallization from dichloromethane layered with hexane. The compound decomposes to a brick red solid on standing over a period of 2 weeks; mp 214 °C dec. Anal. Calcd for $C_{30}H_{24}O_6TiCr_2$: C, 56.97; H, 3.82. Found: C, 57.23; H, 3.87.

Preparation of [η^6-{(Triphenylphosphine)aurio(I)}benzene]tricarbonylchromium(0) (9). A solution of (η^6-lithiobenzene)tricarbonylchromium(0), prepared from the reaction between (η^6-benzene)$Cr(CO)_3$ (0.214 g, 1 mmol) and *n*-butyllithium (0.73 mL, 1.1 mmol in a 1.5 mol/dm^3 solution of hexane) in THF (15 mL) at −40 °C was added dropwise to a stirred solution of (triphenylphosphine)gold(I) chloride (0.49 g, 1 mmol) in THF (−50 °C). The resulting yellow mixture was stirred at −50 °C for 30 min, after which it was stirred at room temperature for 1 h. Repeated washing with hexane (3 × 20 mL) to remove and collect unreacted starting materials left a light yellow powder of $[Au(PPh_3)(\mu\text{-}\eta^1{:}\eta^6\text{-}C_6H_5)Cr(CO)_3]$ (9; 0.102 g, 48%, based on π-arene precursor); mp 93–95 °C. Anal. Calcd for $C_{27}H_{20}O_3PCrAu$: C, 48.23; H, 3.00. Found: C, 47.51; H, 2.73.

Preparation of [η^6-{(Triphenylphosphine)aurio(I)}-*o*-fluorobenzene]tricarbonylchromium(0) (10). The title compound was synthesized by the procedure described for the preparation of 9, starting with 0.232 g (1 mmol) of (η^6-fluorobenzene)tricarbonylchromium(0). Yellow crystals of $[Au(PPh_3)(\mu\text{-}\eta^1{:}\eta^6\text{-}o\text{-}C_6H_4F)Cr(CO)_3]$ (10) were obtained after recrystallization from dichloromethane–pentane (1.04 g, 62%); mp 65–67 °C. Anal. Calcd for $C_{27}H_{19}O_3FPCrAu$: C, 46.87; H, 2.77. Found: C, 46.63; H, 2.70.

Crystal Structure Analyses. All diffraction measurements were performed at room temperature on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å) at room temperature (22 °C). The unit cell parameters were determined using 25 centered reflections (15 with $\theta > 11°$ for 2, 25 with $14° < \theta < 17°$ for 3). The relevant crystal data for 2 and 3 are summarized in Table I. All the data were corrected for Lorentz and polarization effects. A variable but maximum scan speed of 5.49° min^{-1} and a maximum scan time of 60 s/reflection were employed for both crystals. Three standard

Scheme I[a]



[a] Legend: (i) [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$], R = H (**1**), *o*-F (**2**), *p*-Me (**3**), *m*-Me (**4**); (ii) [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$], R = 5 × Me, CH$_2$ (**5**); (iii) $^1/_2$[Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$], R = H (**6**), *p*-Me (**7**); (iv) Au(PPh$_3$)(Cl), R = H (**9**), *o*-F (**10**).

reflections for each crystal were measured at regular intervals, to check orientations and crystal stability, and the decay of 5.2% in the data for **2** was corrected. The data for **3** showed no significant decay. An empirical absorption correction was applied to the data for **3** by measuring the intensities of nine reflections with χ near 90° for different ψ values ($0 \leq \psi \leq 360°$, every 10°) and using the EAC program, from the Enraf-Nonius package.[14] The maximum and minimum correction factors were 1.00 and 0.89, with an average value of 0.95. Both structures were solved by Patterson and Fourier methods[15] and refined by full-matrix least-squares techniques using SHELX.[16] All the hydrogen atoms in both structures were placed in calculated positions and refined with a common isotropic thermal parameter for each structure that converged to $U_{\text{iso}} = 0.055$ (7) Å^2 for **2** and $U_{\text{iso}} = 0.099$ (6) Å^2 for **3**. All the non-hydrogen atoms in both structures were refined anisotropically using $\sigma^2(F_o)$ weights. Scattering factors for Ti and Cr were taken from the literature.[17]

Results and Discussion

Synthesis. Metalation of (η^6-C$_6$H$_5$R)Cr(CO)$_3$ (R = H, F, Me) with *n*-butyllithium in THF at −78 °C afforded suitable nucleophilic precursors for reactions with transition-metal complexes that contain halogen ligands. The strong nucleophilic center, created on the arene, is largely localized on the metalated carbon. Upon addition of the (π-lithioarene)tricarbonylchromium(0) compounds to titanocene dichloride in THF at low temperatures (see path i in Scheme I), the red solution rapidly turns blue-green. The intensely blue complexes [Ti(Cp)$_2$(Cl){μ-(η^1:η^6-C$_6$H$_4$R)}Cr(CO)$_3$] (R = H (**1**), *o*-F (**2**), *p*-Me (**3**)) were isolated in high yields.

In addition to **3**, the blue band obtained from the residue from the reaction of Cp$_2$TiCl$_2$ with (η^6-LiC$_6$H$_4$Me)Cr(CO)$_3$ contained a mixture of two isomeric forms which could not be separated by column chromatography. However, **3** was purified after repeated recrystallizations from dichloromethane–pentane mixtures. ^{1}H NMR spectra revealed an isomeric mixture of para- and meta-substituted toluene dimers in a product ratio *p*:*m* of 76:24. By contrast, ratios of *o*:*m*:*p* product distributions of 10:45:45 (53% yield) and 6:41:22, obtained by lithiation of (π-toluene)Cr(CO)$_3$ with *n*-BuLi and subsequent alkylation with organic reagents, were recorded by Semmelhack and co-workers[18] and Card and Trahanovsky,[12] respectively. These results favor meta

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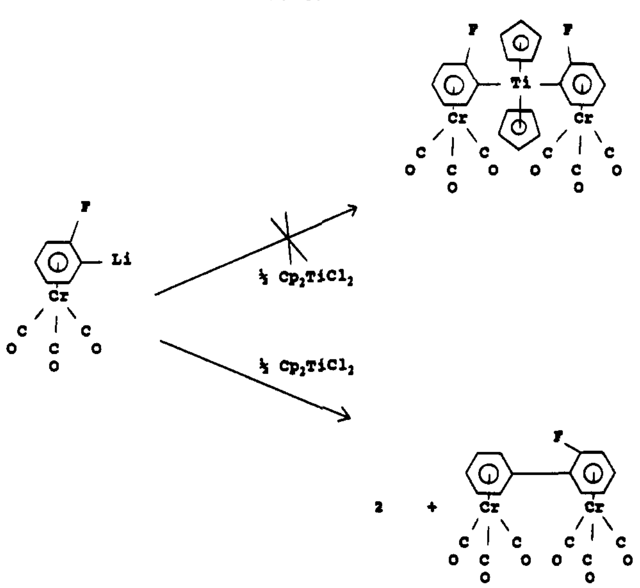
metalation and very low yields of the para product. In addition, competition between ring H and benzylic H abstraction was found, the latter being the thermodynamically favored process.[19] The steric and electronic effects of substituents on site selectivity have been correlated with the frontier orbitals of the arene complex (LUMO),[20] as well as the influence of charge induced by the $Cr(CO)_3$ conformation.[21] The increased electron density on the arene ligand of **3** (vide infra) will electronically favor the formation of para- and ortho-disubstituted products over a meta-substituted dimer, while the steric bulk of the titanium substituent favors the para product above the ortho dimer. Interestingly, we were unable to isolate a bimetallic complex with a bridging benzyl ligand. This we ascribe to a greater instability of bimetallic complexes with bridging benzyl ligands compared to those with bridging benzene ligands (complex **5** is far less stable than **1**–**3**).

The distinctive blue observed for the bimetallic complexes **1**–**3** is seldom found for π-arene complexes of chromium, for which the normal colors vary from yellow to red. A broad absorption band with λ_{max} at ca. 580 nm in the UV and visible spectra of **1**–**3** was observed. The spectra are complex, and it was impossible to unambiguously make assignments to absorption bands which might indicate a ligand-mediated intermetallic charge-transfer process. We are presently studying the electronic spectra of bimetallic compounds in different solvents and at low temperatures.

We have also reacted lithiated (η^6-hexamethylbenzene)tricarbonylchromium(0)[13] with Cp_2TiCl_2 to study the ease of formation, as well as structural aspects, of compounds containing a methylene group between the phenyl ring and the titanium atom. Instead of a similar blue product, a less stable orange compound formulation identical to the other compounds, i.e. $[Ti(Cp)_2(Cl)\{\mu\text{-}\eta^1:\eta^6\text{-}C_6Me_5CH_2\}Cr(CO)_3]$ (**5**), was obtained in low yield. We ascribed the low yield to either ineffective metalation of the hexamethylbenzene (Bz*) ring or the inability of the lithiated methylene to displace a chloride.

Addition of double the stoichiometric amount of lithiated (arene)chromium species to titanocene dichloride afforded the trimetallic products $[(\mu\text{-}Ti(Cp)_2)\{(\eta^1:\eta^6\text{-}C_6H_4R)Cr(CO)_3\}_2]$ (R = H (**6**), *p*-Me (**7**)) in reasonable yields (path iii in Scheme I). Irrespective of whether 1 or 2 equiv of the lithiated fluorobenzene derivative was used, only one chloride was consistently displaced to afford **2**. An orange-red solid, identified as $[(\mu\text{-}\eta^6:\eta^6\text{-}o\text{-}FC_6H_4C_6H_5)\{Cr(CO)_3\}_2]$ (**8**), was also obtained in low yields from the reaction with 2 equiv of lithiated reagent (Scheme II). We attribute the formation of **8** to the reaction of lithiated fluorobenzene complex with a nonmetalated fluoroarene substrate present in the reaction mixture. These results are also in agreement with observations by Argarwal and co-workers[22] that the desired bis(chromioarenyl)titanocene does not form upon treatment of $(\eta^6\text{-}LiC_6F_5)Cr(\eta^6\text{-}C_6H_6)$ with titanocene dichloride but that homopolymerization takes place instead. The displacement of only one chlorine atom from titanocene dichloride upon treatment with $(\eta^6\text{-}o\text{-}LiC_6H_4F)Cr(CO)_3$ is contrary to expectations from literature observations based on lithiated cyclopentadienyl precursors[4,6] and the results obtained for the benzene and toluene derivatives from which the trimetallic compounds **6** and **7** were isolated. The corresponding non-benzenoid trinuclear compounds of manganese,[6a] $[Ti(Cp)_2\{(\eta^1:\eta^5\text{-}C_5H_4)Mn(CO)_3\}_2]$, and iron,[6b] $[Ti(Cp)_2\{(\eta^1:\eta^5\text{-}C_5H_4)Fe(Cp)\}_2]$, are formed from the reactions of titanocene dichloride with $[Mn(\eta^5\text{-}LiC_5H_4)(CO)_3]$ and ferrocenyllithium in a 1:2 molar ratio. The trimetallic compounds **6** and **7** are air- and moisture-sensitive and decompose thermally to give unidentified brick red residues.

Scheme II



Treatment of a THF solution (−78 °C) of the gold(I) chloride compound with metalated $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ yielded the neutral heterobimetallic complexes $[Au(PPh_3)\{\mu\text{-}\eta^1:\eta^6\text{-}C_6H_4R\}Cr(CO)_3]$ (R = H (**9**), *o*-F (**10**); path iv in Scheme I). The new complexes were isolated as golden yellow solids which are soluble in hexane, chloroform, dichloromethane, and acetone and have remarkably low melting points compared to those of the titanium analogues. Complex **9** decomposed rapidly in most solvents, as well as in the benzene–hexane mixtures used to attempt crystallization. The complex **10** gave only fine needles, unsuitable for a single-crystal X-ray determination, even after numerous attempts of crystallization from different solvent mixtures.

All new complexes were characterized by elemental analysis (except **4**) and IR, NMR, and mass spectroscopy (Tables II–IV).

Spectroscopic Studies. Two well-resolved stretching modes for the terminal CO groups are observed in the infrared spectra of all the compounds (Table II) in accordance with the symmetry of $C_{3v}(A + E)$ for the $Cr(CO)_3$ groups. The expected two bands are at lower wavenumbers (15–21 cm^{-1}) than the corresponding bands for the arene precursors,[1,23] indicating a strengthening of the Cr–CO bond. Since compounds of metalated Cr(0) (d^6) have high basicity and those of Ti(IV) (d^0) have high Lewis acidity, transfer of electron density via a donor/acceptor type of interaction or electrostatic attraction is a strong possibility. Therefore, displacement of H by the $Ti(Cp)_2Cl$ entity leads to an increased residual electron density on the arene ring, resulting in lower wavenumbers for the carbonyl vibrations of **1**–**4**. The IR spectra of **9** and **10** also display two bands at lower wavenumbers, again indicating increased electron density on the arene ring. Because of

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Table II. Infrared and Mass Spectral Data for the Bimetallic Complexes Derived from Cp_2TiCl_2 and $Au(PPh_3)Cl$

	ν_{CO} (CH_2Cl_2),[a] cm^{-1} for $Cr(CO)_3$ fragment		
complex	A_1 (s)	E (s, br)	mass peaks, *m/e* (*I*, %)
1	1952	1872	427 (13) [M^+], 343 (7) [M^+ – 3CO], 278 (12) [–Cp], 148 (19) [$Ti(\eta^5-C_5H_5)Cl^+$], 130 (15) [$Cr(\eta^6-C_6H_6)^+$]
2	1958	1878	444 (14) [M^+], 360 (40) [M^+ – 3CO], 295 (8) [–Cp], 148 (60) [$Ti(\eta^5-C_5H_5)Cl^+$; $Cr(\eta^6-C_6H_6)^+$]
2[b]	1980	1916	
3	1949	1868	440 (9) [M^+], 356 (16) [M^+ – 3CO], 292 (11) [–Cp], 228 (15) [$Cr(\eta^6-C_6H_5Me)(CO)_3^+$], 148 (14) [$Ti(\eta^5-C_5H_5)Cl^+$], 144 (40) [$Cr(\eta^6-C_6H_5Me^+$]
5	1930	1850	
6	1953	1876	604 (9) [M^+], 520 (5) [M^+ – 3CO], 436 (9) [M^+ – 6CO], 228 (28) [$Cr(\eta^6-C_6H_5Me)(CO)_3^+$], 148 (8) [$Ti(\eta^5-C_5H_5)Cl^+$], 144 (40) [$Cr(\eta^6-C_6H_5Me)^+$]
7	1966	1889	
8	1970 (sh)	1902 (sh)	444 (35) [M^+], 360 (32) [M^+ – 3CO), 276 (53) [M^+ – 6CO], 224 (29) [$Cr(\eta^6-C_6H_4FC_6H_5)^+$], 205 (19) [$Cr(\eta^6-C_6H_5-C_6H_5)^+$], 152 (24) [$C_6H_5-C_6H_5^+$]
9	1951	1878	
10	1958 (vs)	1877	690 (11) [M^+], 606 (23) [M^+ – 3CO], 554 (16) [$Au(\eta^1-C_6H_4F)PPh_3^+$], 459 (31) [$AuPPh_3^+$], 262 (83) [$PPh_3^+$], 148 (3) [$Cr(\eta^6-C_6H_5F)^+$]

[a] Abbreviations: s (strong), vs (very strong), br (broad), sh (shoulder). [b] Spectrum obtained in hexane.

Table III. ^1H NMR Spectral Data for Bi- and Trimetallic Complexes Derived from Cp_2TiCl_2 and $Au(PPh_3)Cl$

		chem shift, δ, ppm (*J*, Hz)					
			arene[a] protons				
complex	solvent	C_5H_5	ortho [ortho′]	meta [meta′]	para	CH_2	CH_3
1	C_6D_6	5.76 (s, 10 H)	4.64 (dd, 2 H, *J* = 6.2, 1.2)	4.34 (t, 2 H, *J* = 6.2)	4.61 (dt, 1 H, *J* = 6.2, 1.2)		
2	C_6D_6	6.24 (s, 5 H) 5.55 (s, 5 H)	4.50 (m, 1 H)	3.82 (m, 1 H) [4.67 (m, 1 H)]	4.67 (m, 1 H)		
	CD_3COCD_3	6.80 (s, 5 H) 6.51 (s, 5 H)	5.46 (m, 1 H)	4.85 (m, 1 H) [5.71 (m, 1 H)]	5.71 (m, 1 H)		
3	C_6D_6	5.81 (s, 10 H)	4.80 (d, 2 H)	4.53 (d, 2 H)			1.68 (s, 3 H)
	$CDCl_3$	6.39 (s, 10 H)	5.03 (br s, 2 H)	4.87 (d, 2 H)			2.03 (s, 3 H)
4	C_6D_6	5.46 (s, 5 H) 5.29 (s, 5 H)	4.59 (m, 1 H) [4.76 (s, 1 H)]	4.26 (d, 1 H)	4.35 (d, 1 H)		1.73 (s, 3 H)
5	$CDCl_3$	6.28 (s, 10 H)				4.76 (s, 2 H)	2.22 (s, 3 H) 2.21 (s, 3 H) 2.13 (s, 6 H) 2.11 (s, 3 H)
	CD_3COCD_3	6.38 (s, 10 H)				4.66 (s, 2 H)	2.28 (s, 6 H) 2.18 (s, 3 H) 2.16 (s, 6 H)
6	C_6D_6	5.73 (s, 10 H)	4.58 (d, 4 H, *J* = 6.5)	4.48 (t, 4 H, *J* = 6.1)	4.58 (t, 2 H, *J* = 6.5)		
7	C_6D_6	5.79 (s, 10 H)	4.67 (dt, 4 H)	4.19 (d, 4 H)			1.66 (s, 6 H)
8	$CDCl_3$[b]		5.32 (m, 1 H)	4.96 (dt, 1 H) [5.59 (tq, 1 H)]	5.81 (dt, 1 H)		
			5.71 (dd, 2 H)	5.38 (t, 1 H)	5.44 (dt, 1 H)		
9	C_6D_6		5.28 (m, 2 H)	4.76 (t, 2 H)	4.59 (tt, 1 H)	7.45 (m, 6 H)[c] 6.97 (m, 9 H)[c]	
10	C_6D_6		4.68 (m, 1 H)	4.26 (m, 1 H) [4.94 (m, 1 H)]	5.38 (m, 1 H)	7.43 (br m, 6 H)[c] 6.96 (m, 9 H)[c]	

[a] Signals (*o*, *m*, *p*) were assigned relative to metal substituent; brackets denote position nearest to the nonmetal substituent. [b] First set of values denotes chemical shifts for protons in C_6H_4F part of molecule; second set denotes chemical shifts for C_6H_5. [c] $P(C_6H_5)_3$.

the higher electron density of the gold moiety (d^{10}), we inferred that in this instance a polarized covalent interaction between the arene ring and $Au(PPh_3)$ is more probable.

The general fragmentation pattern in the mass spectra (Table II) obtained for compounds 1–3 comprises the initial loss of all carbonyls, followed by loss of one of the two cyclopentadienyl rings on titanium to give the fragment ion $[Cr(\eta^1:\eta^6-C_6H_4R)Ti(\eta^5-C_5H_5)Cl]^+$. The Ti–C(arene) σ-bond is subsequently fragmented to afford the ions $[Cr(\eta^6-C_5H_4R)]^+$ and $[Ti(\eta^5-C_5H_5)Cl]^+$. The absence of a peak at an *m/e* value corresponding to the fragment $[Ti(\eta^6-C_6H_4R)(\eta^5-C_5H_5)Cl]^+$ or any ion with the unit Ti-($\eta^6-C_6H_4R$) confirms preferential rupture of the Ti–C(arene) σ-bond before the Cr–C(arene) π-bond. Less significant degradation paths for the molecular ions correspond to those reported by Nesmeyanov and co-workers[24] for bis(cyclopentadienyl) derivatives of titanium and are omitted. In contrast, the mass spectrum of 10 indicates the exact opposite, and fragmentation of the Cr–C(arene) π-bond precedes that of the Au–C(arene) σ-bond.

In the ^1H NMR spectra of 1–7 (Table III) the signals for the resonances of the protons of the cyclopentadienyl rings on the titanium uniformly occur at lower fields than the ring protons of the σ,π-bridged arene of the $Cr(CO)_3$ moiety and are shifted upfield from those reported for Cp_2TiCl_2.[25] The ^1H and ^{13}C (Table IV) NMR spectra of complexes 1, 3, and 5–7 show a singlet for the individual complexes in the region of δ 5.8 ppm (10 H) because of the

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Table IV. ^{13}C NMR Spectral Data[a] for Bi- and Trimetallic Complexes Derived from Cp_2TiCl_2 and $Au(PPh_3)Cl$

		chem shift								
				arene[b] carbon						
complex	solvent	C_{CO}	C_5H_5	ipso (F)	ipso	ortho	meta [meta′]	para	CH_2	CH_3
1	C_6D_6	235.7	118.0		107.4	104.1	91.6	95.4		
2	CD_3COCD_3	236.4	120.3	148.5 (d, $\underline{C}F$, $^1J_{CF}$ = 264.0)	unobsd	108.9 (d, $^3J_{CF}$ = 15.7)	89.5 [83.3, (d, $^2J_{CF}$ = 32.1)]	96.8 (d, $^3J_{CF}$ = 7.9)		
			119.6							
	C_6D_6	235.2	119.3	147.2 (d, $\underline{C}F$, $^1J_{CF}$ = 263.7)	112.6	107.2 (d, $^3J_{CF}$ = 15.1)	87.1 [80.7 (d, $^2J_{CF}$ = 31.5)]	93.3 (d, $^3J_{CF}$ = 7.4)		
3	C_6D_6	234.8	118.1		105.0	93.6	101.6			35.9
6	$CDCl_3$	234.7	116.8		108.5	106.0	104.6	103.7	62.8	14.4 14.1 13.8
7	C_6D_6	235.5	117.6		105.5	101.5	92.6	93.7		
8[c]	$CDCl_3$	231.6		144.9 (d, $\underline{C}F$, $^1J_{CF}$ = 261.9)	110.5 (d, $\underline{C}C$, $^2J_{CF}$ = 14.5)	90.2 (d, $^2J_{CF}$ = 21.9)	95.1 (d, $^2J_{CF}$ = 21.9)	93.1		
		230.5								
					106.8 (d, $C\underline{C}$, $^2J_{CF}$ = 4.8)	94.5 (d, $^4J_{CF}$ = 0.2)	93.2	85.2		
9[d]	C_6D_6	236.8								
10[d]	C_6D_6	235.8		151.83 (d, J_{CF} = 261)	93.9 (d, $^2J_{CF}$ = 261)	104.3 (d, $^3J_{CF}$ = 19.6)	93.6 (d, $^4J_{CF}$ = 7.0) [82.3 (d, $^2J_{CF}$ = 28.9)]	90.5 (s)		

[a] δ in ppm; J in Hz. [b] Assignment of resonances always relative to metal substituent; the prime denotes position nearest to the substituent F or CH_3. [c] First set of values denotes chemical shifts of carbons in C_6H_4F groups; second set denotes chemical shifts of carbons in C_6H_5 part of molecule. [d] Not uniquely assigned.

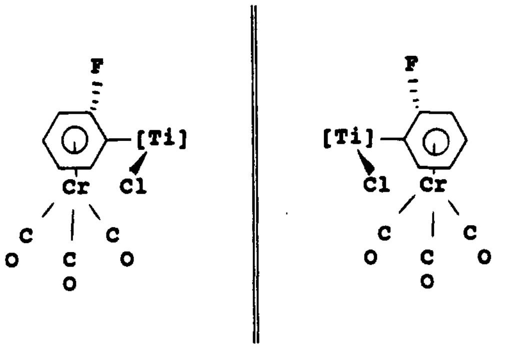

Figure 1. Planar chirality of **2**.

equivalent cyclopentadienyl rings on titanium. This differs from the corresponding spectra for **2** and **4**, where two distinct singlets, one for each cyclopentadienyl ring, are observed, indicating different environments. The nonequivalence of the two Cp rings is not unprecedented in the literature,[26] but explanations are valid for the specific compounds studied. Two possible reasons for the duplication of the Cp signals of **2** and **4** were considered. First, a barrier to rotation about the Ti–C_{sp^2} vector could give rise to different environments for the cyclopentadienyl rings. However, the occurrence of restricted rotation on steric grounds for **4** or on electronic grounds for **2** and **4**, and not for **5** and the others, seems unlikely. Furthermore, evidence against restricted rotation was found from a variable-temperature ^{1}H NMR study of **2**, the spectra of which, apart from signals due to decomposition, did not change significantly. Second, the cyclopentadienyl rings in **2** and **4** have become diastereotopic as a result of the unsymmetrically substituted arene ligand. A chiral plane exists in molecules of **2** and **4** (Figure 1), and the duplication of resonances was ascribed to the existence of a racemic mixture of two stereoisomers. Examples of organometallic complexes exhibiting planar chirality have been reported in the literature.[27] Attempts to separate these isomers by chromatography were unsuccessful. Even though the difference in chemical shift for the two resonances in the proton NMR spectrum is substantial, the two resonances in the ^{13}C NMR spectrum of **2** differ in chemical shifts by only 0.7 ppm in acetone-d_6 and by 1.8 ppm in benzene-d_6.

The ^{1}H and ^{13}C NMR results for the bimetallic and trimetallic complexes show similar trends, revealing very little change in the nature of the σ Ti–C(arene) bond on going from a complex with two metal units to one with three. The ^{1}H NMR spectra display the signals expected for substituted benzene rings,[28] i.e. an AA′BB′C pattern for **1**, an ABCD pattern for the ortho- and meta-disubstituted benzene in **2** and **4**, and an AA′BB′ pattern for the para-disubstituted benzene in **3**. Unfortunately, experimental data on the lithiated arene are limited because of its instability and the only documented ^{1}H NMR spectrum in THF at −20 °C shows multiplets at δ values of 5.21 and 4.89 ppm.[12b] In contrast, a ^{1}H NMR spectrum of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in THF, also at −20 °C, displays a singlet at δ 5.30 ppm. Extrapolation of results obtained in different deuterated solvents reveals that the arene proton resonances for the complexes $(\eta^6\text{-}C_6H_5X)Cr(CO)_3$ (X = H, Li, Cp_2TiCl) change with increasing field strength in the order H < Cp_2TiCl < Li.

The heterobimetallic complexes **9** and **10**, which have the $Au(PPh_3)$ unit σ-bonded to an arene carbon atom of the chromium tricarbonyl moiety, also show the trends in their proton and carbon resonances of the arene ring associated with the shielding effects of the titanium fragment above. Thus, the bridging benzene ligand is shielded by both the electron-poor Ti and the electron-rich Au when

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Table V. Fractional Coordinates (×10⁴) and Equivalent Thermal Factors (×10³ Å²) for $C_{19}H_{14}ClFO_3CrTi$ (Compound 2)

	x/a	*y/b*	*z/c*	U_{eq}[a]
Cr	1555 (1)	1386 (1)	2190 (1)	33 (1)
C(1)	−24 (9)	658 (7)	1978 (7)	39 (2)
O(1)	−1006 (6)	222 (5)	1844 (5)	56 (2)
C(2)	1779 (9)	674 (8)	1114 (7)	43 (2)
O(2)	1907 (7)	166 (6)	436 (5)	72 (2)
C(3)	606 (10)	2412 (8)	1399 (7)	44 (3)
O(3)	−24 (7)	3096 (6)	897 (5)	69 (2)
F	3563 (5)	3447 (4)	2734 (4)	56 (1)
C(4)	3165 (10)	2466 (7)	2995 (6)	40 (3)
C(5)	2147 (9)	2473 (8)	3463 (6)	43 (3)
C(6)	1738 (9)	1535 (9)	3812 (6)	41 (2)
C(7)	2383 (9)	606 (8)	3641 (6)	42 (2)
C(8)	3370 (9)	609 (7)	3146 (5)	34 (2)
C(9)	3866 (8)	1570 (7)	2819 (5)	32 (2)
Ti	5764 (1)	1527 (1)	2375 (1)	31 (1)
Cl	5592 (2)	−305 (2)	2037 (2)	49 (1)
C(10)	4811 (9)	1566 (8)	599 (6)	43 (2)
C(11)	4350 (10)	2452 (8)	999 (6)	42 (3)
C(12)	5441 (10)	3105 (8)	1423 (6)	52 (3)
C(13)	6583 (11)	2608 (9)	1273 (7)	53 (3)
C(14)	6165 (10)	1629 (9)	784 (6)	51 (3)
C(15)	7968 (9)	1844 (9)	3342 (7)	48 (3)
C(16)	7617 (10)	929 (8)	3691 (7)	51 (3)
C(17)	6578 (11)	1104 (9)	4102 (7)	57 (3)
C(18)	6319 (10)	2181 (10)	4031 (7)	55 (3)
C(19)	7166 (10)	2637 (8)	3568 (6)	48 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table VI. Fractional Coordinates (×10⁴) and Equivalent Thermal Factors (×10³ Å²) for $C_{20}H_{17}O_3ClCrTi$ (Compound 3)

	x/a	*y/b*	*z/c*	U_{eq}[a]
Cr	1334 (1)	1182 (1)	−1886 (1)	47 (1)
C(1)	712 (6)	882 (6)	−2669 (3)	74 (2)
O(1)	309 (4)	697 (5)	−3179 (3)	122 (2)
C(2)	2399 (6)	1187 (6)	−2398 (3)	71 (2)
O(2)	3078 (4)	1171 (5)	−2731 (3)	118 (2)
C(3)	1504 (6)	−131 (6)	−1755 (4)	68 (2)
O(3)	1621 (5)	−961 (4)	−1689 (3)	111 (2)
C(4)	1915 (5)	2327 (5)	−1188 (3)	47 (2)
C(5)	1351 (6)	2777 (5)	−1693 (3)	62 (2)
C(6)	417 (6)	2484 (6)	−1784 (3)	57 (2)
C(7)	47 (5)	1733 (5)	−1372 (3)	49 (2)
C(8)	623 (4)	1287 (5)	−864 (3)	41 (2)
C(9)	1592 (5)	1574 (4)	−750 (3)	39 (2)
Ti	2325 (1)	932 (1)	160 (1)	41 (1)
Cl	1588 (1)	−598 (1)	69 (1)	57 (1)
C(10)	2323 (6)	1436 (7)	1339 (3)	72 (2)
C(11)	2265 (7)	2279 (6)	927 (4)	71 (2)
C(12)	1403 (7)	2267 (6)	606 (3)	66 (2)
C(13)	917 (5)	1422 (6)	779 (3)	59 (2)
C(14)	1489 (6)	918 (6)	1247 (3)	64 (2)
C(15)	3551 (5)	−11 (6)	−373 (4)	63 (2)
C(16)	3544 (5)	903 (7)	−698 (4)	67 (2)
C(17)	3786 (5)	1602 (6)	−207 (5)	76 (2)
C(18)	3965 (5)	1105 (7)	415 (4)	76 (3)
C(19)	3803 (5)	146 (7)	304 (4)	71 (2)
C(20)	−143 (6)	2987 (6)	−2326 (4)	98 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

compared with the unsubstituted arene ligand. The tendency of transition-metal fragments to exert a shielding effect on the protons of the bridging arene ligand was also observed for Cr–Mn[1] and Cr–Fe[29] combinations.

The perspective drawings of molecules 2 and 3 with the atomic numbering scheme used are shown in Figures 2 and 3, respectively. A drawing of projections on the benzene planes of the two molecules 2 and 3 in Figure 4 displays the relative conformations of the arene–Cr(CO)₃ moiety.

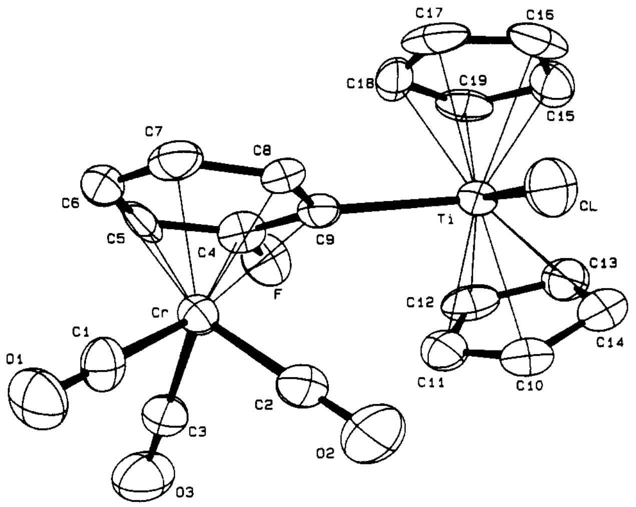

Figure 2. Perspective drawing of the molecular structure of **2**.

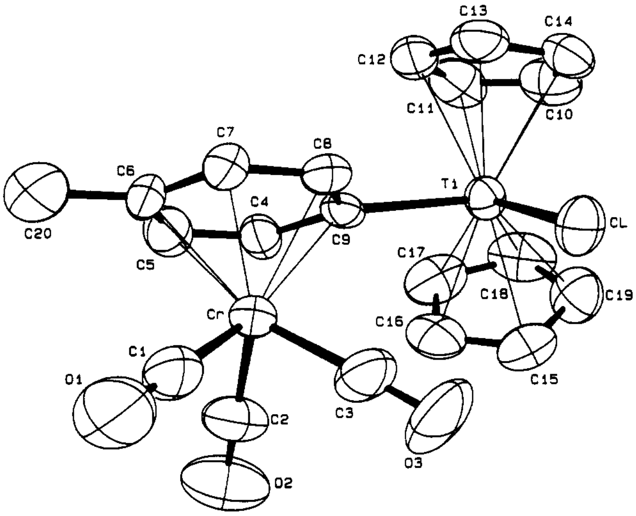

Figure 3. Perspective drawing of the molecular structure of **3**.

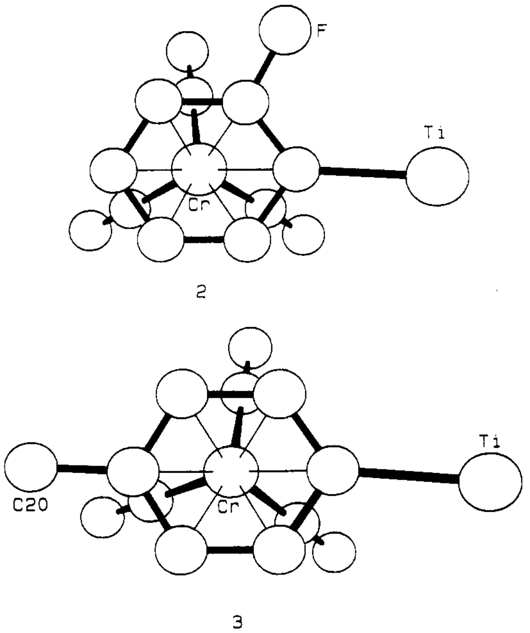

Figure 4. View of **2** and **3** along the Cr–arene bond.

Fractional atomic coordinates and selected and averaged bond lengths and angles for 2 and 3 are given in Tables V–VII, respectively. The points CNT1, CNT2, and CNT3

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Table VII. Selected Bond Lengths (Å) and Angles (deg) for 2 and 3 (Averaged)

	2 (*o*-F)	3 (*p*-Me)
	Bond Distances	
Ti–C_{Cp}	2.367 (9)	2.382 (7)
Ti–C(9)	2.217 (8)	2.213 (6)
Ti–CNT2	2.053 (10)	2.076 (9)
Ti–CNT3	2.060 (10)	2.069 (9)
Ti–Cl	2.333 (3)	2.338 (2)
C_{arene}–C_{arene}	1.398 (12)	1.407 (9)
C(5)–C(6)	1.381 (12)	1.391 (9)
C(8)–C(9)	1.431 (11)	1.441 (8)
Cr–$C_{carbonyl}$	1.812 (10)	1.804 (8)
C–O	1.161 (10)	1.156 (8)
C(4)–F	1.374 (9)	
C(6)–C(20)		1.478 (8)
	Bond Angles	
CNT2–Ti–CNT3	132.4 (5)	132.2 (4)
C(9)–Ti–Cl	93.6 (2)	94.8 (2)
CNT2–Ti–C(9)	109.8 (5)	101.8 (4)
CNT3–Ti–C(9)	100.6 (5)	107.3 (4)
CNT2–Ti–Cl	106.0 (5)	106.9 (4)
CNT3–Ti–Cl	107.6 (5)	107.5 (4)

are the centroids of the arene and two Cp rings, respectively.

The general geometry of **2** and **3** is not without unusual structural features but is in part comparable with those of Cp_2TiCl_2[30] and (π-arene)$Cr(CO)_3$.[31] The titanium atom is displaced from the plane of the η^6-arene ring in **2** by 0.45 (1) Å and in **3** by 0.288 (3) Å, and the fluoro substituent is in an anti configuration with respect to the chloro ligand on the titanium. The conformations of the tripodal moieties (arene–$Cr(CO)_3$) require comparison and some comments. Three different orientations for the $Cr(CO)_3$ tripod with respect to an ortho-substituted arene ligand have been recorded,[31,32] of which the arene ring in **2** adopts the fully staggered orientation, the value of the C(2)–Cr–CNT1–C(9) torsion angle being 32(1)°. The para-substituted arene ring in **3** adopts a distorted staggered conformation which is the expected compromise orientation (vide supra) for two "electron-donating substituents"[31,33] in the 1,4-positions on the arene ring. The C(3)–Cr–CNT1–C(9) torsion angle is –20 (1)°, and the deviation from a syn-eclipsed arrangement relative to titanium is 41 (1)°. The "open clamshell" conformation typical for Cp_2MXY[30] species is reflected by the dihedral angles formed by the least-squares planes for the two coordinating Cp rings in each structure: 49 (1)° in **2** and 50 (1)° in **3**.

The molecular parameters involving C(9) reflect some interactions that need to be addressed. The C(8)–C(9) bond distance is significantly longer than average C_{arene}–C_{arene} bond distances of 1.402 (12) Å (1.431 (11) and 1.441 (8) Å for **2** and **3**, respectively). The C(9)–Ti bond distance is shorter than the observed C(sp^2,phenyl)–Ti bond distance of 2.27 Å for $Cp_2Ti(Ph)_2$[34] but is comparable to the 2.216 Å recorded for $[\{Cp_2Ti(p\text{-}CH_3C_6H_4)\}_2]$[35] (2.217 (9) and 2.213 (6) Å for **2** and **3**, respectively). On the other hand, the C(9)–Ti bond distances correlate well with the reported distances of 2.21 (2) Å observed for the C(sp^3,methyl)–Ti bond of $(\eta^5\text{-}C_9H_7)_2Ti(CH_3)_2$[36] and 2.216 (2) Å for $(MeCp)_2Ti(CH_2OCH_3)Cl$.[37] Furthermore, the small value for the endocyclic bond angle C(4)–C(9)–C(8) (111.3 (7) and 114.6 (6)° for **2** and **3**, respectively) can be understood in terms of the effect of the electropositive Ti atom.[38] The resulting increase manifested in the C(4)–C(9)–Ti bond angle (128.0 (7) and 127.6 (5)° for **2** and **3**, respectively)—trans to the Cl ligand—and the effect of the π-coordinated Cr fragment on the significant distortion around C(9) are not fully appreciated. The Cr–C(9) distances of 2.333 (8) and 2.278 (5) Å for **2** and **3**, respectively, are also significantly larger than the other Cr–C_{arene} distances (2.203 (9) Å, averaged). These effects, as well as the bond angle vs electronegativity correlations of bridging phenyl ligands in heterobimetallic systems, are still under further investigation.

Conclusion. Lithiated arenes of chromium are effective reagents for the synthesis of heterobimetallic complexes when treated with substrates which have halogen ligands. The strong nucleophilicity of these metalated arenes is ascribed to a highly localized negative charge on the arene ring and on the metalated carbon. Noteworthy is the shielding effect observed in the ^1H NMR spectra for the bridging arene ligand due to both the electron-poor titanium and the electron-rich gold fragment. This indicates a polarization of the σ-bond toward the arene ligand and is also supported by structural features around the σ-bonded carbon atom of the arene ligand. We ascribe the similarity of the spectroscopic results for combinations of the (arene)chromium fragment with early (Ti) and late (Au) metal fragments to differences in the nature of the arene–metal σ-bond, the titanium linkage being possibly of a more electrostatic nature and the gold representing a more covalent interaction.

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Registry No. **1**, 138260-95-4; **2**, 138260-96-5; **3**, 138260-97-6; **4**, 138260-98-7; **5**, 138285-61-7; **6**, 138260-99-8; **7**, 138261-00-4; **8**, 138261-01-5; **9**, 138261-02-6; **10**, 138261-03-7; $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, 12082-08-5; $(\eta^6\text{-}C_6H_5F)Cr(CO)_3$, 12082-05-2; $(\eta^6\text{-}C_6H_5Me)Cr(CO)_3$, 12083-24-8; $(\eta^6\text{-}C_6Me_6)Cr(CO)_3$, 12088-11-8; Cp_2TiCl_2, 1271-19-8; $Au(PPh_3)Cl$, 14243-64-2.

Supplementary Material Available: Tables listing anisotropic thermal parameters, hydrogen fractional coordinates and isotropic thermal parameters, and bond angles and distances for **2** and **3**, ^1H NMR, IR, and mass spectra for **1**, ^1H and ^{13}C NMR spectra for **2**, ^1H NMR and mass spectra for **6** and **8**, and ^1H and ^{13}C NMR spectra for **9** (20 pages); tables of calculated and observed structure factors for **2** and **3** (18 pages). Ordering information is given on any current masthead page.

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