Heterobimetallic Complexes with Phenylcyclopentadienyl Ligand: Syntheses and Structures of Tricarbonylchromium−η^6,η^5-Phenylcyclopentadienyl−Transition Metal Complexes[1]

Changtao Qian,* Jianhua Guo, and Jie Sun

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,
354 Fenglin Lu, Shanghai, 200032, China

Jian Chen and Peiju Zheng

Center of Analysis and Measurement, Fudan University, Shanghai, 200433, China

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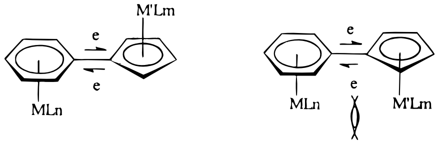
A new synthetic method of heterobimetallic complexes bridging with a π,π-phenylcyclopentadienyl ligand, tricarbonylchromium−η^6,η^5-phenylcyclopentadienyl−transition metal complexes, was developed through the reactions of (η^6-$C_6H_5C_5H_5$)Cr(CO)$_3$ or its sodium salt with transition metal complexes. The method is suitable for most transition metal elements with the advantages of easy manipulation, mild reaction conditions, and moderate to high yields. As indicated by ^{1}H NMR spectra, the interactions between the two π systems of phenyl and cyclopentadienyl rings were weak. X-ray crystal structures of seven complexes were studied. Compound **23**, [η^6-C_6H_5Cr(CO)$_3$]$_2C_{10}H_{10}$, crystallizes in orthorhombic space group *Pbca* with cell constants $a = 29.616(8)$ Å, $b = 12.861(5)$ Å, $c = 12.397(7)$ Å, $V = 4721(6)$ Å^3, $Z = 8$, $R = 0.045$, and $R_w = 0.045$. Compound **3**, (η^6-$C_6H_5C_9H_7$)Cr(CO)$_3$, crystallizes in monoclinic space group $P2_1/c$ with cell constants $a = 7.901(3)$ Å, $b = 14.799(2)$ Å, $c = 12.917(2)$ Å, $\beta = 99.72(2)°$, $V = 1488.7(4)$ Å^3, $Z = 4$, $R = 0.044$, and $R_w = 0.051$. Compound **7**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ti(CO)$_2$(η^5-C_5H_5), crystallizes in monoclinic space group $P2_1/c$ with cell constants $a = 12.361(4)$ Å, $b = 12.487(6)$ Å, $c = 12.531(7)$ Å, $\beta = 93.48(4)°$, $V = 1930$ Å^3, $Z = 4$, $R = 0.047$, and $R_w = 0.048$. Compound **13**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Mo(CO)$_3$Br, crystallizes in monoclinic space group $P2_1/c$ with cell constants $a = 14.685(2)$ Å, $b = 8.509(3)$ Å, $c = 14.960(3)$ Å, $\beta = 104.46(1)°$, $V = 1810.0(7)$ Å^3, $Z = 4$, $R = 0.037$, and $R_w = 0.037$. Compound **19**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_9H_6$)Mn(CO)$_3$, crystallizes in triclinic space group P_{-1} with cell constants $a = 11.660(4)$ Å, $b = 12.578(5)$ Å, $c = 6.987(2)$ Å, $\alpha = 100.03(3)°$, $\beta = 104.19(2)°$, $\gamma = 71.99(3)°$, $V = 939.3(6)$ Å^3, $Z = 2$, $R = 0.048$, and $R_w = 0.065$. Compound **21**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ru(PPh$_3$)$_2$Cl, crystallizes with one molecule of EtOH in triclinic space group P_{-1} with cell constants $a = 14.033(4)$ Å, $b = 16.163(6)$ Å, $c = 10.411(3)$ Å, $\alpha = 104.22(3)°$, $\beta = 103.50(2)°$, $\gamma = 90.81(3)°$, $V = 2219(1)$ Å^3, $Z = 2$, $R = 0.081$, and $R_w = 0.096$. Compound **22**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Co(CO)$_2$, crystallizes in orthorhombic space group $P2_12_12_1$ with cell constants $a = 15.083(5)$ Å, $b = 16.391(5)$ Å, $c = 6.351(4)$ Å, $V = 1570(1)$ Å^3, $Z = 4$, $R = 0.036$, and $R_w = 0.039$. The *trans* configurations of the two metal atoms in these molecules were found as expected; the phenyl and cyclopentadienyl or indenyl rings in the molecules were found to be not coplanar.

Introduction

Heterobimetallic complexes incorporating hydrocarbons as bridges between metal atoms have become increasingly interesting.[2,3] With two metal atoms in close proximity, the synergism of two different metal centers in these compounds may generate unique reaction patterns or enhanced reactivity. Considering the diverse reactivity and wide range applications of (π-arene)[4,5] and cyclopentadienyl transition metal complexes,[6] heterobimetallic complexes containing both types of species which were bridged by hydrocarbon ligands are especially interesting. Heterobimetallic complexes with a bridging π,π-phenylcyclopentadienyl ligand are very typical ones of this class (Scheme 1).

Scheme 1



In these complexes, two π systems were combined closely. The possible electronic interactions through the bridging ligand or synergism between the two proximate organometallic species may produce novel properties. Because (π-arene)Cr(CO)$_3$ are representative π-arene complexes,[7−9] we intend to synthesize

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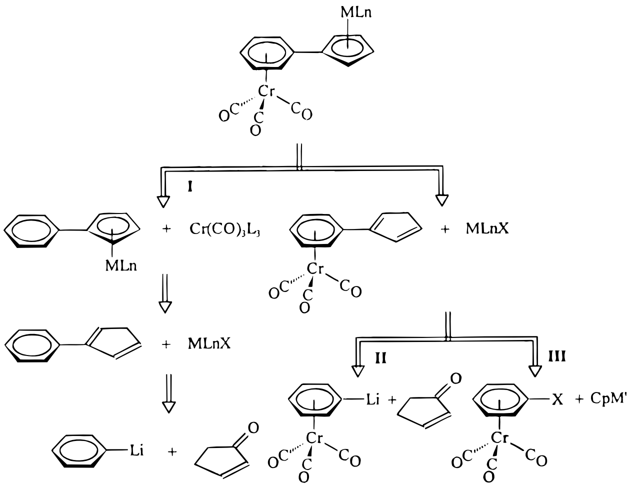
S0020-1669(95)01630-2 CCC: $14.00

Scheme 2



Cp=C$_5$H$_5$

tricarbonylchromium—η^6,η^5-phenylcyclopentadienyl—transition metal complexes.

There are three possible synthetic routes (as shown in Scheme 2). Compared with route III, routes I and II are more complicated and forcing reaction conditions are needed.[10−13] We will introduce later in this paper that route III is a general method for the syntheses of these compounds, with advantages of easy manipulation, mild reaction conditions, and moderate to high yields.

Results and Discussion

Synthesis. The synthetic methods of some tricarbonylchromium—η^6,η^5-phenylcyclopentadienyl—transition metal complexes were summarized in Scheme 3.

(η^6-$C_6H_5C_5H_5$)Cr(CO)$_3$ (**1**) can be prepared in excellent yield by nucleophilic substitution between (η^6-C_6H_5F)Cr(CO)$_3$ and CpK, as reported by F. Gottardi et al.[14] Though **1** is unstable in solution at room temperature, it can be stored in solid state at low temperature for several days. **1** reacted with NaH in THF at 0 °C to produce the corresponding sodium salt (**2**). 3-[(Tricarbonylchromio) phenyl]indene (**3**)[14] and its sodium salt (**4**) could be obtained similarly. When **2** was treated with equimolecular CpTiCl$_3$ or CpZrCl$_3$·DME, complexes Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ti(η^5-C_5H_5)Cl$_2$ (**5**) and Cr(CO)3(η^6,η^5-C_6H_5-C_5H_4)Zr(η^5-C_5H_5)Cl$_2$ (**6**) were formed. It is interesting to find that **5** was a green powder. As most Ti(IV) organometallic complexes are red, the special color of **5** may arise from unclear interactions between Ti and Cr atoms.[15] The color of **6** was yellow as expected. When **5** was treated with Mg/HgCl$_2$ under carbon monoxide atmosphere, a Ti(II) carbonyl complex (**7**), Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ti(CO)$_2$(η^5-C_5H_5), was obtained which was a very air-sensitive red solid.

2 reacted with M(CO)$_3$(RCN)$_3$ (M = Cr, Mo, W; R = Me, Et) to produce compounds **8**, **9**, and **10**, respectively, which were used as solutions without purification. Methylation, bromination, and nitrosolation of these sodium salts were carried out by reacting them with CH$_3$I, Br$_2$, and Diazald. For Mo and W, expected products can be obtained in moderate yields. For Cr only nitrosolation was successfully processed.

2 reacted with [Mn(CO)$_4$Br]$_2$ to produce compound **18**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Mn(CO)$_3$. The synthesis of **18** has been completed through route I shown in Scheme 2 by two groups.[11,13] Compared with their methods, our synthetic method is superior in the following aspects: mild reaction conditions, easy manipulation, and high yield. In addition, when [Mn(CO)$_4$Br]$_2$ was treated with **4**, a heterobimetallic compound with the bridging phenylindenyl ligand ((tricarbonylchromio)-η^6,η^5-phenylindenyl))tricarbonylmanganese (**19**) was obtained (Scheme 4).

It is difficult to prepare **19** by following the literature procedure for **18**, for complicated mixtures may form. Indenyl complexes are known to be different from cyclopentadienyl transition metal complexes in many aspects.[16−18] The synthesis of other tricarbonylchromium—η^6,η^5-phenylindenyl—transition metal complexes with a similar method is in progress.

Considering the unique applications of CpRu(PPh$_3$)$_2$Cl in organic synthesis,[19] we are interested in the synthesis of compound **21**, Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ru(PPh$_3$)$_2$Cl. Following the literature procedure for the preparation of CpRu(PPh$_3$)$_2$Cl[20] (**1**), RuCl$_3$·3H$_2$O, excess PPh$_3$, and EtOH were mixed and heated to reflux for several hours. A reaction did occur with the color of the mixture changing from dark green to bright yellow. But compound **20** instead of **21** was obtained after workup. The replacement of the arene coordinated to Cr(CO)$_3$ by PPh$_3$ in the reaction process can explain this result. It seemed a milder reaction condition was necessary for **21**. When **1** and RuCl$_2$(PPh$_3$)$_3$ were mixed in benzene and stirred at room temperature, **21** indeed formed. We also found that addition of zinc powder to the reaction system can speed up this reaction.[21]

A Cr/Co complex (**22**), Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Co(CO)$_2$, can also be prepared by reaction between **1** and Co$_2$(CO)$_8$ using *t*-BuCH=CH$_2$ as a hydrogen abstractor.[22,23] The reaction needed gentle reflux in CH$_2$Cl$_2$. Though dimerization of some **1** took place in the process, the yield of **22** was still satisfactory.

The synthesis of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Pd(η^3-C_3H_5), from the reaction of **2** with (η^3-C_3H_5)Pd$_2$Cl$_2$, was unsuccessful. The product was too unstable to be isolated.

In summary, starting from **1**, tricarbonylchromium—η^6,η^5-phenylcyclopentadienyl—transition metal complexes of some group IVB, VIB, VIIB, and VIII elements were successfully synthesized.

Spectra. The infrared spectra of these complexes display the anticipated ν_{CO} stretching bands of virtual A and E symmetry of the Cr(CO)$_3$ moiety.[24] To our surprise, though the metal atoms connected to the Cp′ ring (Cp′ = C$_5$H$_4$) are quite different, the ν_{CO} values were almost the same. In **1**, the ν_{CO}(THF) were 1960 cm^{-1} (A) and 1886 cm^{-1} (E) for the local C_{3v} symmetry of Cr(CO)$_3$. Except for compound **5**, very small frequency shifts (about 3 cm^{-1}) were observed for A and E peaks of all other

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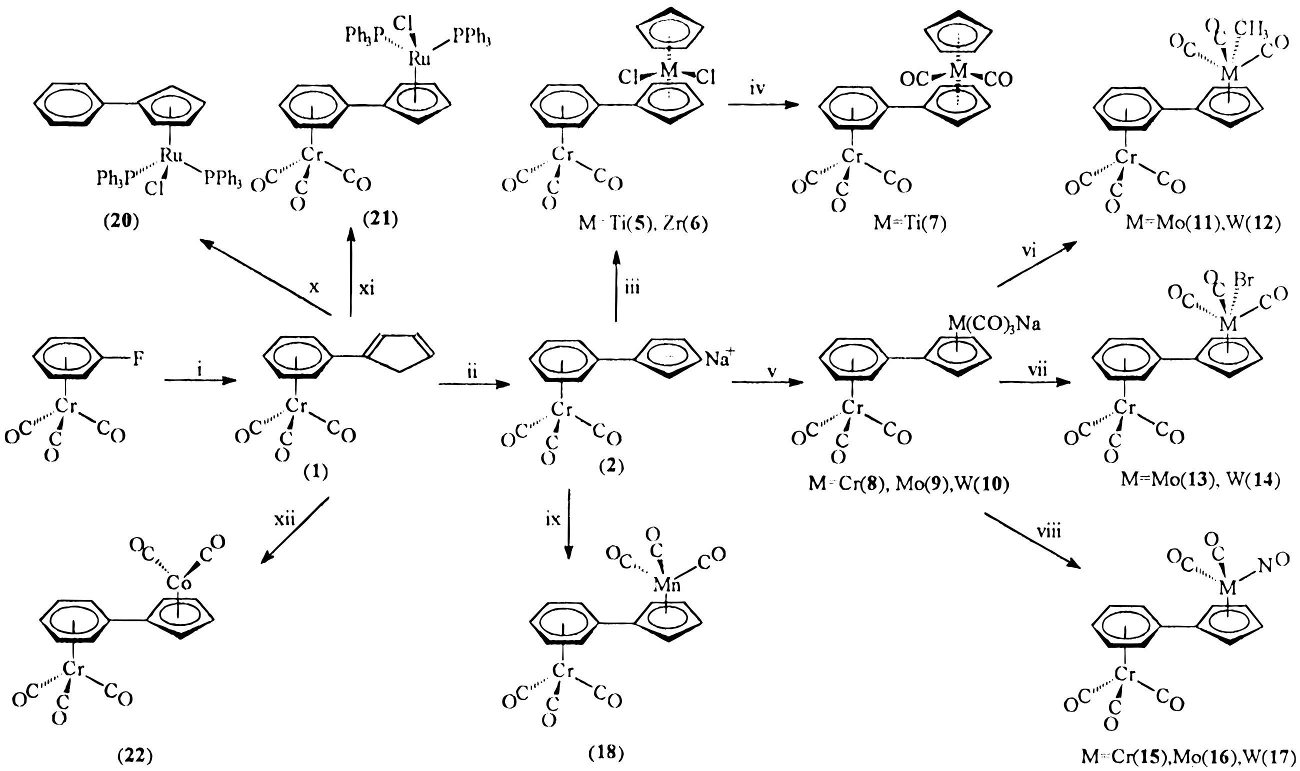
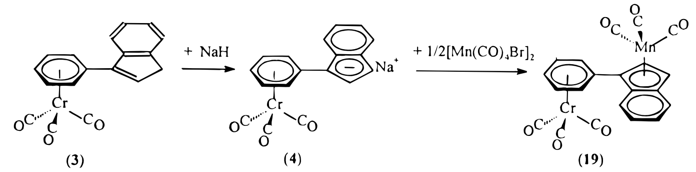
Scheme 3. Summary of the Synthesis of Tricarbonylchromium−η^6,η^5-Phenylcyclopentadienyl−Transition Metal Complexes[a]



[a] (i) CpK, DME, 0 °C; (ii) NaH, THF, 0 °C; (iii) $CpTiCl_3$ or $CpZrCl_3$·DME, THF, rt; (iv) Mg, $HgCl_2$, CO; (v) $M(CO)_3(RCN)_3$, rt; (vi) MeI, 0 °C; (vii) Br_2/THF, −78 °C → rt; (viii) Diazald, 0 °C → rt; (ix) $[{}^1/_2Mn(CO)_4Br]_2$, rt; (x) $RuCl_3·3H_2O$, PPh_3 (excess), EtOH, reflux; (xi) $RuCl_2(PPh_3)_3$, Zn, benzene, rt; (xii) *t*-BuCH=CH_2, $Co_2(CO)_8$, CH_2Cl_2, reflux.

Scheme 4



complexes. For **5**, a 19 cm^{-1} to high-frequency shift for A and a 28 cm^{-1} to low-frequency shift for E were found. It might arise from unclear interaction between Cr and Ti atoms. There were some overlaps of the ν_{CO} stretching bands for carbonyls attached to other metal atoms in some cases. For instance, ν_{CO} of the $Mo(CO)_3Me$ moiety in **11** was expected to appear as three peaks because of its local C_s symmetry.[25] But only two bands at 2018 and 1927 cm^{-1} were found. The ν_{NO} in **15**−**17** were also obviously found at 1699, 1670, and 1664 cm^{-1} for Cr, Mo, and W, respectively.

Under EI mass spectra conditions, the carbonyls in these compounds were found to dissociate successively from the molecular ion and then two metal atoms were lost one by one from the ligand. The ligand ion can still easily lose C_2H_2 to produce corresponding fragments.

The ^{1}H NMR spectra of these complexes were expected to display a AA′BB′X pattern for the protons on the substituted η^6-phenyl ring and an AA′BB′ pattern for the protons on the η^5-Cp′ ring. In $CDCl_3$ or THF-d_8, the protons on the phenyl rings in most of these complexes were consistent with the adoption of a substituted η^6-arene bonding mode, displaying a characteristic AA′BB′X pattern at room temperature. But the protons on the Cp′ ring usually resonated as two singlets. In some cases there was some overlap for the chemical shifts of protons on the phenyl and Cp′ rings. For example, in THF-d_8, the ortho, para, and meta resonances of the phenyl ring of **5** appear at 5.51 (t), 5.59 (t), and 6.09 (d) ppm, while the protons on the Cp′ ring resonances appeared at 6.64 (s) and 6.78 (s) ppm. The resonance of the protons on the Cp ring are at 6.60 (s) ppm. The difference between the chemical shifts of protons on Cp′ and Cp was small. The chemical shifts of the α and β position protons on Cp′ in **20** and **21** showed remarkable difference, which were 3.34 (s, βH) and 4.59 (s, αH) for **21** and 3.52 (s, βH) and 4.63 (s, αH) for **22**, respectively. These results are similar to those of some literature reports,[26] such as $(CH_3C_5H_4)RuCl(PPh_3)_2$ (3.30, 4.0 ppm) and $(CH_3COC_5H_4)$-$RuCl(PPh_3)_2$ (3.6, 5.1 ppm). The unusual differences may be ascribed to a special property of ruthenium metal.[27] From **20** to **21**, a downfield shift of 0.18 ppm for the β protons and 0.04 ppm for the α protons was observed. It implied that complexation of $Cr(CO)_3$ to the phenyl ring only results in a small change for the chemical shifts of Cp′ protons. Similar results were also found for other compounds. The small differences indicate that interactions between the two organometallic moieties are quite weak.

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Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

formula	$C_{28}H_{20}O_6Cr_2$ (**23**)	$C_{18}H_{12}CrO_3$ (**3**)	$C_{21}H_{14}O_5CrTi$ (**7**)	$C_{17}H_9O_6BrCrMo$ (**13**)	$C_{21}H_{11}O_6CrMn$ (**19**)	$C_{50}H_{39}O_3ClCrP_2Ru$ (**21**)	$C_{16}H_9O_5CrCo$ (**22**)
formula weight	556.45	328.29	446.23	537.09	466.25	984.39	392.17
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	P_{-1} (No. 2)	P_{-1} (No. 2)	$P2_12_12_1$ (No. 19)
a, Å	29.616(8)	7.901(3)	12.361(4)	14.685(2)	11.660(4)	14.033(4)	15.083(5)
b, Å	12.861(5)	14.799(2)	12.487(6)	8.509(3)	12.578(5)	16.163(6)	16.391(5)
c, Å	12.397(7)	12.917(2)	12.531(7)	14.960(3)	6.987(2)	10.411(3)	6.351(4)
α, deg					100.03(3)	104.22(3)	
β, deg		99.72(2)	93.48(4)	104.46(1)	104.19(2)	103.50(2)	
γ, deg					71.99(3)	90.81(3)	
V, Å^3	4721(6)	1488.7(4)	1930(1)	1810.0(7)	939.3(6)	2219(1)	1570(1)
Z	8	4	4	4	2	2	4
d_{calc}, g cm^{-3}	1.565	1.465	1.535	1.971	1.648	1.473	1.659
μ(Mo Kα), cm^{-1}	9.64	7.569	10.06	35.36	12.87	7.64	17.69
T, °C	20	20	20	20	20	20	20
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
R [a]	0.045	0.044	0.047	0.037	0.048	0.081	0.036
R_w [b]	0.045	0.051	0.048	0.037	0.065	0.096	0.039

[a] $R = \sum_{i=1}^{n}(|F_o|_i - |F_c|_i)/\sum_{i=1}^{n}|F_o|_i$. [b] $R_w = [\sum_{i=1}^{n}w_i(|F_o|_i - |F_c|_i)^2/\sum_{i=1}^{n}w_i|F_o|^2]^{1/2}$.

Scheme 5

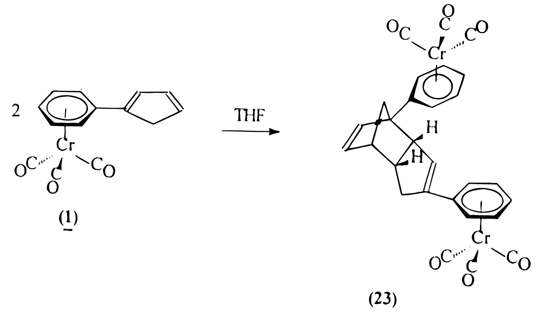

Table 2. Selected Bond Lengths (Å) and (deg) of **23**

Cr(1)−C(17)	2.235(8)	Cr(1)−C(20)	2.193(9)
Cr(1)−C(26)	1.85(1)	Cr(2)−C(1)	2.228(9)
Cr(2)−C(4)	2.248(7)	Cr(2)−C(23)	1.83(1)
O(1)−C(23)	1.159(10)	O(6)−C(26)	1.138(10)
C(4)−C(7)	1.50(1)	C(8)−C(9)	1.53(1)
C(9)−C(10)	1.50(1)	C(10)−C(11)	1.32(1)
C(14)−C(15)	1.51(1)	C(15)−C(16)	1.33(1)
C(15)−C(17)	1.48(1)		
C(17)−Cr(1)−C(26)	95.3(3)	C(18)−Cr(1)−C(26)	87.8(3)
C(26)−Cr(1)−C(27)	87.5(4)	C(3)−Cr(2)−C(25)	94.5(4)
C(4)−Cr(2)−C(25)	94.6(3)	C(23)−Cr(2)−C(24)	89.5(4)
C(3)−C(4)−C(5)	116.9(7)	C(11)−C(7)−C(12)	106.0(6)
C(7)−C(8)−C(9)	94.2(6)	C(9)−C(13)−C(14)	117.0(8)
C(14)−C(15)−C(16)	111.6(7)	C(18)−C(17)−C(22)	116.4(8)
C(9)−C(13)−H(15)	102.9		

Crystal Structures. X-ray crystal structures of seven complexes were determined. Crystallographic data are listed in Table 1.

For the use of structural comparison, we tried to determine the crystal structures of **1** and **3**. But **1** was unstable in solution and easily dimerized to 1,4-bis[(tricarbonylchromio)phenyl]-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**23**) after recrystallization in THF/hexane at 0 °C (Scheme 5).

Shown in Figure 1 is an ORTEP diagram of the molecular structure of **23**. Selected bond distances and bond angles are listed in Table 2.

As can be seen from Figure 1, **23** is the *endo* Diels−Alder addition product of **1**. The angle of C(9)−C(13)−C(14) is 117.0(8)°. Taking two phenyl rings as reference, we found that the two Cr(CO)$_3$ fragments are both in peripheral positions, avoiding strong steric interaction. The structural parameters of the two Cr(CO)$_3$ moieties are very similar. The two phenyl rings were outward distorted by the substituent as indicated by the δd value proposed by Hunter.[28,29] One apparent difference between the two (arene)Cr(CO)$_3$ moieties is the relative (arene)-Cr(CO)$_3$ conformations. Diverse conformations of (arene)Cr(CO)$_3$ attracted much attention due to its significant influence on the regioselectivity of nucleophilic/electrophilic attack on arene.[9] For monosubstituted arene, the conformation of (arene)-Cr(CO)$_3$ is either syn-eclipsed for an electron-withdrawing substituent or anti-eclipsed for an electron-donating substituent. As can be seen from Figure 2, Cr(1)(CO)$_3$ has approximately an anti-eclipsed conformation, while Cr(2)(CO)$_3$ is obviously a staggered conformation. The reason for the difference is unclear, but may arise from the different steric environments.

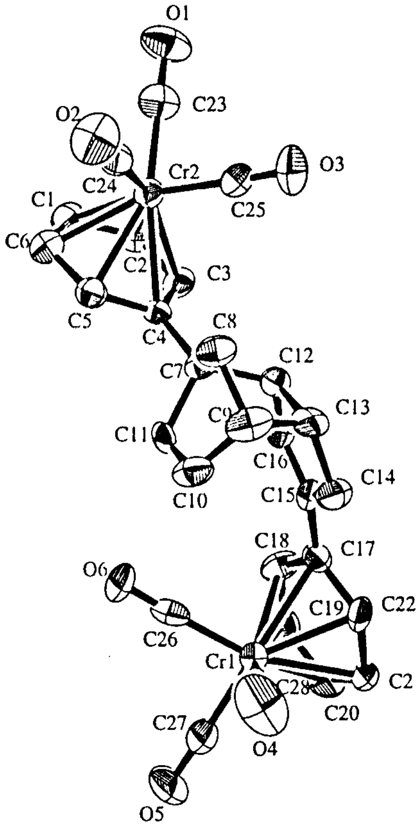

Figure 1. Molecular structure of compound [η^6-$C_6H_5Cr(CO)_3]_2C_{10}H_{10}$ (**23**).

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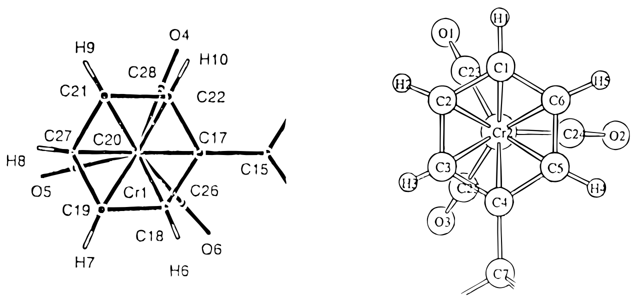

Figure 2. Top view of (arene)Cr(CO)$_3$ of **23**.

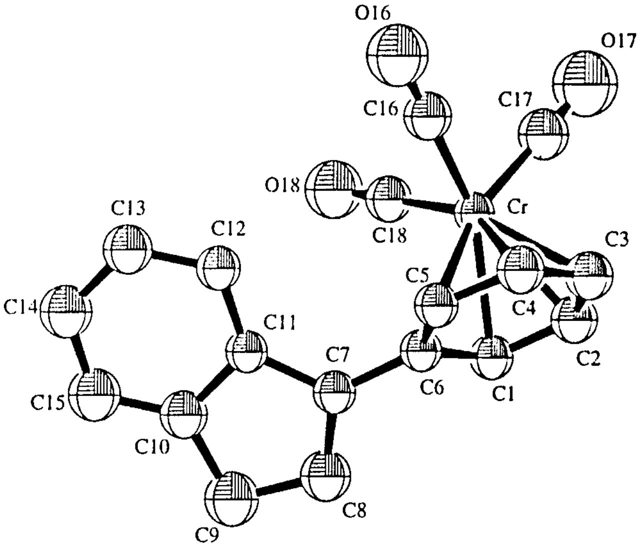

Figure 3. Molecular structure of compound Cr(CO)$_3$-η^6-$C_6H_5C_9H_7$ (**3**).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of **3**

Cr−C(3)	2.213(4)	Cr−C(6)	2.242(4)
Cr−C(16)	1.831(5)	C(16)−O(16)	1.157(6)
C(6)−C(7)	1.472(7)	C(7)−C(8)	1.343(6)
C(1)−Cr−C(18)	92.1(2)	C(6)−Cr−C(18)	89.1(2)
C(16)−Cr−C(17)	88.2(2)	C(1)−C(6)−C(5)	118.4(4)
C(8)−C(7)−C(11)	109.2(4)	C(8)−C(9)−C(10)	102.5(4)
H(91)−C(9)−H(92)	107.0(4)	Cr−C(16)−O(16)	179.4(5)

The dihedral angle between the plane of C(12)−C(16)−C(15)−C(14) and C(17)−C(18)−C(19)−C(20)−C(21)−C22 was found to be 14.99°. Thus the conjugation between C(15)−C(16) and the C(17)−C(18)−C(19)−C(20)−C(21)−C(22) ring was small.

Crystals of 3-[(tricarbonylchromio)phenyl]indene (**3**) suitable for X-ray analysis were obtained from a THF/hexane solution. The ORTEP diagram of **3** is shown in Figure 3, while selected bond parameters are listed in Table 3.

The relative (arene)Cr(CO)$_3$ conformation of **3** is staggered. The special conformation may arise from the bulky substituent on the phenyl ring. An outward distortion of the phenyl ring was also found. The dihedral angle between the C_6H_5 and indenyl rings is 47.30°. The structure features do not result in steric interactions between the metal atom and the substituent; the distances between chromium and the subsituent atoms are longer than 3.2 Å.

Crystals of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ti(CO)$_2C_5H_5$ (**7**) suitable for X-ray analysis were obtained from a THF/hexane solution. The ORTEP diagram of **7** is shown in Figure 4, and selected bond distances and bond angles are listed in Table 4.

As expected, in **7** the two metal atoms lie opposite the bridge due to the steric effects. A staggered conformation of Cr(CO)$_3$ relative to the phenyl ring was found. It may arise from the bulky substitutent of (Cp′)CpTi(CO)$_2$. The (Cp′)CpTi(CO)$_2$ moiety adopts an eclipsed configuration as found in Cp$_2$Ti(CO)$_2$.[30] The OC−Ti−CO angle in the (CO)$_2$Ti(Cp′)Cp moiety is nearly 90° (88.9(3)°). The dihedral angle between Cp′ and Cp is 38.34°. In contrast to the outward distortion of the phenyl ring, an inward distortion of the Cp′ ring was found. Due to the Cp′ being linked on (arene)Cr(CO)$_3$, the C−C bond lengths and the distances between Ti and the carbon atoms of the Cp′ ring were longer than those of the Cp ring. The following data show this trend: $[(C-C)_{Cp}]_{av}$, 1.38 Å; $[(C-C)_{Cp'}]_{av}$, 1.415 Å; $[(Ti-C)_{Cp}]_{av}$, 2.233 Å; $[(Ti-C)_{Cp'}]_{av}$, 2.362 Å; Ti−Cp(plane), 2.017 Å; Ti−Cp′(plane), 2.031 Å. It is unexpected that the phenyl and Cp′ rings are not coplanar. The dihedral angle between the two planes is 17.22°.

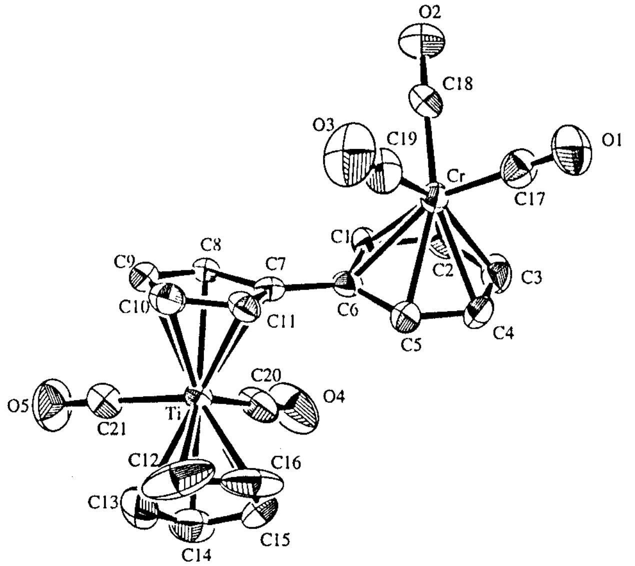

Figure 4. Molecular structure of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ti(CO)$_2$-Cp (**7**).

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of **7**

Cr−C(11)	2.258(6)	Cr−C(14)	2.228(6)
Cr−C(21)	1.826(7)	Ti−C(1)	2.330(8)
Ti−C(6)	2.384(6)	Ti−C(9)	2.336(6)
O(1)−C(17)	1.151(7)	Ti−C(17)	2.025(7)
C(1)−C(2)	1.39(1)	O(5)−C(21)	1.150(7)
C(6)−C(10)	1.423(8)	C(11)−C(12)	1.414(8)
C(9)−C(11)	1.481(8)		
C(11)−Cr−C(19)	89.5(3)	C(19)−Cr−C(20)	89.6(3)
C(9)−Ti−C(17)	78.9(2)	C(17)−Ti−C(18)	88.9(3)
Ti−C(9)−C(11)	124.3(4)	C(8)−C(9)−C(10)	107.4(5)
C(12)−C(11)−C(16)	117.6(5)	Cr−C(11)−C(9)	130.3(4)
Ti−C(17)−O(1)	179.1(6)	Cr−C(19)−O(3)	179.5(7)

Crystals of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Mo(CO)$_3$Br (**13**) suitable for X-ray analysis were obtained from a THF/hexane solution. The ORTEP diagram of **13** is shown in Figure 5, and selected bond distances and bond angles are listed in Table 5.

Similar to the result of **7**, Cr and Mo atoms are also in a *trans* position of the phenylcyclopentadienyl ligand in **13**. Outward distortion of the phenyl ring was found. The conformation of Cr(CO)$_3$ is in pseudoeclipsed form. Mo(CO)$_3$Br adopts the usual irregular “four-legged piano stool” arrangement of typical CpM(CO)$_3$X (M = Cr, Mo, W) derivatives. Boyle et al.[31] found that the distance between Mo and C of the carbonyl *trans* to Br, $[Mo-C(CO)_{trans}]$, is shorter than that of the corresponding $[Mo-C(CO)_{cis}]$, due to the greater extent of back-

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(30) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1976**, *96*, C4.

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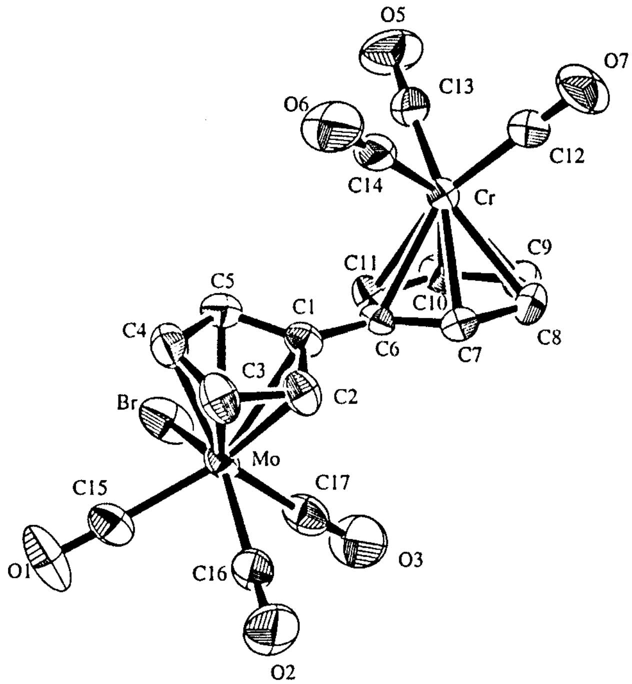

Figure 5. Molecular structure of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Mo(CO)_3Br$ (**13**).

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) of **13**

Mo−Br	2.640(1)	Mo−C(1)	2.346(5)
Mo−C(3)	2.276(7)	Mo−C(15)	2.019(7)
Mo−C(16)	2.002(7)	Mo−C(17)	1.990(8)
Cr−C(6)	2.224(5)	Cr−C(9)	2.212(7)
Cr−C(12)	1.848(7)	O(7)−C(12)	1.151(7)
O(1)−C(15)	1.140(8)	C(1)−C(2)	1.422(8)
C(1)−C(6)	1.471(8)	C(6)−C(11)	1.400(8)
Br−Mo−C(1)	97.9(1)	Br−Mo−C(15)	77.3(2)
Br−Mo−C(16)	136.1(2)	Br−Mo−C(17)	77.2(2)
C(15)−Mo−C(16)	80.1(3)	C(15)−Mo−C(17)	110.9(3)
C(16)−Mo−C(17)	76.5(3)	C(12)−Cr−C(13)	90.9(3)
C(2)−C(1)−C(5)	106.0(6)	Mo−C(1)−C(6)	122.2(4)
Cr−C(6)−C(1)	129.4(4)	C(7)−C(6)−C(11)	118.9(6)
Mo−C(15)−O(1)	177.7(7)	Cr−C(12)−O(7)	178.6(6)

bonding to the *trans* carbonyl. On the contrary, we found that [$Mo-C(CO)_{cis}$], Mo−C(17) 1.990(8) Å in **13**, was shorter than [$Mo-C(CO)_{trans}$], Mo−C(16) 2.002(7) Å, although the difference is only 0.01 Å. Unlike that in **7**, the Cp′ ring has no obvious distortion. In **13** the dihedral angle between the phenyl and Cp′ rings was 25.03°.

The crystal structure of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_9H_6)Mn(CO)_3$ (**19**), a heterobimetallic compound with a bridging phenylindenyl ligand, was also determined. Suitable crystals were obtained from a THF/hexane solution. The ORTEP diagram of **19** is shown in Figure 6, and selected bond distances and bond angles are listed in Table 6.

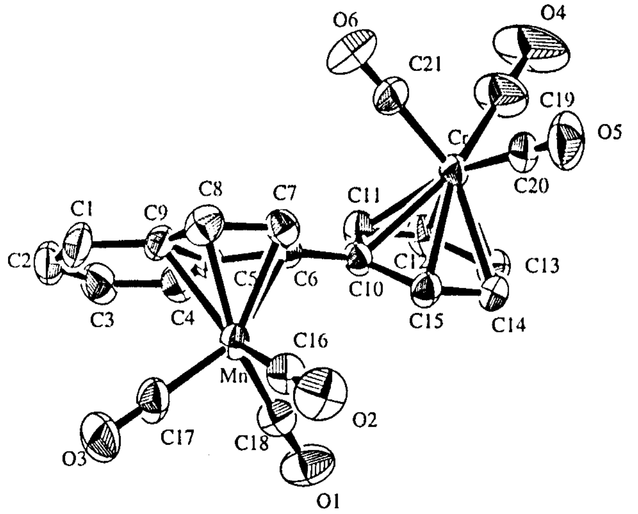

Figure 6. Molecular structure of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_9H_6)Mn(CO)_3$ (**19**).

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) of **19**

Mn−C(5)	2.201(4)	Mn−C(9)	2.222(4)
Mn−C(16)	1.788(5)	Cr−C(10)	2.240(4)
Cr−C(13)	2.213(5)	Cr−C(19)	1.850(6)
O(1)−C(18)	1.144(6)	O(4)−C(19)	1.146(8)
C(5)−C(6)	1.452(6)	C(6)−C(10)	1.479(6)
C(7)−C(8)	1.417(7)	C(10)−C(11)	1.421(6)
C(16)−Mn−C(17)	90.9(2)	C(19)−Cr−C(20)	89.0(3)
C(10)−Cr−C(21)	88.8(2)	C(5)−C(6)−C(7)	106.8(4)
Mn−C(6)−C(10)	126.5(3)	Cr−C(10)−C(6)	128.3(3)
C(11)−C(10)−C(15)	118.5(4)	Cr−C(19)−O(14)	178.8(6)
Mn−C(16)−O(2)	178.7(5)		

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) of **21**

Ru−Cl	2.454(3)	Ru−P(1)	2.316(4)
Ru−P(2)	2.339(4)	Ru−C(10)	2.27(1)
Ru−C(12)	2.17(1)	Cr−C(4)	2.20(1)
Cr−C(7)	2.16(2)	P(1)−C(20)	1.83(2)
O(2)−C(2)	1.16(2)	C(4)−C(5)	1.38(2)
C(4)−C(10)	1.49(2)	C(10)−C(11)	1.42(2)
Cl−Ru−P(1)	90.1(1)	Cl−Ru−P(2)	94.2(1)
Cl−Ru−C(10)	91.5(4)	P(1)−Ru−P(2)	101.5(1)
C(1)−Cr−C(2)	89.7(8)	C(39)−P(2)−C(45)	95.7(6)
Ru−P(1)−C(20)	108.3(5)	Cr−C(4)−C(10)	127.5(9)
Cr−C(2)−O(2)	178(2)	C(5)−C(4)−C(9)	118(1)
Ru−C(10)−C(4)	130.4(9)	C(11)−C(10)−C(14)	108(1)

In **19**, Cr and Mn atoms are in a *trans* position too. For the (arene)$Cr(CO)_3$ moiety, outward distortion of the phenyl ring and a staggered conformation of $Cr(CO)_3$ were found. Though the Mn was bonded with the C(5)−C(9) five-membered ring in a η^5 fashion, differences among the C−C bond lengths are obvious. C(5)−C(6) is obviously longer than the other C−C bonds. It indicates that the bonds between Mn and Cp′ are not symmetrical in our structure. Butler et al.[32] have also found there are different C−C bond lengths in the Cp ring of $CpMn(CO)_3$. The reason for the difference was attributed to electronic effects other than the arrangement style in the solid state. The phenyl and indenyl rings are also not coplanar. The dihedral angle is 38.30°, which is smaller than the one in compound **3** (47.30°), which has no coordination of $Mn(CO)_3$ with the indenyl ring.

We obtained single crystals of the EtOH adduct of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Ru(PPh_3)_2Cl$ (**21**) in the process of recrystallization of **21** from CH_2Cl_2/hexane. The ORTEP diagram of **21** is shown in Figure 7, and selected bond distances and bond angles are listed in Table 7.

Though Ru was bonded to PPh_3 instead of carbonyls, Cr and Ru are still in the *trans* position of the ligand like in **7**, **13**, and **19**. Outward distortion of the phenyl ring and a staggered conformation of $Cr(CO)_3$ were found. In contrast to the inward distortion of the Cp′ ring in **7**, an outward distortion of the Cp′ plane was found, i.e., Ru−C(10) is longer than other Ru−C(Cp′). The Ru−Cl distance of 2.454(3) Å is similar to that found in $CpRu(PPh_3)_2Cl$ (2.453(2) Å).[33] The two Ru−P bonds

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(32) Fitzpatrick, P. J.; Page, Y. L.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852.

(33) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.

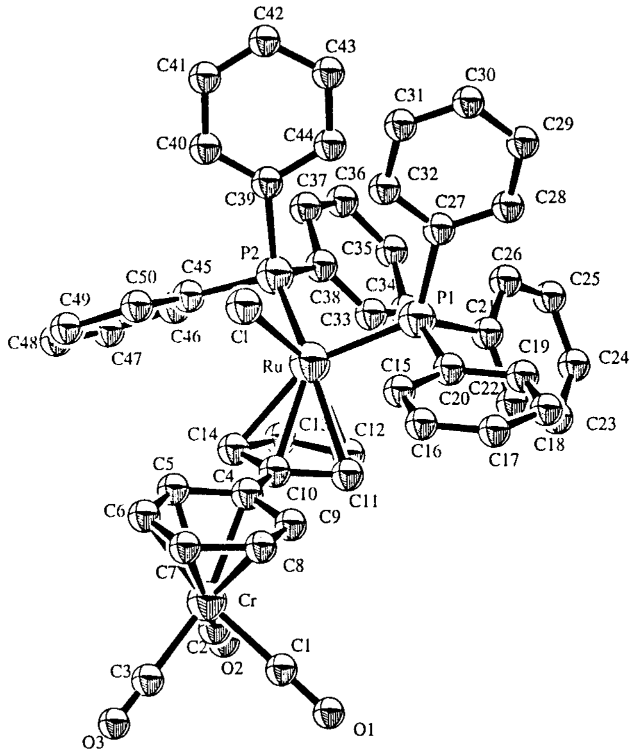


Figure 7. Molecular structure of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Ru(PPh_3)_2Cl$ (**21**).

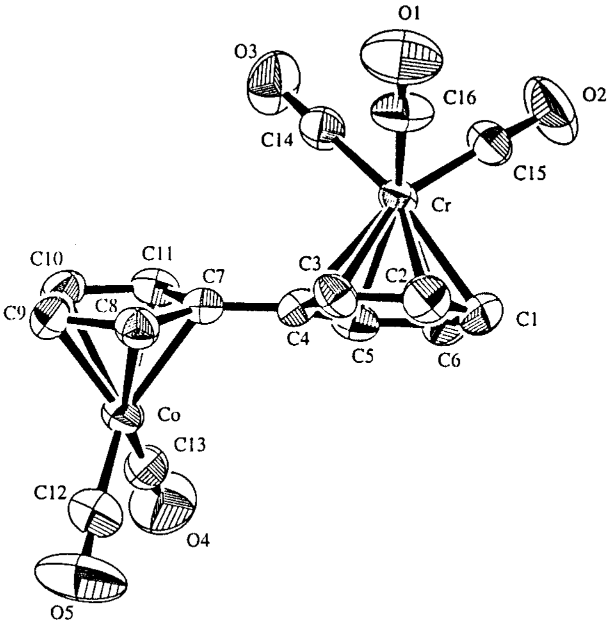


Figure 8. Molecular structure of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Co(CO)_2$ (**22**).

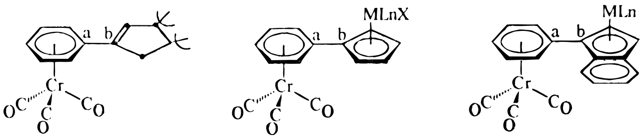
were unequal with a difference of 0.023 Å. It is interesting to note that the dihedral angle between the phenyl and Cp′ rings is 9.31°.

We also obtained suitable crystals of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Co(CO)_2$ (**22**) from a THF/hexane solution and determined its structure.[1] The ORTEP diagram of **22** is shown in Figure 8, and selected bond distances and bond angles are listed in Table 8.

Table 8. Selected Bond Lengths (Å) and Bond Angles (deg) of **22**

Co−C(7)	2.129(8)	Co−C(10)	2.095(9)
Co−C(12)	1.75(1)	Cr−C(1)	2.21(1)
Cr−C(4)	2.258(8)	Cr−C(14)	1.827(9)
O(1)−C(16)	1.16(1)	O(4)−C(13)	1.16(1)
C(3)−C(4)	1.42(1)	C(4)−C(7)	1.45(1)
C(7)−C(8)	1.43(1)		
C(7)−Co−C(13)	119.1(4)	C(12)−Co−C(13)	94.8(5)
C(4)−Cr−C(14)	90.2(3)	C(14)−Cr−C(15)	89.5(4)
Cr−C(4)−C(7)	131.2(6)	C(3)−C(4)−C(5)	116.6(9)
Co−C(7)−C(4)	126.2(6)	C(8)−C(7)−C(11)	104.9(8)
Co−C(13)−O(4)	179.4(9)	Cr−C(14)−O(3)	178.1(9)

Scheme 6



(**23**) (**7**): M=Ti, L=CO, n=2, X=Cp (**19**): M=Mn, L=CO, n=3

(**13**): M=Mo, L=CO, n=3, X=Br

(**21**): M=Ru, L=PPh$_3$, n=2, X=Cl

(**22**): M= Co, L=CO, n=2

Like before, Cr and Co atoms lie in the *trans* position of the ligand too. Outward distortion of the phenyl ring and a staggered conformation of $Cr(CO)_3$ were found. Similar to that of **21**, an outward distortion of the Cp′ ring was found, i.e., Co−C(7) of 2.219(8) Å is longer than other Co−C(Cp′) bonds. Like $CpCo(CO)_2$,[34] the plane formed by Co and two coordinated carbonyls is perpendicular to the Cp′ ring with a dihedral angle of 91.34°. The phenyl ring and the Cp′ ring are not coplanar either; the dihedral angle is 25.00° (Scheme 6).

Table 9 summarizes some important structural data of the above-mentioned compounds.

Though the poor crystal quality of **21** generated some incoherent results, it can be seen from these data that the bond parameters of (arene)$Cr(CO)_3$ moieties in these complexes are very similar, although the metal atoms attached to the Cp′ ring are quite different. On the other hand, except for the similar C−C bond distances of the Cp′ ring, the bond parameters of Cp′ML$_n$X moieties are obviously different. For the first-row transition metals, along the sequence of Ti, Mn, and Co, the distances of $[M-C(Cp')]_{av}$, $[M-C(carbonyl)]_{av}$, and [M−PL-(Cp′)] have an obvious tendency to decrease. The dihedral angles of the phenyl and Cp′ planes vary for different metal atoms and ligands.

General Comments. A good synthetic method for heterobimetallic complexes with bridging phenylcyclopentadienyl ligands of the type tricarbonylchromium−η^6,η^5-phenylcyclopentadienyl−transition metal complexes was developed. The method has advantages such as suitability for most transition metal complexes, mild reaction conditions, easy manipulation, and moderate to high yields. Spectroscopic properties of the complexes were studied. An X-ray crystallographic study of five heterobimetallic compounds was completed, and some interesting structural features were also found.

Experimental Section

All procedures were performed using standard Schlenk techniques under an atmosphere of dry oxygen-free argon. Tetrahydrofuran, diethyl ether, 1,2-dimethoxyethane, benzene, toluene, and hexane were distilled from sodium benzophenone ketyl under argon. Chloroform, dichloromethane, and acetonitrile were distilled from calcium hydride or P_2O_5 under argon. THF-d_8 was treated with a sodium−potassium alloy and was deoxygenated by several freeze−pump−thaw cycles.

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(34) Yu, M.; Struchkov, Y. T.; Chernega, A. N.; Meidine, M. F.; Nixon, J. F. *J. Organomet. Chem.* **1992**, *436*, 79.

Table 9. Comparison of Some Selected Bond Parameters

length (Å) and angle (deg)	**23**[a]	**3**	**7**	**13**	**19**	**21**	**22**
$[(C-C)\text{arene}]_{av}$	1.40	1.410	1.403	1.400	1.404	1.39	1.40
$[Cr-C(\text{arene})]_{av}$	2.218	2.224	2.225	2.213	2.214	2.19	2.213
$[Cr-C(\text{carbonyl})]_{av}$	1.84	1.833	1.832	1.840	1.846	1.85	1.82
Cr−PL(arene)[b]	1.721	1.720	1.727	1.713	1.712	1.687	1.718
[C(a)−C(b)]	1.48	1.472	1.481	1.471	1.479	1.49	1.45
$[(C-C)Cp']_{av}$			1.415	1.415	1.427	1.41	1.42
$[M-C(Cp')]_{av}$			2.362	2.235	2.170	2.21	2.087
$[M-C(\text{carbonyl})]_{av}$			2.033	2.004	1.793		1.74
M−PL(Cp′)[c]			2.031	1.986	1.799[g]	1.857	1.700
PL(arene)∧PL(Cp′)[d]	14.99[e]	47.30[f]	38.34	25.03	38.30[g]	9.31	25.00

[a] Cr(1) fragment of the compound. [b] PL(arene) represents the plane of C_6H_5. [c] PL(Cp′) represents the plane of C_5H_4. [d] The dihedral angle between the two planes. [e] For **23** the PL(Cp′) is replaced by the plane formed by the four bold carbon atoms in Figure 1. [f] For **3** the PL(Cp′) is replaced by the plane of C_9H_7. [g] Here PL(Cp′) is replaced by PL(C_9H_6).

$CDCl_3$ was dried by being allowed to stand for several hours with molecular sieves (4A) and was purified by vacuum transfer from CaH_2. ^{1}H NMR spectra were recorded with a Bruker AM-300 spectrometer; chemical shifts are reported in ppm relative to internal TMS. IR spectra of solution in THF were recorded on a Perkin-Elmer Model 983 spectrometer. Mass spectra were recorded on an HP5989A instrument. Elementary analyses were performed on an Italian Carlo-Eyba Model 1106 analyzer. Melting points were determined in sealed argon-filled capillaries and were uncorrected. $ZrCl_4$ was sublimed before use. Other reagent grade chemicals were used without further purification. The following compounds were prepared by following literature procedures: (η^6-$C_6H_5C_5H_5$)Cr(CO)$_3$,[14] (η^6-$C_6H_5C_9H_7$)Cr(CO)$_3$,[14] Cp_2TiCl_2,[35] $C_5H_5SiMe_3$,[36] $CpTiCl_3$,[37,38] $CpZrCl_3$(DME),[39] Cr(CO)$_3$(CH$_3$CN)$_3$,[40] Mo(CO)$_3$(CH$_3$CN)$_3$,[40] W(CO)$_3$(EtCN)$_3$,[41] Mn(CO)$_5$Br,[42] [Mn(CO)$_4$Br]$_2$,[43] RuCl$_2$(PPh$_3$)$_3$,[44] and (η^3-C_3H_5)$_2$Pd$_2$Cl$_2$.[45] All column chromatography was completed using deactivated neutral alumina (Al_2O_3).

Synthesis of (η^6-$C_6H_5C_5H_5$)Cr(CO)$_3$ (1). At 0 °C, 33 mL of a 0.86 M CpK (28.2 mmol) solution in DME was added dropwise to the stirred solution of (C_6H_5F)Cr(CO)$_3$ (1.09 g, 4.7 mmol) in 15 mL of DME. After being stirred at 0 °C for an additional 2.5 h, the reaction was quenched by deoxygenated NH_4Cl-saturated aqueous solution and the organic layer was separated. The aqueous layer was extracted by Et_2O (40 mL × 3), and the Et_2O extractant was combined with the organic layer. After distillation of the solvent and cyclopentadiene in vacuo, 40 mL of Et_2O was added to the residue and the solution was dried over $MgSO_4$. Chromatographic separation on Al_2O_3 (Et_2O/hexane = 1:5) afforded 1.2 g of a yellow mixture of compounds **1** and **1′** (92% yield, mp 92−94 °C). IR (THF, cm^{-1}): ν_{CO} 1960 vs, 1886 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.83−6.53 (m, 3H), 5.55−5.53 (m, 5H), 3.30 (m, 2H). Mass spectrum (EI): *m/z* (relative intensity) 278 (M$^+$, 33.09%), 250 (M$^+$ − CO, 5.61%), 222 (M$^+$ − 2CO, 33.65%), 194 (M$^+$ − 3CO, 100%), 142 (M$^+$ − Cr(CO)$_3$, 7.49%), 80 (Cr(CO), 5.95%), 52 (Cr, 73.12%).

Synthesis of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)TiCl$_2$(Cp) (5). To a solution of **1** (0.38 g, 1.4 mmol) in 20 mL of THF was added NaH (60 mg, excess) in portions at 0 °C. The mixture was stirred for 1 h at 0 °C. After centrifugation, a yellow solution of **2** was obtained. $CpTiCl_3$ (0.30 g, 1.4 mmol) in THF (10 mL) was added to the solution dropwise. After being stirred at room temperature overnight, the solvent was removed under vacuum. The solid residue was placed in a Soxhlet extractor and was extracted using CH_2Cl_2. After removal of the solvent under reduced pressure, 0.4 g (63%) of **5** was obtained as a dark green crystalline solid, mp 196−199 °C dec. Anal. Calcd for $C_{19}H_{14}Cl_2CrO_3Ti$: C, 49.49; H, 3.06. Found: C, 49.24; H, 2.72. IR (THF, cm^{-1}): ν_{CO} 1979 vs, 1858 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.78 (s, 2H), 6.64 (s, 2H), 6.60 (s, 5H), 6.09 (d, 2H), 5.59 (t, 2H), 5.51 (t, 1H). Mass spectrum (EI): *m/z* (relative intensity) 376 (M$^+$ − 3CO, 23%), 341 (M$^+$ − 3CO − Cl, 6%), 311 (M$^+$ − 3CO − Cp, 7%), 254 (M$^+$ − 3CO − Cr − 2Cl, 100%), 193 ([$C_{11}H_9$ + Cr]$^+$, 57%), 141 ($C_{11}H_9^+$, 64%), 115 ($C_9H_7^+$, 39%), 65 (Cp$^+$, 15%), 52 (Cr$^+$, 35%).

Synthesis of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)ZrCl$_2$(Cp) (6). Following the procedure for **5**, $CpZrCl_3$(DME) (0.48 g, 1.4 mmol) and the sodium salt of **1** (0.38 g, 1.4 mmol) were used, and **6** was obtained as a yellow powder (0.40 g, 49%), mp 203−205 °C dec. Anal. Calcd for $C_{19}H_{14}Cl_2CrO_3Zr$: C, 45.24; H, 2.80. Found: C, 44.72; H, 2.92. IR (THF, cm^{-1}): ν_{CO} 1960 vs, 1888 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.61 (m, 2H), 6.50 (m, 7H), 5.85 (m, 2H), 5.58 (m, 3H). Mass spectrum (EI): *m/z* (relative intensity) 446 (M$^+$ − 2CO, 5%), 418 (M$^+$ − 3CO, 60%), 366 (M$^+$ − 3CO − Cr, 23%), 331 (M$^+$ − 3CO − Cr −Cl, 100%), 301 (M$^+$ − 3CO − Cp − Cr, 76%), 296 (M$^+$ − 3CO − Cr − 2Cl, 39%), 193 ([$C_{11}H_9$ + Cr]$^+$, 44%), 141 ($C_{11}H_9^+$, 26%), 65 ($C_9H_7^+$, 12%), 52 (Cr$^+$, 51%).

Synthesis of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Ti(CO)$_2$(Cp) (7). **5** (0.75 g, 1.6 mmol), magnesium powder (0.16 g, 6.4 mmol), and 30 mL of THF were placed into a Schlenk tube and stirred magnetically. The tube was flushed with carbon monoxide for 5 min, and $HgCl_2$ (0.4 g, 1.5 mmol) was then added while carbon monoxide was allowed to flow slowly over the solution through the side-arm stopcock and out to a mercury overpressure valve. The reaction mixture was stirred in the carbon monoxide atmosphere for 1 h at room temperature, during which time the color changed from green to dark red. The clear solution was decanted, and the solvent was removed under vacuum. The residue was chromatographed on deactivated alumina. Eluting with Et_2O/hexane (1:10) produced a yellow band which was unreacted **1**. Further elution with Et_2O/hexane (2:10) produced a yellow band which was the dimer of **1**. Further elution with Et_2O/hexane (4:10) produced a red band that was collected and the solvent removed under vacuum. A red powder was obtained (0.30 g, 41%). **7**: mp 132−135 °C dec. Anal. Calcd for $C_{21}H_{14}CrO_5Ti$: C, 56.52; H, 3.16. Found: C, 57.18; H, 3.42. IR (THF, cm^{-1}): ν_{CO} 1959 vs, 1887 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.79−5.36 (m, 9H), 5.03 (s, 5H). Mass spectrum (EI): *m/z* (relative intensity) 390 (M$^+$ − 2CO, 14%), 334 (M$^+$ − 4CO, 8%), 254 (M$^+$ − 5CO − Cr, 43%), 194 ([$C_{11}H_{10}$ + Cr]$^+$, 100%), 141 ($C_{11}H_9^+$, 41%), 115 ($C_9H_7^+$, 29%), 65 (Cp$^+$, 33%), 52 (Cr$^+$, 98%).

Synthesis of Cr(CO)$_3$(η^6,η^5-$C_6H_5C_5H_4$)Mo(CO)$_3$CH$_3$ (11). To a THF solution of **2** (1.4 mmol) was added Mo(CO)$_3$(CH$_3$CN)$_3$ (0.42 g, 1.4 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. An orange yellow solution of **9** was obtained. The solution was cooled to 0 °C, and CH_3I (1 mL, excess) was added. After the solution was stirred at room temperature for 2 h, the solvent was removed under vacuum. The solid residue was then chromatographed. Eluting with CH_2Cl_2/hexane (1:10 → 2:10) produced two yellow bands which were **1** and a dimer of **1**. Further elution with CH_2Cl_2/hexane (3:10 → 7:10) produced a yellow band that was collected and the solvent removed under vacuum. A yellow powder was obtained (0.39 g, 61%). **11**: mp 164−167 °C. Anal. Calcd for $C_{18}H_{12}CrMoO_6$: C, 45.78; H, 2.56. Found: C, 45.92; H, 2.37. IR (THF, cm^{-1}): ν_{CO} 2018 s, 1964 vs, 1927 vs, 1892 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.57 (d, 2H), 5.46 (t, 2H), 5.37 (m, 4H), 5.30 (t,

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1H), 0.32 (s, 3H). Mass spectrum (EI): *m/z* (relative intensity) 474 (M^+, 17%), 390 ($M^+ - 3CO$, 42%), 375 ($M^+ - 3CO - Me$, 30%), 334 ($M^+ - 5CO$, 31%), 306 ($M^+ - 6CO$, 58%), 291 ($[C_{11}H_9 + Cr + Mo]^+$, 19%), 239 ($[C_{11}H_9 + Mo]^+$, 28%), 193 ($[C_{11}H_9 + Cr]^+$, 10%), 141 ($C_{11}H_9^+$, 59%), 115 ($C_9H_7^+$, 54%), 52 (Cr^+, 100%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)W(CO)_3CH_3$ (12). Following the procedure for **11**, **1** (0.18 g, 0.6 mmol), $W(CO)_3(EtCN)_3$ (0.28 g, 0.6 mmol), and CH_3I (1 mL) were used and a yellow powder (0.26 g, 23%) was obtained. **12**: mp 164−167 °C. Anal. Calcd for $C_{18}H_{12}CrO_6W$: C, 38.59; H, 2.16. Found: C, 38.85; H, 2.11. IR (THF, cm^{-1}): ν_{CO} 2014 s, 1964 vs, 1917 vs, 1892 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.62 (s, 2H), 5.43 (m, 7H), 0.39 (s, 3H). Mass spectrum (EI): *m/z* (relative intensity) 476 ($M^+ - 3CO$, 37%), 461 ($M^+ - 3CO - Me$, 81%), 433 ($M^+ - 4CO - Me$, 50%), 405 ($M^+ - 5CO - Me$, 31%), 392 ($M^+ - 6CO$, 28%), 377 ($[C_{11}H_9 + Cr + W]^+$, 27%), 325 ($[C_{11}H_9 + W]^+$, 26%), 193 ($[C_{11}H_9 + Cr]^+$, 9%), 141 ($C_{11}H_9^+$, 17%), 115 ($C_9H_7^+$, 23%), 52 (Cr^+, 100%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Mo(CO)_3Br$ (13). To a THF solution of **9** (1.2 mmol) was added Br_2 (60 μL, 1.2 mmol) in THF (10 mL) dropwise at −78 °C. The mixture was stirred at −78 °C for 0.5 h and then slowly warmed to room temperature and stirred for an additional 0.5 h. The solvent was removed under vacuum, and the solid residue was purified by chromatography on alumina. Eluting with CH_2Cl_2/hexane (1:10 → 2:10) produced two yellow bands which were **1** and a dimer of **1**. Further elution with CH_2Cl_2/hexane (3:10 → 10:10) produced a red band that was collected and the solvent removed under vacuum. A red powder was obtained (0.28 g, 45%). **13**: mp 160−163 °C. Anal. Calcd for $C_{17}H_9BrCrMoO_6$: C, 38.01; H, 1.69. Found: C, 38.62; H, 2.04. IR (THF, cm^{-1}): ν_{CO} 2047 s, 1963 vs, 1890 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.50−5.42 (m, 9H). Mass spectrum (EI): *m/z* (relative intensity) 318 ($M^+ - 6CO - Cr$, 4%), 239 ($[C_{11}H_9 + Mo]^+$, 14%), 193 ($[C_{11}H_9 + Cr]^+$, 11%), 141 ($C_{11}H_9^+$, 98%), 115 ($C_9H_7^+$, 100%), 52 (Cr^+, 14%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)W(CO)_3Br$ (14). Following the procedure for **13**, $W(CO)_3(EtCN)_3$ (0.43 g, 1.0 mmol), (**1**) (0.28 g, 1.0 mmol), and Br_2 (51 μL, 1.0 mmol) were used to produced a yellow powder (0.26 g, 42%). **14**: mp 172−174 °C dec. Anal. Calcd for $C_{17}H_9BrCrO_6W$: C, 32.67; H, 1.45. Found: C, 33.00; H, 1.69%. IR (THF, cm^{-1}): ν_{CO} 2020 s, 1964 vs, 1924 vs, 1892 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.56−5.28 (m, 9H). Mass spectrum (EI): *m/z* (relative intensity) 545 ($M^+ - Br$, 6%), 512 ($M^+ - 4CO$, 6%), 488 ($M^+ - 3CO - Cr$, 15%), 461 ($M^+ - 3CO - Br$, 25%), 433 ($M^+ - 4CO - Br$, 41%), 432 ($M^+ - 5CO - Cr$, 51%), 405 ($M^+ - 5CO - Br$, 51%), 404 ($M^+ - 6CO - Cr$, 100%), 377 ($[C_{11}H_9 + Cr + W]^+$, 29%), 325 ($[C_{11}H_9 + W]^+$, 33%), 193 ($[C_{11}H_9 + Cr]^+$, 15%), 141 ($C_{11}H_9^+$, 91%), 115 ($C_9H_7^+$, 66%), 52 (Cr^+, 39%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Cr(CO)_2NO$ (15). A solution of **8** was obtained in following the procedure for **9**, with **1** (0.23 g, 0.8 mmol) and $Cr(CO)_3(CH_3CN)_3$ (0.21 g, 0.8 mmol). The solution was cooled to 0 °C, and Diazald (0.18 g, 0.8 mmol) in THF (10 mL) was added slowly. The mixture was warmed to room temperature and was stirred for 3 h. After filtration, the solvent was removed under vacuum. The solid residue was purified by column chromatography. Eluting with CH_2Cl_2/hexane (1:10 → 2:10) produced two yellow bands which were **1** and a dimer of **1**. Further elution with CH_2Cl_2/hexane (3:10 → 10:10) produced an orange band that was collected and the solvent removed under vacuum. An orange powder was obtained (0.19 g, 55%). **15**: mp 171−174 °C dec. Anal. Calcd for $C_{16}H_9Cr_2NO_6$: C, 46.28; H, 2.18. Found: C, 46.93; H, 2.26. IR (THF, cm^{-1}): ν_{CO} 2021 s, 1963 vs, 1890 vs; ν_{NO} 1699 s. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.32−5.01 (m, 9H). Mass spectrum (EI): *m/z* (relative intensity) 415 (M^+, 9%), 331 ($M^+ - 3CO$, 23%), 275 ($M^+ - 5CO$, 100%), 273 ($M^+ - 4CO - NO$, 47%), 245 ($M^+ - 5CO - NO$, 18%), 193 ($[C_{11}H_9 + Cr]^+$, 46%), 141 ($C_{11}H_9^+$, 6%), 115 ($C_9H_7^+$, 3%), 52 (Cr^+, 17%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Mo(CO)_2NO$ (16). Following the procedure for **15**, $Mo(CO)_3(MeCN)_3$ (0.37 g, 1.3 mmol), **1** (0.36 g, 1.3 mmol), and Diazald (0.28 g, 1.3 mmol) were used to produce a yellow powder (0.36 g, 60%). **16**: mp 161−164 °C dec. Anal. Calcd for $C_{16}H_9CrMoNO_6$: C, 41.85; H, 1.98. Found: C, 42.06; H, 2.21. IR (THF, cm^{-1}): ν_{CO} 2017 s, 1963 vs, 1938 vs, 1890 vs; ν_{NO} 1670 s. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.60−5.30 (m, 9H). Mass spectrum (EI): *m/z* (relative intensity) 461 (M^+, 6%), 377 ($M^+ - 3CO$, 40%), 375 ($M^+ - 2CO - NO$, 35%), 321 ($M^+ - 5CO$, 89%), 319 ($M^+ - 4CO - NO$, 100%), 291 ($M^+ - 5CO - NO$, 18%), 267 ($M^+ - 4CO - NO - Cr$, 23%), 213 ($M^+ - 4CO - NO - Cr - C_2H_2$, 16%), 141 ($C_{11}H_9^+$, 6%), 115 ($C_9H_7^+$, 4%), 52 ($Cr^+$, 31%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)W(CO)_2NO$ (17). Following the procedure for **15**, $W(CO)_3(EtCN)_3$ (0.42 g, 1.0 mmol), **1** (0.27 g, 1.0 mmol), and Diazald (0.21 g, 1.0 mmol) were used to produce a yellow powder (0.30 g, 56%). **17**: mp 161−164 °C dec. Anal. Calcd for $C_{16}H_9CrNO_6W$: C, 35.12; H, 1.66. Found: C, 35.80; H, 1.81. IR (THF, cm^{-1}): ν_{CO} 2007 s, 1963 vs, 1923 s, 1890 vs; ν_{NO} 1664 s. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.57−5.22 (m, 9H). Mass spectrum (EI): *m/z* (relative intensity) 491 ($M^+ - 2CO$, 6%), 463 ($M^+ - 3CO$, 30%), 461 ($M^+ - 2CO - NO$, 24%), 407 ($M^+ - 5CO$, 81%), 405 ($M^+ - 4CO - NO$, 76%), 377 ($M^+ - 5CO - NO$, 13%), 353 ($M^+ - 4CO - NO - Cr$, 14%), 299 ($M^+ - 4CO - NO - Cr - C_2H_2$, 10%), 193 ($[C_{11}H_9 + Cr]^+$, 3%), 141 ($C_{11}H_9^+$, 7%), 115 ($C_9H_7^+$, 5%), 52 ($Cr^+$, 100%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Mn(CO)_3$ (18). To a solution of **2** (0.9 mmol) was added $[Mn(CO)_4Br]_2$ (0.23 g, 0.5 mmol) in THF (10 mL) slowly. The mixture was stirred overnight, and some precipitants formed. After filtration, the solvent was evacuated to dryness. Chromatography of the residue was performed over an alumina column. After two small yellow fractions (eluted with CH_2Cl_2/hexane = 2:10), a main yellow fraction (eluted with CH_2Cl_2/hexane = 4:10 → 1:1) was obtained. A yellow powder was obtained after removal of the solvent (0.31 g, 79%). **18**: mp 179−182 °C dec. Anal. Calcd for $C_{17}H_9CrMnO_6$: C, 49.06; H, 2.18. Found: C, 49.17; H, 2.38. IR (THF, cm^{-1}): ν_{CO} 2022 s, 1964 vs, 1934 s, 1891 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.43 (m, 4H), 5.29 (m, 1H), 5.12 (s, 2H), 4.82 (s, 2H). Mass spectrum (EI): *m/z* (relative intensity) 416 (M^+, 13%), 322 ($M^+ - 3CO$, 44%), 276 ($M^+ - 5CO$, 41%), 249 ($M^+ - 4CO - Mn$, 23%), 248 ($M^+ - 6CO$, 100%), 196 ($[C_{11}H_9 + Mn]^+$, 29%), 193 ($[C_{11}H_9 + Cr]^+$, 79%), 141 ($C_{11}H_9^+$, 16%), 115 ($C_9H_7^+$, 10%), 55 (Mn^+, 13%), 52 (Cr^+, 27%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_9H_6)Mn(CO)_3$ (19). To a solution of **3** (0.29 g, 0.9 mmol) in THF (20 mL) at 0 °C was added NaH (60 mg, excess) in portions. The reaction mixture was stirred for 1 h at 0 °C. After centrifugation, a yellow solution of **4** was obtained. To a solution of **4** (0.9 mmol) was added $[Mn(CO)_4Br]_2$ (0.23 g, 0.5 mmol) in THF (10 mL) slowly. The mixture was stirred overnight at room temperature. After filtration, the solvent was evacuated to dryness. Chromatography of the residue was performed over an alumina column. After two small yellow fractions (eluted with CH_2Cl_2/hexane = 2:10), a main yellow fraction (eluted with CH_2Cl_2/hexane = 3:10) was obtained. A yellow powder was obtained after removal of the solvent (0.31 g, 75%). **19**: mp 150−152 °C dec. Anal. Calcd for $C_{21}H_{11}CrMnO_6$: C, 54.09; H, 2.38. Found: C, 54.41; H, 2.25. IR (THF, cm^{-1}): ν_{CO} 2021 s, 1963 vs, 1933 s, 1890 vs. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.77−7.20 (m, 4H), 5.87 (s, 1H), 5.70 (s, 1H), 5.46−5.28 (m, 5H). Mass spectrum (EI): *m/z* (relative intensity) 466 (M^+, 8%), 382 ($M^+ - 3CO$, 27%), 326 ($M^+ - 5CO$, 32%), 299 ($M^+ - 4CO - Mn$, 21%), 298 ($M^+ - 6CO$, 78%), 246 ($[C_{15}H_{11} + Mn]^+$, 6%), 243 ($[C_{15}H_{11} + Cr]^+$, 100%), 191 ($C_{15}H_{11}^+$, 35%), 165 ($C_{13}H_9^+$, 8%), 55 (Mn^+, 8%), 52 (Cr^+, 36%).

Synthesis of $(\eta^5\text{-}C_6H_5C_5H_4)Ru(PPh_3)_2Cl$ (20). **1** (0.49 g, 1.8 mmol), $RuCl_3\cdot 3H_2O$ (0.38 g, 1.4 mmol), PPh_3 (3 g, 11.4 mmol), and EtOH (100 mL) were mixed and refluxed for 8 h. The color of the mixture changed from dark green to orange. After being cooled to room temperature, the reaction mixture was filtered and the filtrate was evacuated to dryness and chromatographed on an alumina column. After two small yellow fractions (CH_2Cl_2/hexane = 2:10), a main red orange fraction (CH_2Cl_2/hexane = 3:10 → 1:1) was obtained. An orange powder was obtained after removal of the solvent (0.47 g, 41%). **20**: mp 178−181 °C dec. Anal. Calcd for $C_{47}H_{39}ClP_2Ru$: C, 70.36; H, 4.90. Found: C, 69.46; H, 4.69. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.85 (m, 5H), 7.37−6.94 (m, 30H), 4.59 (s, 2H), 3.34 (s, 2H). Mass spectrum (EI): *m/z* (relative intensity) 540 ($[C_{11}H_9 + Ru(PPh_3)Cl]^+$, 2%), 505 ($[C_{11}H_9 + Ru(PPh_3)]^+$, 3%), 262 ($[PPh_3]^+$, 100%), 183 ($[PPh_3 - C_6H_7]^+$, 79%), 108 ($[PPh]^+$, 31%), 115 ($C_9H_7^+$, 4%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Ru(PPh_3)_2Cl$ (21). To a mixture of **1** (0.57 g, 2.0 mmol) and $RuCl_2(PPh_3)$ (1.96 g, 2.0 mmol) in benzene (40 mL) was added zinc powder (0.2 g, excess). The mixture was stirred for 48 h at room temperature. After centrifugation, the clear solution was evaporated to dryness and chromatographed on an alumina column. After two small yellow fractions (CH_2Cl_2/hexane = 2:10), a main red orange fraction (CH_2Cl_2/hexane = 3:10 → 1:1) was obtained. An orange solid was obtained after removal of the solvent (0.86 g, 45%). **21**: mp 164−166 °C dec. Anal. Calcd for $C_{50}H_{39}ClCrO_3P_2Ru$: C, 64.00; H, 4.19. Found: C, 64.35; H, 3.96. IR (THF, cm^{-1}): ν_{CO} 1957 vs, 1883 vs. ^1H NMR ($CDCl_3$): δ (ppm) 7.47−7.07 (m, 30H), 5.50−5.27 (m, 5H), 4.63 (s, 2H), 3.52 (s, 2H). Mass spectrum (EI): *m*/*z* (relative intensity) 505 ($[C_{11}H_9 + Ru(PPh_3)]^+$, 7%), 428 ($[C_{11}H_9 + Ru(PPh_2)]^+$, 2%), 262 ($[PPh_3]^+$, 100%), 183 ($[PPh_3 - C_6H_7]^+$, 69%), 108 ($[PPh]^+$, 23%), 115 ($C_9H_7^+$, 3%), 52 ($Cr^+$, 3%).

Synthesis of $Cr(CO)_3(\eta^6,\eta^5\text{-}C_6H_5C_5H_4)Co(CO)_2$ (22). A mixture of **1** (0.43 g, 1.5 mmol), $Co_2(CO)_8$ (0.3 g, 0.9 mmol), *t*-BuCH=CH_2 (0.4 mL), and CH_2Cl_2 (30 mL) was heated to gentle reflux for 10 h. After the solution was cooled to room temperature, the solvent was removed under vacuum. The solid residue was chromatographed on an alumina column. Eluting with CH_2Cl_2/hexane = 1:10 produced one small yellow band of **1** at first, followed by a main red fraction. A red powder was obtained after removal of the solvent (0.37 g, 61%). **22**: mp 107−109 °C dec. Anal. Calcd for $C_{16}H_9CoCrO_5$: C, 49.00; H, 2.31. Found: C, 49.26; H, 2.33. IR (THF, cm^{-1}): ν_{CO} 2025 s, 1962 vs, 1890 vs. ^1H NMR ($CDCl_3$): δ (ppm) 5.52 (d, 2H), 5.43 (t, 2H), 5.35 (s, 2H), 5.29 (t, 1H), 5.16 (s, 2H). Mass spectrum (EI): *m*/*z* (relative intensity) 364 ($M^+ - CO$, 20%), 336 ($M^+ - 2CO$, 32%), 308 ($M^+ - 3CO$, 36%), 280 ($M^+ - 4CO$, 64%), 252 ($M^+ - 5CO$, 100%), 196 ($[C_{11}H_9 + Co]^+$, 21%), 193 ($[C_{11}H_9 + Cr]^+$, 69%), 141 ($C_{11}H_9^+$, 29%), 115 ($C_9H_7^+$, 25%), 52 (Cr^+, 19%).

Formation of 1,4-Bis[tricarbonylchromio)phenyl]tricyclo[5.2.1.0^{2,6}]-deca-3,8-diene (23). Yellow crystals of compound **23** were obtained from the THF/hexane solution of **1** after being allowed to stand at about 0 °C for several days. **23**: mp 163−165 °C. Anal. Calcd for $C_{28}H_{20}Cr_2O_6$: C, 60.43; H, 3.62. Found: C, 59.95; H, 3.79. IR (THF, cm^{-1}): ν_{CO} 1959 vs, 1886 vs. ^1H NMR ($CDCl_3$): δ (ppm) 6.21−5.98 (m, 3H), 5.57−5.30 (m, 10H), 3.75−3.09 (m, 3H), 2.53 (m, 1H), 2.01−1.69 (m, 3H). Mass spectrum (EI): *m*/*z* (relative intensity) 472 ($M^+ - 3CO$, 3%), 420 ($M^+ - 3CO - Cr$, 4%), 388 ($M^+ - 6CO$, 6%), 364 ($M^+ - 5CO - Cr$, 3%), 336 ($M^+ - 6CO - Cr$, 39%), 334 ($M^+ - 6CO - Cr - 2H$, 100%), 52 (Cr^+, 99%).

X-ray Structural Determinations. Single crystals were sealed in thin-walled glass capillaries under argon. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer for **3** and on a Rigaku AFC7R diffractometer for other compounds, using graphite-monochromated Mo Kα radiations in the $\omega - 2\theta$ scan mode at 20 °C. Final lattice parameters were obtained by a least-squares refinement of the 2θ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. The metal atom was located by the Patterson method, and the other non-hydrogen atoms were located by difference Fourier method. All positional parameters and anisotropic thermal parameters for non-hydrogen atoms were refined by the full-matrix least-squares technique. Finally, all hydrogen atoms were introduced in calculated positions. Scattering factors were taken from ref 46. All calculations for **3** were made on a Micro VAX-II computer with SDP plus ORTEP prorams. All calculations for other compounds were performed using the teXsan[47] crystallography software package of the Molecular Structure Corporation. The crystallography data are listed in Table 1.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **23**, **3**, **7**, **13**, **19**, **21**, and **22** are available. Access information is given on any current masthead page.

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(47) *teXsan, Crystal Structure Analysis Package*, Molecular Structure Corporation, 1985 and 1992.