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Structural, Stereochemical, and Electronic Features of Arene–Metal Complexes

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I. Introduction

Metal atoms,[1] metal surfaces,[2] and metal compounds[3] interact with aromatic hydrocarbons and often form stable complexes through overlap of the ring π and π^* orbitals with appropriate orbitals of the metal atom(s). Hein and his co-workers[4] isolated the first molecular arene–metal complexes in 1919, but definitive compositional and structural characterization of these complexes was not achieved until the mid-fifties. In a general context, the structural features of molecular arene–metal complexes are well-defined. For example, the metal–carbon and carbon–carbon bond distances can be predicted to within certainly 0.05 and 0.02 Å, respectively, for any new or noncrystallographically defined transition-metal complex with a benzene or simple alkyl-substituted benzene ligand. Also, it is generally feasible to anticipate the direction that substituent atoms or groups will bend out of the C_6 ring plane on complexation with a metal. Such general aspects as well as systematic considerations will be addressed in this analysis. Our initial motivation in this structural analysis was to discern minor structural or stereochemical perturbations that might provide clues to mechanistic features for reactions of arene–metal complexes. The primary focus of our studies of arene–metal complexes has been the mechanism of (a) arene–metal bond formation,[5,6] (b) arene exchange between the arene–metal complex and unbound arene,[5,6] and (c) solution-phase hydrogenation of an arene by a coordination complex.[7] In all three of these reactions, we have supposed that stereochemical transformations of the arene ligand may play a key role—for example, interconversions of the form

$$\eta^6\text{-arene–M} \rightleftharpoons \eta^4\text{-arene–M} \rightleftharpoons \eta^2\text{-arene–M}$$

where the η^x notation is the standard hapto notation[8] in which the x superscript denotes the number of carbon atoms of the arene ligand that are within bonding distance of the metal center. Not only are all three structural forms of interest in this analysis, but also of interest are structural forms intermediate between the idealized η^6-, η^4- and η^2-arene–metal structures—should the intermediate structural forms exist in the ground state (crystallographically defined) of the molecular species. We also consider the electronic driving forces behind geometric distortions for (η^x-arene)metal complexes from a molecular orbital point of view.

Because our interest in arene–metal interactions spans molecular mononuclear and polynuclear metal complexes and metal surfaces, all are included in this analysis. For the molecular complexes, only crystallographic or electron diffraction data are considered. No structural parameters have been established for arene–metal interactions on metallic surfaces, but qualitative stereochemical information is included for discussion of this class. Primary consideration in this structural analysis is for benzene and alkylbenzenes as the aromatic hydrocarbon ligand in these complexes; these simple and basic aromatic hydrocarbons have been the primary base for the chemistry of interest to us.

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II. Sandwich Complexes

A. Definitions

"Sandwich" is organometallic jargon and a pervasive qualifier for a family of complexes in which a metal atom is complexed to two planar and parallel, or nearly parallel, sets of ligands. The largest class within this family is based on planar C_nH_n ligands. For the benzene subclass, the paradigm is bis(benzene)chromium. Mixed sandwich systems comprise metal complexes with different types of C_nH_n ligands—in the arene system, an example is $[C_6H_6Fe(C_5H_5)^+]$. In a structural, stereochemical, and electronic context, the subclass of paramount importance is that of the bis(arene)metal complexes. Although a relatively small number of crystallographic investigations of complexes in this subclass have been reported, the extant crystallographic data appear to provide a fair overview. Missing are structural data for a bis(arene) complex of second- or third-row transition metals, complexes with tri-, tetra-, and pentasubstituted benzene ligands, and complexes based on condensed arene ligands. Actually, accurate crystallographic analyses are available only for complexes with benzene, hexamethylbenzene, and disubstituted benzene; all structural data for bis(η^6-arene)metal complexes are summarized in Table I.

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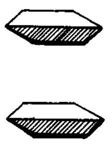
B. Bis(arene)metal Complexes

A sandwich complex like the classic bis(benzene)chromium molecule, which is formally an 18-electron, coordinately saturated complex, should have a geometry in which the metal is sandwiched between parallel planar benzene ligands. Figure 1 shows the construction of the valence molecular orbitals on the left and metal 3d, 4s, and 4p atomic levels on the right. A shorthand representation has been used for the in-phase and out-of-phase combinations of π orbitals that emphasizes their nodal characteristics. For example, **1** and **2** are equivalent to **3** and **4**, respectively. The a_{1g}, a_{2u}, and e_{1u} benzene π sets are stabilized by metal s and p orbitals. The benzene molecular e_{1g} orbital is also stabilized by chromium xz and yz orbitals (see the coordinate system at the top center of Figure 1). So there are a total of six strong bonding interactions between chromium and the two benzene molecules. Metal x^2-y^2 and xy orbitals are stabilized (in $1e_{2g}$) to a small extent by the benzene π^* combination of e_{2g} symmetry. This overlap is of δ symmetry and is necessarily smaller



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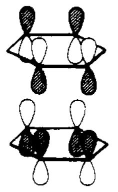

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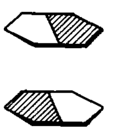

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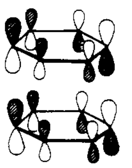

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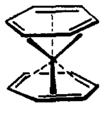
than the σ bonding in $1a_{1g}$ and $1a_{2u}$ or the π type in $1e_{1g}$ and $1e_{1u}$. Furthermore, there is a high-lying σ set on benzene of e_{2g} symmetry derived from combinations of the carbon p_x and p_y atomic orbitals that is also of δ symmetry and will mix into $1e_{2g}$ in an antibonding manner. The a_{1g} benzene π set lies in the nodal region of d_{z^2}. Therefore, the molecular orbital $2a_{1g}$ is almost totally metal d_{z^2} in character. What this means is $1e_{2g}$ and $2a_{1g}$ are effectively nonbonding. Six electrons will be housed in these levels plus twelve electrons in the six bonding levels to give the eighteen electrons previously mentioned. We have described the bonding for bis(benzene)chromium within a delocalized molecular orbital framework. A localized valence-bond view could have been developed by constructing six equivalent d^2sp^3 hybrids.[9] The hybrid bonds point toward the vertices of an octahedron, and the six π bonds of the benzene molecules match them perfectly in a spatial sense to produce six Cr–olefin bonds given by the resonance structures 5 and 6. The remaining three atomic orbitals at chromium that are not used in the hybridization scheme (z^2, $x^2 - y^2$, xy) are left unbonding.



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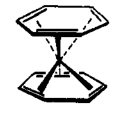

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In the delocalized picture of Figure 1 there is a cylindrical symmetry about the sixfold axis of the complex which is apparent. The a_{1g} and a_{2u} orbitals are cylindrically symmetrical to begin with. Two others come as doubly degenerate sets. The particular degenerate sets that have been presented are convenient, familiar ones. However, there is an infinite number of others. One can construct a linear combination of the two members of an e set that produces two alternative orbitals that are as good as the first set. This creates cylindrical symmetry. Taking the two resonance structures 5 and 6 together also creates a cylindrically symmetric situation. There are two consequences of this. First, maximal electron density in the six Cr–benzene bonds is not concentrated along the C–Cr vectors or along C–C-midpoint–Cr vectors. It is distributed equally. Second, cylindrical symmetry in the absence of steric effects requires that there be a low rotational barrier about the benzene–chromium axis. Therefore, the energy difference between eclipsed, D_{6h}, and staggered, D_{6d}, forms must be small. An extended Hückel calculation[10] on bis(benzene)chromium has placed the eclipsed conformation 0.9 kcal/mol more stable than the staggered one. This is consistent with an electron diffraction study[11] of gaseous $(C_6H_6)_2Cr$ which established D_{6h} symmetry with a C–C bond distance of 1.423 ± 0.002 Å—if there is an alternation of C–C bond distances in the rings, the difference in distances can be no more than ~0.01 Å. A similar interpretation has been made for the molecule in the crystalline state with an average C–C distance of 1.420 (3) Å, although there may have been rotational disorder in the crystal.[12] No uniform bond alternation has been seen in the structures of three CF_3 derivatives.[13] In this comparative study of potential substituent effects in bis(η^6-arene)metal complexes, the crystal structures of $Cr[1,4\text{-}C_6H_4(CF_3)_2]_2$, $Cr[1,3\text{-}C_6H_4(CF_3)_2]_2$, and $Cr[1,3\text{-}C_6H_4Cl(CF_3)]_2$ were evaluated.[13] One complex, the one with meta Cl and CF_3 substituents, is perfectly eclipsed. The other two are rotated by 10° and 17° toward the staggered geometry (for which the rotation angle would be 30°). This again points to a small rotational barrier.

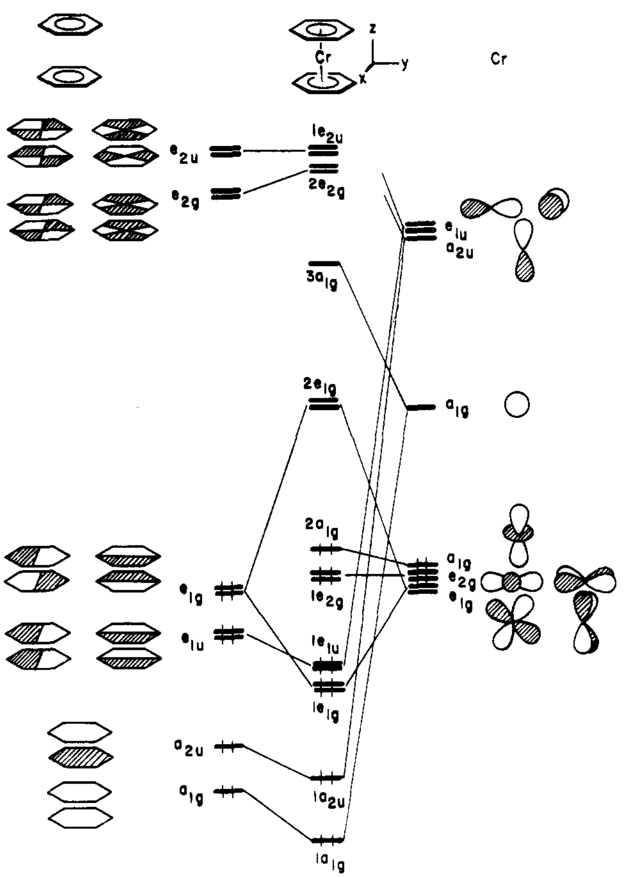


Figure 1. A generalized molecular orbital diagram for bis(benzene)metal complexes of D_{6h} symmetry following the analysis of $(C_6H_6)_2Cr$ by: Shustorovich, E.; Dyatkina, M. E. *Dokl. Akad. Nauk. SSSR* **1959**, *128*, 1234. Photoelectron spectroscopic studies of gaseous bis(benzene), bis(toluene), and bis(mesitylene) complexes of Cr, Mo, and W agree in assigning the lowest ionization energy to ionization from $2a_{1g}$. This ionization energy from the $^2A_1$ ground state is 5.4–5.5, 5.2–5.3, and 5.0–5.2 eV for the benzene, toluene, and mesitylene complexes, respectively. Generally, the chromium and molybdenum complexes have the lowest and highest ionization energy, respectively, for a given arene ligand set. The next band has been assigned to the $^2E_{2g}$ ion state and the next two (unresolved for chromium) successively to the $^2E_{1u}$ and $^2E_{1g}$ ion states. For a general discussion of photoelectron studies of (arene)metal complex, see: Green, J. C. *Struct. Bonding*, **1981**, *43*, 37.

TABLE I. Structural Data for $(\eta^6\text{-arene})_2M$ Complexes[a]

molecule or complex	C–C(ring)	M–C(ring)	M–C_6(grav.)[b]	ring planarity[c]	orientation of rings[d]	C–S(subst. atom)	angle S–C_6 plane[e]	ref
C_6H_6 (g)	1.398 (9)			P		1.077		38
$Cr(C_6H_6)_2$	1.417 (3)	2.142 (2)	1.606 (1)	P	E	0.94 (3)		12
$Cr(C_6H_6)_2$ (g)	1.423 (2)	2.150 (2)	1.613 (5)	P	E	1.090 (5)	–	11
$Cr[p\text{-}(CF_3)_2C_6H_4]_2$	1.390 (10)	2.145 (6)	1.626	P	~E	1.472 (11)		13
$Cr[m\text{-}(CF_3)_2C_6H_4]_2$[f]	1.404 (7)	2.147 (5)	1.624	P	E	1.492 (7)	–	13
$Cr[m\text{-}(CF_3)(Cl)C_6H_4]_2$	1.408 (5)	2.137 (3)	1.609	P	E	1.497 (4)C 1.740 (3)Cl	– –	13
$Cr(C_6H_6)_2{}^+I^-$	1.40	2.13 (4)			E			16
$Cr(C_6H_5CH_3)_2{}^+I^-$	1.42	2.08	1.53		E	1.50, C		17
$Cr(C_6H_5CH_3)_2{}^+$ $[C_{12}H_4N_4{}^-]$	1.38 (4)	2.11 (3)	1.61 (4)		E			18
$Cr(C_6H_5CH_3)_2{}^+$ $[C_{12}H_4N_4{}^-]\cdot C_{12}H_4N_4$	1.40 (4)	2.18 (3)	1.67 (4)		E			19a
$Cr(C_6H_5C_2H_5)_2{}^+I^-\cdot OH_2$	1.40 (5)	2.08 (4)		P	E	1.57 (3)	+	19b
$V(C_6H_6)_2$		2.17	1.66					15
C_6H_5F	1.383[g] 1.396[h]					1.354, F 1.082, H		k
$V(1,4\text{-}C_6H_4F_2)_2$	1.386 (4)[g] 1.415 (4)[h]	2.204 (2)[i] 2.187 (3)[j]	1.671	NP	~E	1.362 (3), F 0.98 (4), H	+, F	21
$C_6(CH_3)_6$ (s)	1.391 (12)			P		1.498 (5)	±	44a
$Co[C_6(CH_3)_5]_2{}^+PF_6{}^-$	1.398 (5)	2.257 (2)	1.770	P	E	1.519 (5)	+	22

[a] Distances in Å. [b] Distance between metal atom and C_6 ring center of gravity. [c] P indicates planar ring; NP indicates substantial deviation from planarity. [d] E indicates carbon atoms of rings are eclipsed; S indicates staggered. [e] + indicates substituent atom or group is bent away from metal; – indicates it is bent toward metal. [f] Dihedral angle between C_6 planes was 2.6°. [g] C(H)–C(F) bond length. [h] C(H)–C(H) bond length. [i] M–C(F) bond length. [j] M–C(H) bond length. [k] Nygaard, L.; Bojesen, I.; Pederson, T.; Rastrup-Andersen, J. *J. Mol. Struc.* **1968**, *2*, 209.

For the gaseous state of bis(benzene)chromium, the hydrogen atoms appear to be bent slightly out of the C_6 plane toward the metal atom.[11] This has been ascribed[14] to better ring orbital overlap with the metal *xz*, *yz* (e_{1g}) set. The atomic p_z orbitals on the ring become pointed more toward the metal. Substituents on the ring, such as CH_3 or CF_3, are displaced slightly away from the ring, presumably to avoid steric contacts.

There are a number of structures available with one electron fewer than $(C_6H_6)_2Cr$. Referring back to Figure 1, this electron would be removed from $2a_{1g}$ which is nonbonding (d_{z^2}). Consequently, one would not expect much in the way of structural differences between the 17- and 18-electron systems. Inspection of Table I shows this to be the case. Crystallographic data[15] for $(C_6H_6)_2V$ have been presented, but a full structural determination was not completed. Also, there was a low-temperature study[16] of $(C_6H_6)_2Cr^+I^-$ in which the 17-electron chromium(I) sandwich compound appeared to be structurally and stereochemically analogous to the parent neutral molecule, but the data set was small and the accuracy of the determination was not high. Related were studies of salts of $(\eta^6\text{-}CH_3C_6H_5)_2Cr^+$. Unfortunately, the accuracies were again low, but within this qualification, the $Cr(C_6)_2$ core structures had approximately D_{6h} symmetry.[17–19a] The reported average C–C bond distances were 1.42, 1.38, and 1.40 Å for the three salts, and the methyl substituents are fully distal to each other and are bent slightly away from the chromium atom. A similar stereochemistry was reported for the analogous ethylbenzene complex in the salt $[(\eta^6\text{-}C_2H_5C_6H_5)_2Cr^+]I^-\cdot OH_2$, but the precision of the crystallographic determination was low.[19b] The structures of $(\eta^{12}$-[3.3]paracyclophane)$Cr^+I_3{}^-$ and $PF_6{}^-$ have also been determined.[20] It is interesting that there are no significant geometrical distortions in the paracyclophane ring upon introduction of the metal.

Two sandwich complexes with substituted benzene ligands have been structurally determined with relatively high accuracy. Bis(1,4-difluorobenzene)vanadium(0) approaches an idealized bis(η^6-arene)M geometry with nearly eclipsed ring carbon atoms and D_2 symmetry.[21] Ring C–C distances were not equivalent; the C(H)–C(H) values are 1.415 (4) Å and the C(H)–C(F) values are 1.386 (4) Å, identical to within experimental error with the analogous C–C separations in gaseous C_6H_5F. Conformation of the C_6 rings was nearly planar, but a significant departure toward the boat conformation is reflected in the inequivalent V–C (ring C–H) and V–C (ring C–F) distances of 2.187 (3) and 2.204 (2) Å. The ring hydrogen atoms appeared to be displaced slightly from the C_4(H) plane described by the four carbon atoms bearing hydrogen substituents toward the metal atom, a displacement consistent with that in $(C_6H_6)_2Cr$. This structure is to be compared with bis(benzene)vanadium(0) where the C–V distances are similar. Although this latter vanadium complex crystal structure determination did not possess a high degree of accuracy, the complex does *appear* to have D_{6h} symmetry with V–C (av) = 2.17 Å and V–C_{grav} = 1.66 Å.[15]

Of special note is the structure of the 20-electron complex, $Co[C_6(CH_3)_6]_2{}^+$, established for the hexafluorophosphate salt.[22] There is again a close approach to idealized D_{6h} symmetry for this cationic bis(arene)cobalt complex although it is required to possess only C_{2h} site symmetry in this crystal. No significant difference in the ring C–C bond lengths was observed; the average ring C–C bond distance is 1.398 (7) Å. The C_6 ring carbon atoms are coplanar to within 0.003 Å and the two rings are in parallel planes. However, there are significant departures from the idealized D_{6h} symmetry—in terms of the $Co(C_6)_2$ core structure; this departure comprised a slippage of each C_6 ring center of gravity off the idealized sixfold axis in the crystallographic mirror plane. This slippage produced small, but statistically significant, differences in the Co–C(ring) separations, which range from 2.235 (2) to 2.278 (2) Å (an identical situation occurs in the 20-electron nickelocene[23a]). The average Co–C(ring) distance is 2.257 (14) Å, which is about 0.06 Å longer than those for 18-electron, first-row transition-metal–arene complexes. Referring back to Figure 1, the extra two electrons go into $2e_{1g}$. If the two rings remain parallel and η^6, then the ground state will be one where the two electrons in $2e_{1g}$ are not paired, i.e., a triplet state, which is the case here. The longer Co–C distances are a reflection of the fact that the metal xz and yz in $2e_{1g}$ are antibonding with respect to the benzene π set. The methyl carbon atoms lie out of the C_6 ring planes by 0.04 to 0.07 Å and are bent away from the cobalt metal atom. Although the rings are eclipsed, there is no inter-ring contact less than the van der Waals sum.

Summarial features for this class of complexes are as follows: (1) the two C_6 rings are planar and parallel and have an eclipsed orientation for benzene and alkylbenzene derivatives; unusual electron-withdrawing or -releasing substituents like fluorine may effect upon the C_6 rings a departure from planarity; (2) the ring C–C distances are equal to within experimental accuracy for C_6H_6 or $C_6(CH_3)_6$ arene ligands; (3) the ring C–C distances are not significantly different from those of the parent gaseous arene molecule; (4) the metal–carbon (ring) distances for first-row transition metals in 18-electron complexes are ~2.15 Å and the metal to C_6 center of gravity separations range from about 1.6 to 1.7 Å; and (5) the ring substituents are slightly out of the C_6 ring plane with hydrogen substituents bent slightly toward the metal atom to achieve a more effective M–C overlap, but bulkier substituents like a methyl group tend to be bent away from the metal atom for steric reasons. In first-row transition-metal complexes with more than 18 electrons, the additional electrons typically reside in the metal–carbon antibonding orbitals resulting in an increase (~0.1 Å) in the metal–carbon bond distance. Second-row (and presumably third-row) transition-metal complexes that have 20 electrons may be different. They may be diamagnetic, 18-electron complexes with one arene ligand η^6 in character and the other an η^4-diene ligand, as discussed below.

None of the stereochemical or conformational features of the bis(η^6-arene)metal structures provide any clues about (arene)metal reaction mechanisms that might involve (η^x-arene)metal species with $x < 6$. The sandwich structure of the 20-electron $Co[C_6(CH_3)_6]_2^+$ complex suggests that metal–carbon bonding can be reduced with retention of a sandwich structure if low-lying unoccupied molecular orbitals are largely metal–carbon antibonding.

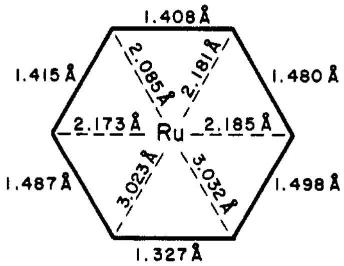
C. Bis(arene)metal Ligand Complexes

The bis(arene)metal sandwich complexes discussed in the previous section formally were 17-, 18-, or 20-electron complexes. Metals of the titanium and vanadium groups also form bis(arene)metal complexes, but these are respectively 16- and 17-electron complexes. Compounds of these metals (see previous section) should have η^6-arene bonding, with the two arene C_6 rings in nearly parallel planes. There is the possibility of conversion of the 16-electron complexes to 18-electron complexes by either donor ligand addition or by oxidative addition of two radical ligands. In either case, the resultant complexes should not have the two η^6-arene ligands in parallel planes; rather they should be canted as are the cyclopentadienyl ligand planes in the analogous bis(cyclopentadienyl)ML_x complexes.[23b]

Bis(benzene)titanium reversibly complexes carbon monoxide, and this carbonyl complex should have the η^6-arene ring planes canted so that the normals to the ring planes generate an angle in the 130–150° range. Recently, the crystal structure of bis(toluene)zirconium bis(trimethylstannyl) has been determined, and the angle formed by the normals to the ring planes is 138.9° and the Sn–Zr–Sn angle is 81.14°.[23c] From the preliminary data reported in this paper, it appears that the η^6-toluene ligands have unexceptional parametric features—the methyl group appears to be bent out of the C_6 plane away from the metal and the Zr–C distances essentially identical to within experimental error (average Zr–C distances are 2.48 (1) Å). In an isoelectronic and related cyclopentadienyl complex, $(\eta^5\text{-}C_5H_5)_2MoBr(SnBr_3)$, the angle generated by the normals to the ligand ring planes is 128.3° and the Br–Mo–Sn angle is 80.2°.[23d] Electronically and structurally, the $(\eta^6\text{-arene})_2ZrX_2$ and $(\eta^5\text{-}C_5H_5)_2MoX_2$ complexes are formally analogous, as are $(\eta^6\text{-arene})_2Cr$ and $(\eta^5\text{-}C_5H_5)_2Fe$. An electronic or theoretical analysis of $(\text{arene})_2ML_x$ or $(\text{arene})_2MX_y$ complexes can be developed in a fashion analogous to that[23b] for the cyclopentadienylmetal analogues. Presumably, this class of bis(arene)metal ligand complexes will have substantial scope within the titanium and vanadium group metals.

D. Arene–Metal Complexes with η^4-Arene Ligands

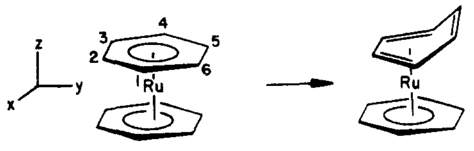
Bis(hexamethylbenzene)ruthenium(0) within our view is one of the most unusual organometallic structures reported to date. One ring, bound in a conventional η^6-fashion, is essentially planar with the methyl substituents expectedly bent out of the ring plane away from the metal atom. Within this η^6-ring ligand, the C–C bond distances vary in a nonalternant fashion between 1.361 (11) and 1.453 (11) Å; the average value is 1.410 Å. The second arene ligand is nonplanar.[24] Only four ring carbon atoms are within bonding distance of the ruthenium atom (2.082 to 2.185 Å), and these carbon atoms are coplanar to within 0.009 Å. The carbon–carbon separations are consistent with those for a diene-like η^4-arene ligand with the two uncomplexed carbon atoms separated by only 1.327 Å, representative of a conventional C–C double bond distance. The other η^4-arene–ruthenium distances are as denoted in the schematic representation 7.



7

Fully analogous is the $(\eta^6\text{-}C_6H_6)Ru[\eta^4\text{-}C_6(C_6H_5)_6]$ complex which has nearly identical structural parameters to the bis(hexamethylbenzene)ruthenium structure.[25] Interestingly, the η^6-arene ligand is benzene, the better donor of the two arenes. Also closely related is $(\eta^5\text{-}C_5H_5)Rh[\eta^4\text{-}C_6(CF_3)_6]$, which is fully isoelectronic to the classic bis(hexamethylbenzene)ruthenium complex. In fact, the structural parameters[26] for the η^4-arene ligand in the two complexes are very similar (*within the accuracy of the two structure determinations*), even though the electronic character of the $\eta^4\text{-}C_6(CH_3)_6$ and $\eta^4\text{-}C_6(CF_3)_6$ ligands are relatively disparate.

The distortion of a 20-electron $(C_6H_6)_2M$ complex from the η^6–M–η^6 to η^6–M–η^4 mode is relatively easy to visualize. Pairing the extra two electrons in $2e_{1g}$ (Figure 1) creates a Jahn–Teller instability. The complex may distort from D_{6h} (or D_{6d}) to a lower symmetry to remove the degeneracy. The specific distortion that takes one ring from η^6 to η^4 bonding is illustrated in 8 → 9. In this distortion, the C_6 centroid–Ru vector of the Ru$(\eta^6\text{-}C_6H_6)$ fragment moves off the center of the other C_6 ring (see 8) toward the C_2–C_3 bond. Also, the C_5–C_6 portion moves up from the plane of the other four carbon atoms away from the metal. The orbitals of $2e_{1g}$ are explicitly drawn out in 10. The lower component of $2e_{1g}$ is stabilized in the 8 → 9 rearrangement because some overlap between metal yz and the top benzene π level is lost. Furthermore, metal y and a higher lying benzene π^* orbital are allowed to mix into this orbital as shown in 11, with the reduction in symmetry. The resultant orbital is indicated by 12. The upper component of $2e_{1g}$ is destabilized somewhat. As C_5–C_6 move out of the plane, the bonding to C_1 and C_4 in this orbital is diminished. Notice that slipping the $\eta^6\text{-}C_6H_6$–Ru portion does not decrease the antibonding of metal xz to the benzene π orbital in the η^4 portion. Thus the a′ orbital in 10 goes down and a″ rises in energy along the distortion path and a sizable gap between the highest occupied and lowest unoccupied levels ensues. However, the energy difference between *triplet* 8 and *singlet* 9 must be small since we are presented examples of each by nature—namely paramagnetic $Co[\eta^6\text{-}C_6(CH_3)_6]_2{}^+$ and the isoelectronic but diamagnetic $[\eta^6\text{-}C_6(CH_3)_6]Ru-\eta^4\text{-}C_6(CH_3)_6]$ complex.



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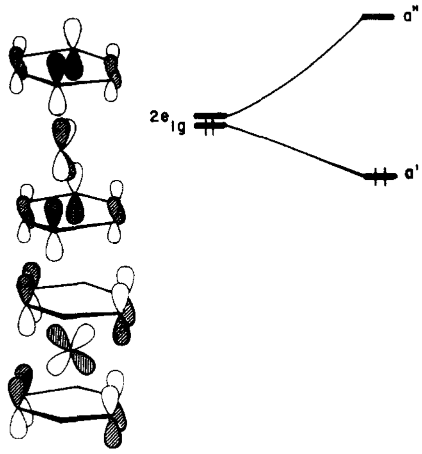

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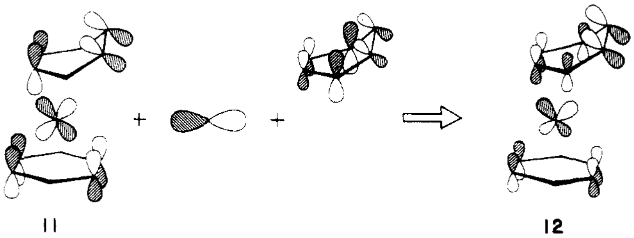
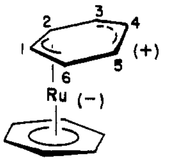


11 12

There are an infinite number of deformations permissible—namely any normal mode or linear combination of modes for D_{6h}–$M(C_6H_6)_2$ that remove the degeneracy. One plausible alternative is conversion to $(\eta^4\text{-}C_6H_6)_2M$ (*formally* a square-planar 16-electron species for d^8 metal configuration). Another is the movement of the $\eta^6\text{-}C_6H_6M$ or specifically the $\eta^6\text{-}C_6H_6Ru$ unit toward C_1 in 8 taking the C_3–C_4–C_5 portion out of the plane, away from the metal. This will destabilize the lower component of $2e_{1g}$ in 10 and stabilize the upper one. The resultant structure, 13, now contains an $\eta^3\text{-}C_6H_6$ moiety. Electron-donating groups at C_1, C_3, and C_5 will stabilize this structure. One might wonder if an $(\eta^4\text{-}C_6H_6)_2Ru$, $(\eta^6\text{-}C_6H_6)_2Ru$, or $(\eta^6\text{-}C_6H_6)Ru(\eta^3\text{-}C_6H_6)$ (13) species could be the transition state or intermediate state for averaging of ring carbon environments in a fluxional $(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}C_6H_6)$ molecule. Only the first is consistent with the data for the dominant exchange mechanism in $[\eta^6\text{-}C_6(CH_3)_6]Ru[\eta^4\text{-}C_6(CH_3)_6]$ as discussed below. The geometrical motions on going from 9 to 13 require passing through a structure very close to the strongly forbidden $(\eta^6\text{-}C_6H_6)_2Ru$ geometry. Therefore, there should be a sizable barrier on going from 9 to 13.



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Bis(hexamethylbenzene)ruthenium is a stereochemically nonrigid molecule.[27,28] At low temperatures (~ −10 °C), the ^1H NMR methyl group resonances for this complex in solution were consistent with the $(\eta^6$-arene)ruthenium$(\eta^4$-arene) structure established for the solid state whereas at ~50 °C all the methyl ^1H resonances were equivalent on the NMR time scale. A line-shape analysis[28] of the ^1H DNMR spectra showed that the permutational character of the dynamic process is consistent with an $(\eta^6$-arene)Ru$(\eta^4$-arene) $\rightleftharpoons$ Ru$(\eta^4$-arene$)_2$ rearrangement and *not* with either an $(\eta^6$-arene)Ru$(\eta^4$-arene) $\rightleftharpoons$ $(\eta^6$-arene$)_2$Ru rearrangement or an $(\eta^6$-arene)Ru$(\eta^4$-arene) $\rightleftharpoons$ $(\eta^6$-arene)Ru$(\eta^3$-arene) rearrangement. The activation parameters for the process were calculated to be $\Delta H^* = 15.6 \pm 1.3$ kcal/mol and $\Delta S^* = -3 \pm 5$ eu.

Attempts to prepare $(\eta^6$-arene)M$(\eta^4$-arene) complexes with benzene or alkyl-substituted benzene (other than hexamethylbenzene) ligands have been unsuccessful.[29] Interestingly, chemical reductions of $\{Rh(C_6(CH_3)_6]^{2+}\}$ under a limited set of reaction conditions invariably yielded an $(\eta^6$-arene)Rh$(\eta^4$-ligand$)^+$ complex in which the η^4-ligand was not hexamethylbenzene but 1,2,3,4,5,6-hexamethylcyclohexadiene.[22] Structural parameters[22] for this complex, with the expected exception of the saturated carbon centers of the η^4-cyclohexadiene ligand, were very similar to those for $[(\eta^6\text{-}C_6(CH_3)_6]Ru[\eta^4\text{-}C_6(CH_3)_6]$ (Table II). The Rh–C distances in this complex are slightly larger and smaller for the η^6-arene and for the η^4-diene, respectively, than the aforementioned and analogous ruthenium complexes. This displacement of the rhodium atom toward the diene ligand is probably a real electronic effect.[22] The hydrogen substituents in the η^4-cyclohexadiene ligand were exo to the metal center.[30]

Structural data for these sandwich structures with η^4-ligands are summarized in Table II.

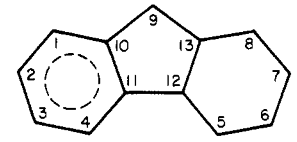
E. Mixed Sandwich Complexes: (η^n-Arene)metal(η^n-C_nH_n) Complexes

This set of arene–metal sandwich structures is potentially large but represented crystallographically only by four complexes, whose structural parameters are listed in Table III.

$[\eta^6\text{-}C_6(CH_3)_6]Fe(\eta^5\text{-}C_5H_5)$ has nearly planar arene and cyclopentadienyl ligands that are in parallel planes (the dihedral angle is only 0.82°). All distance parameters for the arene ligand are indistinguishable, within the precision of this crystallographic analysis,[31] from those of the bis(η^6-arene)metal complexes discussed above. The average aromatic C–C distance is a reasonable 1.38 (1) Å value, but the range is large, 1.324 (10) to 1.417 (13) Å. Unusually long is the apparent Fe–C_5 (center of gravity) distance of 1.79 (1) Å, but this complex is a 19-electron species with one electron in an orbital analogous to $2e_{1g}$ in Figure 1. The trimethylene-bridged analogue based on the ligand $C_5H_4CH_2CH_2CH_2C_6H_5$ has been studied by X-ray diffraction[32] but was disordered, and the precision of the structure determination is too low to permit a meaningful comparison of this structure with the above-described nonbridged analogue.

In the 18-electron $\eta^5\text{-}C_5H_5Ru[\eta^6\text{-}C_6H_5B(C_6H_5)_3]$ complex, the η^5-C_5 and η^6-C_6 rings each are nearly planar and generate a nearly zero dihedral angle (2.95°).[33] The distances between the ruthenium atom and the ring planes are 1.817 (C_5) and 1.701 (C_6) Å; the Ru–C(C_5) distance is 2.170 (6) Å. For the C_6 ring, the carbon atom attached to boron has a Ru–C separation of 2.271 Å which is significantly larger than that for the other five, 2.195 (12) Å, which reflects the fact that this carbon lies slightly out of the arene ring plane away from the ruthenium atom and that the two C–C ring distances for the ring carbon atom attached to boron *appear* to be slightly longer than the other four—1.419 (9) and 1.428 (9) Å, as compared with an 1.40 (1) Å average for the other four. The cyclopentadienyl ligand C–C distance is 1.394 (18) Å. It is significant as an internal and relative reference check that the average ring C–C distance in the η^6-ligand appeared to be larger than for the three, planar uncomplexed phenyl rings—1.410 (4) Å vs. 1.379 (12) Å. Closely analogous is the structure of $(\eta^7\text{-}C_7H_7)Mo[\eta^6\text{-}C_6H_5B(C_6H_5)_3]$.[34] Both ring ligands were *nearly* planar and parallel. Actually, the η^6-C_6H_5B ligand was not exactly planar; the carbon atom bearing the boron substituent was bent out of the mean plane of the other five carbon atoms away from the metal atom. Hence the Mo–C distance for this unique carbon was substantially larger than the mean of the other five distances, 2.430 vs. 2.341 Å. The hydrogen substituents of the η^6-phenyl ring were bent out of the ring plane toward the metal atom. As in the ruthenium complex, the mean C–C ring distance was apparently larger than those of the three uncomplexed phenyl rings, 1.412 (6) vs. 1.394 (6) Å, although when a very conservative 3σ criterion is used, the difference is not significant.

Related to the first two complexes in this class is $[C_5H_5FeC_{13}H_{10}]^+PF_6^-$ where $C_{13}H_{10}$ is the fluorene molecule. Treatment of this 18-electron complex with potassium *tert*-butoxide yielded $C_5H_5FeC_{13}H_9$, a diamagnetic sandwich complex with an η^5-C_5H_5 and an η^6-$C_{13}H_9$ ligand (**14**). Not all six complexed carbon atoms of the latter are coplanar—C_1, C_2, C_3, C_4, and C_{11} are coplanar to within 0.027 Å but C_{10} lies out of this plane by 0.151 and 0.134 Å for molecules A and B in the unit cell (the uncomplexed C_6 ring atoms are coplanar to 0.009 Å).[35] In this C_6 ligand ring, the average C–C separation is 1.419 Å compared with 1.392 Å for the uncomplexed C_6 ring; internally, the difference is significant, but not in an absolute context for comparison with strictly aromatic C_6 ring ligand systems. Average carbon–iron distances are 2.034 and 2.126 Å for the C_5 and C_6 ring systems with the range large for the latter, 2.036 to 2.308 Å. Whether this complex is best represented in an idealized context as zwitterionic $(\eta^5\text{-}C_5H_5)Fe^I(\eta^6\text{-arene})$ (**15a**) or an $(\eta^5\text{-}C_5H_5)Fe^{II}(\eta^5\text{-}C_{13}H_9)$ (**15b**) complex is a moot issue, but the structural parameters appear to favor the former. The basic issue of structure and bonding in (arene)metal complexes with the arene a condensed aromatic is more fully addressed in a later section that deals with the relatively large class of (arene)ML_3 complexes.



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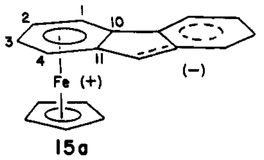
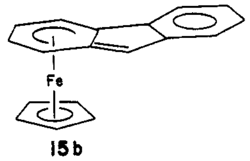


15a



15b

III. η^6-Arene–ML_3 Complexes

A. Classifications

To enable a cohesive and logical discussion of structure and stereochemistry, the large group of η^6-arene–ML_3 structures has been divided into four classes, based on the number and arrangement of substituent groups on the arene ring. The first class consists of structures in which the arene ligand itself possesses a 3-fold or 6-fold symmetry axis; i.e., the ring carbon atoms either have six identical substituent groups or two alternating sets of identical substituents. The second class comprises complexes with monosubstituted benzene rings. The third class comprises complexes with disubstituted and unsymmetrically substituted benzene ligands. In the fourth class, the η^6-arene ligand is part of a larger condensed aromatic molecule. Structural and stereochemical data for these four structural classes are sum-

TABLE II. Structural Data for (η^6-arene)M(η^4-arene) or (η^6-arene)M(η^4-cyclodiene) and (η^5-C_5H_5)M(η^4-arene) Complexes[a]

	η^6-arene ring or η^5-C_5H_5 ring						η^4-cyclodiene ring or η^4-arene ring						
molecule or complex	C-C	M-C	M-C_5 or C_6 (grav.)[b]	C-S[c]	angle S-C_6 plane[d]	δ[e]	C(i)-C(i)[f]	C(i)-C(o)[f]	M-C(i)[f]	M-C(o)[f]	M-C_4-(grav.)[b]	δ(C_6)[g]	ref
$C_6(CH_3)_6$ (s)	1.391 (12)			1.498 (5)	±								44
η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$[h]	1.42 (2)	2.25 (2)	1.750	1.52 (2)	+	5.2	1.41	1.45 (3)	2.12 (4)	2.18 (1)	1.726	42.8	24
η^6-$C_6(CH_3)_6$Rh-η^4-C_6-$(CH_3)_6H_2{}^+PF_6{}^-$	1.38 (1)	2.301 (7)	1.84	1.53 (2)	+	4.7	1.45	1.48 (2)	2.10 (1)	2.14 (1)	1.72	40	22
η^5-C_5H_5Rh-η^4-$C_6(CF_3)_6$[i]	1.39 (3)	2.20 (2)	1.85	1.52		8.9	1.42	1.50 (3)	2.09 (2)	2.13 (2)	1.67	47.9	26
η^6-C_6H_6Ru-η^4-$C_6(C_6H_5)_6$[j]	1.42 (2)	2.25 (1)					1.43	1.46	2.12 (1)	2.17 (1)		46.8	25

[a] Distances in Å and angles in degrees. [b] Distance between metal atom and center of gravity of η^4-diene ligand or η^6/η^5 ring. [c] Distance between ring carbon atom and the substituent atom. [d] + indicates substituent atom or group is bent away from metal; – indicates it is bent toward metal. [e] Dihedral angle defined by η^6-arene (or η^5-C_5H_5) ring plane and C_4 plane of the η^4-diene ligand. [f] i represents the inner carbon atoms and o the outer carbon atoms of the diene ligand. [g] The dihedral angle between the two planes of η^4-arene ligand. [h] The olefinic C–C distance is 1.33 Å. [i] The olefinic C–C distance is 1.31 Å. [j] The olefinic C–C distance is 1.33 Å.

TABLE III. Structural Data for (η^6-arene)M(η^n-C_nH_n) Complexes[a]

	η^6-arene ligand						η^n-C_nH_n ligand				
complex	C-C	M-C	M-C_6-(grav.)[b]	ring planarity[c]	angle S-C_6 plane[d]	δ[e]	C-C	M-C	M-C_n-(grav.)[b]	ring planarity[c]	ref
$C_5H_5FeC_6(CH_3)_6$	1.38 (1)	2.10 (1)	1.60	~P	-	0.82	1.40 (1)	2.144 ( )	1.79	~P	31
$C_5H_5FeC_{13}H_9$ ($C_{13}H_9$ = fluorenyl ligand)	1.42	2.126[g]	1.56	NP		2.7(A), 1.9(B)[f]	1.39	2.034	1.65	P	35
η^5-$C_5H_4(CH_2)_3(\eta^6$-$C_6H_5)Fe^+$	1.36	2.10	1.59	P		7	1.52	2.08	1.62	P	32
$C_5H_5Ru[\eta^6$-$C_6H_5B(C_6H_5)_3]$	1.41	2.20[g]	1.701	NP		2.95	1.39	2.17	1.817	P	33
$C_7H_7Mo[\eta^6$-$C_6H_5B(C_6H_5)_3]$	1.412 (6)	2.341[g,h]	1.887	~P	-(H)	4.2	1.406 (7)	2.275 (5)	1.596	P	34

[a] Distances in Å and angles in degrees. [b] Distance between metal atom and center of gravity of η^6 or η^n ring. [c] P indicates planar ring; NP indicates substantial deviation from planarity. [d] + indicates substituent atom or group is bent away from metal; – indicates it is bent toward metal. [e] Dihedral angle defined by η^6-arene ring plane and η^n-ligand ring plane. [f] Two crystallographically independent molecules in the unit cell. [g] One carbon atom of the ring is substantially farther from the metal atom than the other five. [h] Average value for carbon atoms with hydrogen substituents; the Mo–C(B) distance is 2.430 Å.

TABLE IV. (η^6-Arene)ML_3 Structures with Arenes Possessing 3-Fold or 6-Fold Symmetry Axes[a]

complex	ring[b]	confign (n of C_n)[c]	C-C(ring)	M-C(ring)	M-C_6(grav.)[d]	M-C(CO)	angle S-C_6 plane[e]	ref
C_6H_6	P	D_{6h} (6)	1.398 (9)					38
$C_6(CH_3)_6$	P	D_{3d} (3)	1.391 (12)				+, – (C)	44
$C_6(C_2H_5)_6$	P	D_{3d} (3)	1.402 (1)				+, ± (C, CH_3)	43
$C_6H_6Cr(CO)_3$	P	stag (3)	1.423 (1) 1.406 (1)	2.233 (7)	1.73	1.842 (4)	– (H)	37
$C_6(CH_3)_6Cr(CO)_3$	P	stag (6)	1.42 (3)	2.23 (1)	1.73	1.81 (2)	+ (C)	41
$C_6(C_2H_5)_6Cr(CO)_3$	P	ecl (3)	1.421 (4)	2.235	1.73	1.823 (5)	+, ± (C, CH_3)[f]	43
$C_6(C_2H_5)_6Cr(CO)_2P(C_6H_5)_3$	P	stag (6)	1.424 (10)	2.235	1.73	1.81	+ (C, CH_3)	43
$C_6(CH_3)_6Mo(CO)_3$	P	stag (3)	1.405 (5) 1.441 (9)	2.392 (5)	1.92	1.943 (3)	+ (C)	42
$C_6(C_2H_5)_6Mo(CO)_3$	P	ecl (3)	1.425 (2)	2.384	1.91	1.946 (5)	+, ± (C, CH_3	43

1,3,5-$C_6H_3(CH_3)_3Mo(CO)_3$	P	ecl (3)^g	1.408 (10)	2.372 (5)	1.91	1.946 (10)	+ (C)	42
$\{C_6(CH_3)_6Re(CO)_3{}^+\}$	P	stag		2.33				*k*
$C_6H_6Ru(CO)(GeCl_3)_2$	P	ecl (6)	1.408 (6)	2.29	1.81	1.87 (2)		47
$\{$1,3,5-$C_6H_3(CH_3)_3$-$Mo[(CH_3)_2PC_2H_4P(CH_3)_2]$-$N\}_2$	P	ecl (10–15°) (3)^h	1.410 (10)	2.28 (2)	1.79	2.402 (7)^m	+ (C)	49
$[C_6H_6RuB(pz)_4]^+PF_6{}^-$ ^{t}	P	stag (6)	1.44	2.30 (3)	1.67	2.107 (5)		45
[1,3,5-$C_6H_3(CH_3)_3$]Ru-(4-hydroxy-4-methylpentan-2-one)(acetone)$^{2+}(BF_4{}^-)_2$				2.16–2.20		2.12,2.14^p 2.11^q		50
$C_6H_6RuCl_2[PCH_3(C_6H_5)_2]$	NP^i	stag (6)		2.19^r 2.27^{j,s}		2.335^m 2.410^n		46
[1,3,5-$C_6H_3(CH_3)_3$]-Ru(1-5-η^5-C_8H_9)	NP^u		1.409 (5)	2.224 (3)^v 2.255 (10)^w	1.74		+, +, – (C)	*o*
[1,3,5-$C_6H_3(CH_3)_3$]-Ru(1-3,6,7-η^5-C_8H_9)	NP		1.41 (1)	2.232 (13)	1.74		–, –, – (C)	*o*
$C_6(C_2H_5)_6Cr(CO)_2P(C_2H_5)_3$ ^{l}	P	ecl (6)	1.422	2.230	1.718	1.800	+, ± (C, CH_3)	43b
$C_6(C_2H_5)_6Cr(CO)_2P(C_2H_5)_3$ ^{l}	P	stag (6)	1.421	2.227	1.716	1.814	+, + (C, CH_3)	43b

[a] Distances in A. [b] P indicates planar ring. [c] stag indicates that ring carbon atoms are staggered with respect to the ligands, L. ecl indicates that ring carbon atoms and ligands, L, are eclipsed. C_n is the highest symmetry axis possessed by the arene. [d] Distances between metal atom and center of gravity of arene ring. [e] + indicates substituent atom, S (in parentheses), is bent away from metal; – indicates it is bent toward metal. [f] The methylene carbon atoms are all located on the side of the C_6 plane away from M; however, the methyl carbon atoms project alternatively above and below the plane of the C_6 ring. For the three noneclipsed ethyl groups, the methyl carbon atom is on the metal side of the ring. For the three eclipsed ethyl groups, the methyl carbon atom is located on the side of the ring away from the metal. [g] Methyl groups of arene ligand reside on eclipsed ring carbon atoms. [h] Methyl groups of arene ligand reside on noneclipsed ring carbon atoms. [i] Ring is slightly boat shaped. [j] The two carbon atoms trans to the phosphine ligands are farther from the metal atom than those trans to the Cl ligands. [k] Davis, R. L.; Baenziger, N. C. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 475. [l] One of two conformers. [m] Metal–phosphorus distance. [n] Metal–chlorine distance. [o] Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1981**, *20*, 2353. [p] Metal–oxygen (pentanone) distance. [q] Metal–oxygen (acetone) distance. [r] Four short distances. [s] Two long distances. [t] $B(pz)_4$ = tetrakis(1-pyrazolyl)-borate. [u] Twist-boat distortion of ring. [v] Three short distances. [w] Three long distances.

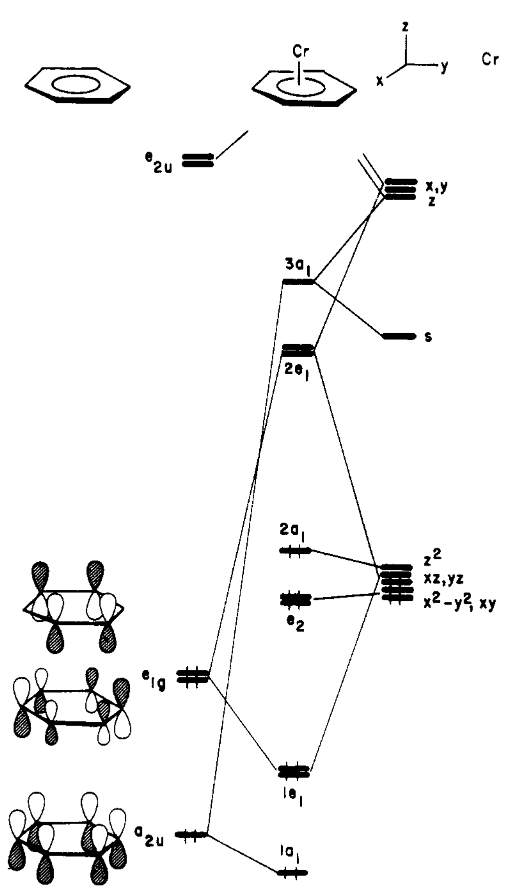
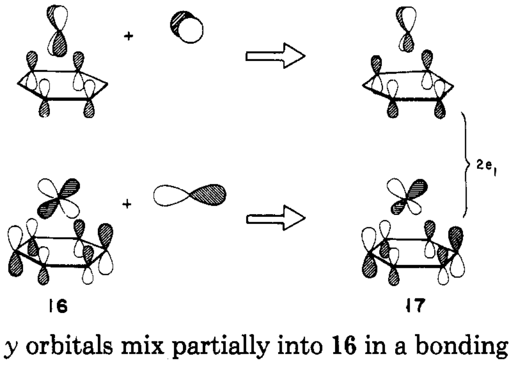


Figure 2. Construction of the valence orbitals in benzene–Cr.

marized in Tables IV–VII, respectively.

B. General Bonding Considerations

One insightful way to describe the orbitals of a benzene–ML_n complex is by interacting the valence orbitals of a benzene–M unit with symmetry-adapted combinations of lone-pair orbitals from the L_n set. This procedure is employed here, and the representation for the benzene–M fragment is then used as a basic construction unit throughout the remainder of this article. Figure 2 illustrates the construction of the valence orbitals in benzene–Cr[14] wherein a familiar pattern emerges. The three filled π levels of benzene, a_{2u} + e_{1g}, are stabilized by chromium orbitals. Three metal orbitals (z^2, $x^2 - y^2$, xy) of $2a_1$ + e_2 symmetry remain "nonbonding". An essentially identical situation was described earlier for bis(benzene)chromium but with the difference that in C_6H_6Cr there are now three empty, low-lying orbitals. The $2e_1$ set consists of metal xz and yz that are antibonding with respect to the benzene e_{1g} orbital, **16**. What keeps $2e_1$ at low energy is that metal



16

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x and y orbitals mix partially into **16** in a bonding (less

TABLE V. η^6-Arene–ML_3 Structures with Monosubstituted Benzene Ligands[a]

complex	ring[b]	configuration[c]	C–C(ring)	M–C(ring)	M–C_6(grav)[d]	M–C(CO)	angle S–C_6 plane[e]	ref
$C_6H_5CH_3Cr(CO)_3$	P	EE (2.2)	1.388 (14)	2.213 (14)	1.72	1.824 (6)	+ (C)	53
$C_6H_5CH_3Re(CO)_3{}^+$	P	E		2.33				*g*
$C_6H_5COOCH_3Cr(CO)_3$	P	E	1.42 (2)	2.22 (1)	1.71	1.85		52
$C_6H_5COOCH_3Cr(CO)_3$	P	E	1.407 (8)	2.22 (1)	1.71	1.842 (5)	+ (C)	54
$C_6H_5OCH_3Cr(CO)_3(1,3,5\text{-}C_6H_3(NO_2)_3)$	P	EE	1.41 (2)	2.23 (2)	1.73	1.79		51
$C_6H_5CH[C(CH_3)_3]_2Cr(CO)_3$	NP[f]	near E (16°)	1.403 (8)	2.24 (4)	1.74	1.827 (1)	+15.4 (C)	55
$C_6H_5COOCH_3Cr(CO)_2CS$	P	E	1.401 (7)	2.23 (1)	1.73	1.849 (2)	– (C)	59
$C_6H_5COCH_3Cr(CO)_3$	P	S (26, 33, 34°)						*h*
$(CH_3)_2PC_6H_5Mo[P(CH_3)_2C_6H_5]_3$	P	E	1.43 (2)	2.28 (2)	1.78	2.43 (1)[p]	+ (P)	*i*
$C_6H_5COOCH_3Cr(CO)_2(CNCOC_6H_5)$		S		2.20–2.24				*j*
$C_6H_5COOCH_3Cr(CO)_2P(C_6H_5)_3$	P	E	1.397 (7)	2.198 (4)	1.70	1.823 (3) 2.34[p]		*k*
$\{C_6H_5P(C_6H_5)_2Cr(CO)_2\}_2$	P	EE (3.5°)		2.19		1.83		*l*
$C_6H_5(C_6H_5)AsCH_2As(C_6H_5)_2Cr(CO)_2$	P	EE (15.9°)	1.403 (27)	2.181 (10)	1.67	1.827 2.406	+ (As)	*m*
$(C_6H_5Cr(CO)_3)_2$	P	S		2.20 (3)				
$[(C_2H_5)_4N][\eta^6\text{-}C_6H_5B(C_6H_5)_3Mo(CO)_3]$	P	S	1.415 (6)	2.372 (5)[q] 2.432 (3)[r]	1.916	1.953		34
$C_6H_5N(C_2H_5)_2Cr(CO)_3$	NP[f]	EE		2.214 (13)[q] 2.369 (2)[r]				58
$C_6H_5C(O)OCH_3Cr(CO)_2PF_3$		S (17.6, 17.7, 19.0°)	1.401	2.201 (10)	1.698 (2)	1.833 (11) 2.132 (3)[p]		60
$C_6H_5P(C_6H_5)_2RuH(P(C_6H_5)_3)_2{}^+BF_4{}^-$				2.28	1.78	2.322 (11)[p]		*n*
$C_6H_5B(C_6H_5)_3Ru(1\text{-}3,5,6\text{-}\eta\text{-}C_8H_{11})$						2.16–2.18[s] 2.23–2.69[t]		*o*
$C_6H_5BF_3Ru(1\text{-}3,5,6\text{-}C_8H_{11})$						2.21–2.27[s] 2.15–2.28[t]		*o*
$C_6H_5COOCH_3Cr(CO)_2CSe$	P	E	1.40 (3)	2.23 (2)	1.742 (1)	1.86 (1)	0°	*u*

[a] Distances in Å. [b] P indicates planar ring; NP indicates nonplanarity. [c] E indicates that three ring carbon atoms and the three ligands, L, are eclipsed; however, the arene substituent resides on a noneclipsed ring carbon atom. EE indicates an eclipsed structure in which the arene substituent resides on one of the three eclipsed ring carbon atoms. S indicates that ring carbon atoms are staggered with respect to the ligands, L. [d] Distance between metal atom and center of gravity of arene ring. [e] + indicates substituent atom, S (in parenthesis), is bent away from metal; – indicates it is bent toward metal. [f] Ring carbon atoms 1 and 4 are displaced out of the plane of the other four ring carbon atoms away from the metal. [g] Davis, R. L.; Baenaiger, N. C. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 475. [h] Dusausoy, Y.; Protas, J.; Besancon, J.; Tirouflet, J. *C. R. Hebd. Seance Acad. Sci., Ser. C.* **1970**, *270*, 1792. [i] Mason, R.; Thomas, K. M.; Heath, G. A. *J. Organomet. Chem.* **1975**, *90*, 195. [j] Le Maux, P.; Simmoneaux, G.; Jaouen, G.; Ouahab, L.; Batail, P. *J. Am. Chem. Soc.* **1978**, *100*, 4312. [k] Andrianov, V. C.; Struchkov, Yu. T.; Baranetzkaya, N. K.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.*, **1975**, *101*, 209. [l] Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *60*, C11. [m] Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1974**, *13*, 1047. [n] McConway, J. C.; Skapski, A. C.; Phillips, L.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1974**, 327. [o] Ashworth, T. V.; Nolte, M. J.; Reimann, R. H.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1977**, 937. [p] Metal-phosphorus distance. [q] Unsubstituted carbon atom. [r] Substituted carbon atom. [s] Olefinic carbon atom. [t] Allylic carbon atom. [u] Saillard, J.-Y.; Grandjean, D. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3772.

TABLE VI. η^6-Arene-ML_3 Structures with Disubstituted Arene Ligands[a] and 1,2,3-Trisubstituted Arene Ligands

complex	ring[b]	configuration[c]	C-C(ring)	M-C(ring)	M-C_6(grav)[d]	M-C(CO)	angle S-C_6 plane[e]	ref
o-$C_6H_4(OCH_3)(COCH_3)Cr(CO)_3$	P	E (OCH_3)	1.42 (6)	2.241 (2)	1.73	1.84 (3)	+ (O), − (C)	61
o-$C_6H_4(OH)(COCH_3)Cr(CO)_3$	P	E (OH)	1.44 (3)	2.25 (6)	1.73	1.84 (2)	− (O), − (C)	61
p-$C_6H_4[C(CH_3)_3](COOH)Cr(CO)_3$	P	~S	1.41 (1)	2.21 (2)	1.70	1.83 (1)	− (C, COOH), + (C)	63
o-$C_6H_4CH_3[C(OH)(C_2H_5)(C_6H_5)]Cr(CO)_3$[f]	P	E (CH_3)	1.42 (2)	2.23 (2)	1.72	1.80 (2)	+ (C, CH_3), + (C)	62
o-$C_6H_4(CHOHCH_3)_2Cr(CO)_3$	P	S	1.42 (1)	2.22 (2)	1.71	1.83 (1)	+ (C)	*m*
o-$C_6H_4(CH_3)[C(OH)(CH_3)(C_2H_5)]Cr(CO)_3$[f]	P	~E (CH_3)	1.44 (4)	2.26 (1)	1.74	1.80 (1)	+ (C, CH_3), − (C)	*n*
o-$C_6H_4(CH_3)(NH_2)Cr(CO)_3$	P	~E (NH_2)	1.40 (2)	2.25 (4)	1.76	1.78 (1)	+ (N)	*o*
(*exo*-2-acetoxybenzonorbornenyl)$Cr(CO)_3$	P	S	1.44 (2)	2.25 (1)	1.73	1.84 (1)	+ (C)	*p*
o-$C_6H_4(CH_3)(CO_2)Cr(CO)_3^-$	P	S		2.21 (1)		1.81 (1)		*q*
m-$C_6H_4(CH_3)(CO_2)Cr(CO)_3^-$	P	S		2.20 (1)		1.83 (1)		*q*
o-$C_6H_4(OCH_3)[CHOH(CH_3)]Cr(CO)_3$	P	E (OCH_3)	1.41 (2)	2.23 (4)	1.73	1.84 (3)	+ (O), − (C)	*r*
o-$C_6H_4(CH_3)[COH(C_6H_5)C_2H_5]Cr(CO)_3$	P	E (CH_3)						*s*
(*exo*-2-methyl-1-indanol)$Cr(CO)_3$		S	1.401	2.213	1.714	1.824		*t*
(*endo*-2-methyl-1-indanol)$Cr(CO)_3$		S	1.404	2.221	1.72	1.835		*t*
[o-$C_6H_4[C(O)(CH_2)_3]]Cr(CO)(CS)(PPh_3)$		S	1.43	2.24	1.72	1.85		*u*
[[2.2]paracyclophane]$Cr(CO)_3$	NP[g]	S	1.398 (8)[v] 1.417 (6)[x] 1.407 (6) (aver)[h]	2.211 (11)[w] 2.342 (2)[g,y]		1.842 (8)	+	64
p-$C_6H_4(CH_3)(CH(CH_3)_2)RuCl_2PCH_3(C_6H_5)_2$	NP[i]	S		2.21[z,j] 2.25[z,j]		2.341 (P) 2.414 (Cl)		46
p-$C_6H_4(t\text{-}C_4H_9)_2Ru(CO)(SiCl_3)_2$	NP[i]	~S	1.41 (1)	2.36 (4)		1.843 (5)	+	*aa*
(*exo*-OMN·Ma)$Cr(CO)_3$[bb]	NP	S	1.42 (2)	2.23 (2)	1.72	1.819 (5)	+, −	77b
[1,2,3-$C_6H_3(OCH_3)_3$]$Cr(CO)_3$	NP[k]	EE[l]		2.252 (15)				58

[a] Distances in Å. [b] P indicates planar ring. [c] E indicates that three ring carbon atoms and the three ligands, L, are eclipsed. The eclipsed arene substituent group is given in parentheses. S indicates that the ring carbon atoms are staggered with respect to the ligands, L. For ortho-substituted arenes, two different staggered orientations are possible. In one orientation, a M-L bond projects onto the C_1-C_2 bond of the arene. In the other orientation, a M-L bond does not project onto the C_1-C_2 arene bond. All of the staggered structures cited here possess the latter orientation. [d] Distance between metal atom and center of gravity of arene ring. [e] + indicates substituent atom, S (in parenthesis), is bent away from metal; − indicates it is bent toward metal. [f] One of two diastereomers. [g] The ring is boat shaped, with the substituted carbon atoms bending away from the Cr atom. However, this bending is no greater than in the parent cyclophane molecule. [h] Although a claim of C-C bond alternation has been made, the standard deviations are relatively large. [i] The ring is slightly boat shaped. [j] The two carbon atoms trans to the phosphine ligands are farther from the metal atom than those trans to the Cl ligands. [k] The ring has an inverted boat shape; the end carbon atoms bend in slightly toward the Cr atom. [l] EE indicates the eclipsed configuration in which two arene substituents reside on eclipsed ring carbon atoms,

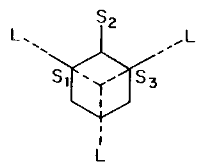

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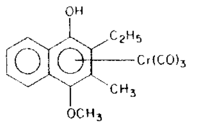
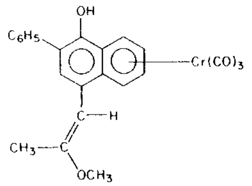
TABLE VII. Condensed Arene-ML_3 Structures[a]

complex (arene)	ring[b]	config.[c]	C-C	Cr-C[d]	Cr-C_6[e]	Cr-C(CO)	angle S-C_6 plane[f]	ref
1-$C_{10}H_7NH_2Cr(CO)_3$ (1-aminonaphthalene)	P (unsubst ring)	~S (24° av)	1.43 (1)	2.25 (4) av 2.22 2.30	1.74	1.76 (5)	+ (C)	72
$C_{10}H_8Cr(CO)_3$ (naphthalene)	NP	~S	1.41 (3)	2.26 (6) av 2.20 2.32	1.70	1.821 (3)		76
$C_{14}H_{12}Cr(CO)_3$ (9,10-dihydrophenanthrene)	P	S	1.403 (12)	2.217 (15) av 2.206 (3) 2.240	1.70	1.833 (8)	+ (C)	*g*
$C_{14}H_{10}Cr(CO)_3$ (phenanthrene, orthorhombic)	NP (end ring)	S	1.41 (2)	2.239 (37) av 2.209 (2) 2.289	1.74	1.84 (1)	+ (C)	73
$C_{14}H_{10}Cr(CO)_3$ (phenanthrene, monoclinic)	P (end ring)	S	1.41 (3)	2.25 (4) av 2.211 (3) 2.284	1.75	1.834 (7)	+ (C)	79
	P	~S	1.42 (2)	2.25 (3) av 2.23 (2) 2.30	1.75	1.83 (2)	+ (C)	*h*
$C_{14}H_{10}Cr(CO)_3$ (anthracene)	NP (end ring)	S	1.42 (2)	2.23 (4) av 2.218 (2) 2.33	1.76	1.842 (8)	+ (C)	78
$C_{14}H_{12}Cr(CO)_3$ (1,4-dihydrophenanthrene)	P (central ring)	S	1.41 (2)	2.24 (3) av 2.22 2.25	1.74	1.81 (2)	+ (C)	79
	P	S	1.41	2.24 av 2.21 2.30				*i*
$Cr(C_{14}H_{10})[P(C_2H_5)_3](CO)_2$ (phenanthrene)	P (end ring)	S	1.408	2.229 av 2.191 2.305		1.86 2.323 (M-P)	+ (C)	77
$Cr(C_{10}H_8)[P(OC_6H_5)_3](CO)_2$ (naphthalene)	NP	S	1.406	2.241 av 2.202 2.320		1.819 2.217 (M-P)		77
$(C_{14}H_{10})Cr(CO)_3 \cdot 1,3,5\text{-}(NO_2)_3C_6H_3$ (phenanthrene)	P (end ring)	S	1.418	2.240 av 2.224 2.272		1.840	+ (C)	80
$C_{18}H_{12}Cr(CO)_3$ (triphenylene)	NP	S	1.407 (6)	2.222 (3) 2.204 (3) 2.258 (2)	1.720	1.837 (3)	+ (C)	71
$C_{12}H_8Cr(CO)_3$ (biphenylene)	P	SS	1.411 (7)	2.226 (3) 2.225 (3) 2.228 (3)	1.724	1.843 (5)	+ (C)	71
$C_{10}H_8$ (naphthalene)	P		1.400					*j*
$C_{10}H_8$ (anthracene)	P		1.409					*j*
$(CH_3)_8C_{10}Cr(CO)_3$[k]	NP	S	1.43 (2)	2.28 (7)	1.75	+, −		77b

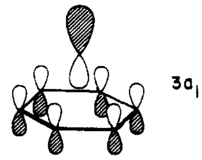
[a] Distances in Å. [b] P indicates planar ring; NP indicates significant departure from planarity. [c] S indicates that the ring carbon atoms are staggered with respect to the ligands, L. For ortho-substituted arenes such as condensed aromatic molecules, two different staggered orientations are possible. In one orientation, a M-L bond projects onto the C_1-C_2 bond of the arene. In the other orientation, a M-L bond does not project onto the C_1-C_2 arene bond. All of the staggered structures cited here are of the latter type. [d] In each group: the first number is the average of the six Cr-C(ring) bond distances; the second number is the average of the Cr-C (ring unsubstituted) bond distances; the third number is the average of the Cr-C (ring junction) bond distances. [e] Perpendicular distance from the metal atom to the plane of the complexed arene ring. [f] + indicates substituent atom, S (in parentheses), is bent away from metal; – indicates it is bent toward metal. [g] Muir, K. W.; Ferguson, G. *J. Chem. Soc. B* **1968**, 476. [h] Dötz, K. H.; Dietz, R.; von Imhof, A.; Lorenz, H.; Huttner, G. *Chem. Ber.* **1976**, *109*, 2033. [i] Dietz, R.; Dötz, K. H.; Neugebauer, D. *Nouv. J. Chim.* **1978**, *2*, 59. [j] Cruichshank, D. W. J.; Sparks, R. A. *Proc. R. Soc. London, Ser. A* **1960**, *258*, 270. [k] Octamethylnaphthalene.

TABLE VIII. Structural Data for η^6-Arene-ML_2 Complexes[a,b]

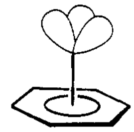
complex	C-C	M-C(4)[c]	M-C(2)[d]	M-C_4(grav)[e]	d[a,f]	θ[b,g]	M-L	L-M-L	ref
$(C_6H_5)_3B(\eta^6\text{-}C_6H_5)Rh[P(C_6H_5)_2CH_2]_2$	1.414 (8)	2.36 (6)	2.281 (3)	1.882	0.06, 0.08	4.2	2.221 (4)	84.3 (0)	*i*
$(\eta^6\text{-}C_6H_6)RuC_8H_{12}$	1.39 (2)	2.255 (4)	2.197 (3)	1.728	0.05, 0.06	5.0			*j*
$\{(\eta^6\text{-}C_6D_6)Rh[1,2\text{-}[(C_6H_5)_2PCH_2]_2\text{-}c\text{-}C_4H_6]^+\}$	1.38 (3)	2.35 (3)	2.299 (2)	1.884	0.02, 0.04	60.6	2.224 (8)	96.2 (1)	85
$[\eta^6\text{-}C_6(CH_3)_6]RuC_8H_8$	1.42 (2)	2.210 (7)[h]	2.172 (8)[h]	2.701[h]	0.05	88.9			91
$(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2$	1.39 (2)	2.126 (6)	2.17 (1)	1.620	−0.01 (1), −0.01 (1)	90°	1.931 (5)	88.3 (3)	89
$(\eta^6\text{-}C_6H_5CH_3)Fe(bpy)$	1.413 (8)	2.106 (2)	2.088 (2)	1.545	0 0	90	1.902 (1)	81.93 (8)	90
$\{(\eta^6\text{-}C_6H_5CH_3)Rh[P(OC_6H_5)_3]_2{}^+\}$	1.38 (3)	2.31 (1)	2.39 (3)	1.863 (9)	0.04, −0.06	81.8	2.184 (4)	90.1 (1)	*k*
$(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$	1.39 (2)	2.168 (5)	2.24 (1)	1.681	−0.06, −0.06	90°	1.891 (4)	87.7 (2)	89
$(\eta^6\text{-}1,3,5\text{-}(CH_3)_3C_6H_3)Ni(C_6F_5)_2$	1.40 (1)	2.191 (4)	2.252 (3)	1.693	−0.06, −0.06	77	1.898 (4)	91.4 (1)	87
$(C_6H_5)_3B(\eta^6\text{-}C_6H_5)Rh[P(OCH_3)_3]_2$	1.42 (1)	2.31 (1)	2.41 (4)	1.841	−0.06, −0.07	79.0	2.18 (1)	90.4 (1)	*l*

[a] Distances in Å. [b] Angles in degrees. [c] Average distance between metal atom and best coplanar four-atom set. [d] Average distance between metal atom and remaining arene carbon atoms. [e] Distance of the metal atom from the plane described in footnote *c*. [f] Distance of noncoplanar carbon atoms from plane described in footnote *e*. Minus (−) signifies away from the metal atom. [g] Angle between the vector defined by the unique para ring atoms and the ML_2 plane such that θ is 90° for conformation **40** and 0° for **41**. [h] Calculated using a five-atom coplanar set. [i] Albano, P.; Areste, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069. [j] Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 132. [k] Uson, R.; Lahuerta, P.; Reyes, J.; Oro, L. A.; Foces-Foces, C.; Cano, F. H.; Garela-Blanco, S. *Inorg. Chim. Acta* **1980**, *42*, 7. [l] Notte, M. S.; Gafner, G. *Acta Crystallogr., Sect. B* **1974**, *B30*, 738.

antibonding) way with respect to the benzene e_{1g} orbital. This hybridizes $2e_1$ out toward the missing ligands, as shown by **17**. Analogously, $3a_1$ is a mixture of metal s and *z* orbitals hybridized out away from the benzene a_{2u} orbital, **18**. In a localized sense, or in valence bond



18



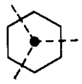
19

terms, three of the metal d^2sp^3 hybrids are interacting with the π orbitals of benzene. There remain three unhybridized metal d orbitals and three unfilled hybrid orbitals, **19**, which are directed away from the benzene ligand. The two pictures, localized and delocalized representations of the benzene-metal bonding, are equivalent; symmetry-adapted combinations of hybrid orbitals in **19** lead to metal orbitals of the same symmetry and radial extension as $2e_1$ and $3a_1$.

From the localized representation of benzene-Cr shown in **19** it is clear that the benzene-Cr fragment is ideally constructed to interact with three donor ligands. These might be carbon monoxide, a phosphine, or the three π bonds of another benzene ligand. From a delocalized point of view, this is illustrated for benzene-ML_3 in Figure 3 where L is taken to be any two-electron σ-donor group. The symmetry-adapted combinations of the three ligand lone pairs are illustrated on the right side of this figure. The lone-pair a_1 combination interacts with $3a_1$ on benzene-Cr and is stabilized. The same situation occurs between the e combination and $2e_1$. To a first approximation, the metal-centered orbitals, $2a_1$ and e_2, are left antibonding. The localized and delocalized bonding descriptions imply cylindrically symmetrical bonding of chromium to the benzene ligand. The rotational barrier about the benzene-Cr axis should then be very small for benzene-CrL_3 complexes. Theoretical calculations[36] and experimental results, as we shall see in the next section, are in agreement with this. The C-C bond lengths of the benzene ligand should also remain equal. This is not quite true. There appears to be a small alternation in bond lengths, a feature that will be discussed in a following section.

C. Arene Ligands with 3- or 6-fold Symmetry Axes

The prototypical η^6-arene-ML_3 structure is η^6-benzene-$Cr(CO)_3$. This complex has been structurally analyzed at low temperatures by both X-ray and neutron diffraction techniques.[37] In the crystalline state, only a mirror plane is crystallographically imposed on the molecule—there is no crystallographically imposed (alternating) inequivalence of the benzene C-C bonds. The staggered conformation, **20**, was found rather than the eclipsed one, **21**. The three ring C-C bonds that



20

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are eclipsed by the CO ligands are significantly longer than the three noneclipsed C-C bonds, 1.423 (1) Å vs.

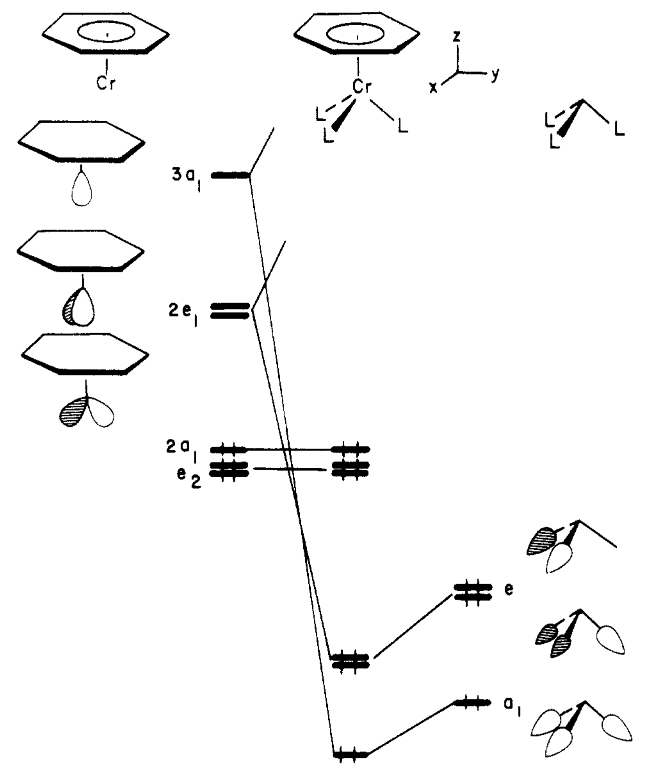


Figure 3. Interaction diagram for benzene–ML_3.

1.406 (1) Å. This C–C bond length alternation reduced the highest-symmetry axis of the benzene ligand to 3-fold; the free benzene molecule, of course, possesses 6-fold symmetry with all C–C bond lengths identical, 1.398 (8) Å.[38] The possibility of bond alternation can also be seen from theoretical considerations. An extended Hückel calculation[36] on benzene–$Cr(CO)_3$ where all C–C distances were equivalent gave larger C–C overlap populations for the staggered bonds than those for the eclipsed set. This implies that the benzene ligand will distort to threefold symmetry in the sense noted above. It is not immediatley obvious why bond alternation occurs in this complex since the bonding pattern developed in the previous section implies that strict cylindrical symmetry is maintained. This is not quite the case. Notice in Figure 3 that the lone-pair e combinations are asymmetric with respect to the *xz* plane. The top component of e lies to the left side of the *xz* plane; the lower component has the majority of its electron density on the right side. On the other hand $2e_1$ (and e_2) in benzene–Cr are left–right symmetric (or antisymmetric). The bonding molecular orbital of e + $2e_1$ can be stabilized even more by mixing some e_2 into it. This is done in such a way that the overlap between chromium orbitals and the lone pairs is increased. Now e_2 carries with it some π^* character that is mixed with the π character of $2e_1$. The net result is to increase C–C π overlap on the staggered bond set and to decrease that overlap on the eclipsed set. So the threefold symmetry of the lone pair L_3 set is behind the bond alternation. An alternative way to approach the problem is to build the orbitals of CrL_3 and interact them with the π and π^* orbitals of benzene. This too produces an intermixing of π and π^* orbitals so that some bond alternation is expected.[39] It is important to bear in mind that this is a minor effect. The rotational barrier is still very small. Electron diffraction results[40] show that the molecule is nearly an unhindered rotor in the gas phase. Just as in the classic sandwich structure, $(\eta^6\text{-benzene})_2Cr$, and for presumably the same reasons, the ring hydrogen atoms in $(\eta^6\text{-benzene})Cr(CO)_3$ bend out of the benzene plane toward the chromium atom. The average displacement from the plane of the benzene ring in the direction of the chromium atom is 0.03 Å.

A staggered orientation is also adopted in the analogous compound containing a fully substituted arene ring, $[\eta^6\text{-}C_6(CH_3)_6]Cr(CO)_3$.[41] Although the six C–C bond lengths are reported to be equal within experimental error (1.42 (3) Å), the accuracy of this determination was not high. The six methyl substituents are all displaced slightly from the mean plane of the arene ring away from the chromium atom. $[\eta^6\text{-}C_6(CH_3)_6]Mo(CO)_3$ likewise adopts a staggered orientation (carbon atoms of ring staggered with respect to carbonyl groups).[42] Here, as in $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, the eclipsed C–C bonds of the ring *appear* to be longer than the noneclipsed bonds, 1.441 (9) Å vs. 1.405 (5) Å; but within the precision of the analysis, the difference is not significant. The methyl carbon atoms are displaced out of the mean plane of the C_6-arene ring away from the molybdenum atom by 0.060 (8) Å.

When the substituent group is changed from methyl to ethyl, the orientation of the CO ligands with respect to the carbon atoms of the arene ring changes from staggered to eclipsed.[43] In both $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_3$ and $[\eta^6\text{-}C_6(C_2H_5)_6]Mo(CO)_3$, the carbon monoxide ligands are eclipsed with respect to three carbon atoms of the arene ring (and three ethyl substituents). Although the C–C bond lengths in the arene rings are all equal in these structures, the arenes possess only 3-fold symmetry, because the ethyl substituents adopt a "cogwheel" orientation. While the methylene carbon atoms of the six ethyl substituents are all located on the side of the arene ring away from the central metal atom, the methyl carbon atoms project alternately above and below the plane of the arene ring. For the three eclipsed ethyl groups, the methyl carbon atom is located on the side of the ring away from the metal atom. It should be noted that the free molecules of both hexamethylbenzene[44] and hexaethylbenzene[43] adopt similar cogwheel orientations in the solid state, with the substituents alternating above and below the arene C_6 planes.

Replacement of a carbonyl ligand in $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_3$ by $P(C_6H_5)_3$ or $P(C_2H_5)_3$ leads to striking changes in the solid-state structure.[43] Whereas $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_3$ adopts an eclipsed configuration with the methyl groups alternately toward and away from the metal atom, one of the conformers of $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_2P(C_2H_5)_3$ retains the eclipsed arene–M–L_3 orientation with only the methyl group trans to the phosphine remaining tipped toward the metal side of the arene.[43b] The second structure found for $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_2P(C_2H_5)_3$[43b] and that of $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_2P(C_6H_5)_3$[43a] have a staggered array of arene carbons with respect to the L_3 set, and all six methyl groups of the arene are directed away from the metal atom.

In these phosphine-substituted compounds, the C–C bond lengths do not alternate in a systematic fashion around the arene ring. However, there appears to be a modest variation in the bond lengths of $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_2P(C_6H_5)_3$—from 1.404 (7) Å to 1.435 (7) Å, although the range is small with respect to the precision of the determination (these values bracket the results reported for both structures of $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_2P(C_2H_5)_3$). The existence of the two cocrystalline conformers of $[\eta^6\text{-}C_6(C_2H_5)_6]Cr(CO)_2P(C_2H_5)_3$ in the same unit cell of the crystal incisively shows how small the energy difference is between the eclipsed and staggered structures.

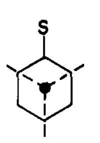
As in $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, a staggered orientation is adopted in both $[(\eta^6\text{-}C_6H_6)RuB(pz)_4]^+PF_6^-$ [$B(pz)_4$ = tetrakis(1-pyrazolyl)borate][45] and $(\eta^6\text{-}C_6H_6)RuCl_2(PCH_3(C_6H_5)_2)$.[46] $(\eta^6\text{-}C_6H_6)Ru(CO)(GeCl_3)_2$, however, provides an exception; it adopts an eclipsed orientation in which the CO and $GeCl_3$ ligands eclipse arene carbon atoms.[47] This again points to a very small rotational barrier for the benzene–ML_3 system.[48] The ring C–C bond lengths in $(\eta^6\text{-}C_6H_6)Ru(CO)(GeCl_3)_2$ are equal within experimental error (1.408 (6) Å), so the benzene C_6 ring locally maintains a 6-fold symmetry axis.

Only three η^6-arene–ML_3 structures containing 1,3,5-substituted arenes have been reported, $(1,3,5\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$,[42] $\{(1,3,5\text{-}C_6H_3(CH_3)_3)Mo[(CH_3)_2PC_2H_4P(CH_3)_2]N\}_2$,[49] and $[\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3]Ru$(4-hydroxy-4-methylpentan-2-one)(acetone)$^{2+}(BF_4^-)_2$.[50] The first two compounds adopt an eclipsed orientation, while the detailed stereochemistry of the last compound has not been reported. In $[\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$, the methyl groups of the arene ligand reside on eclipsed ring carbon atoms. This fits a pattern that shall be discussed electronically in the next section: M–L bonds eclipse electron-donor-substituted arene carbons. This conformational preference has electronic origins, and its magnitude depends upon the strength of the donor substituent, which is weak for a methyl or alkyl group. In $\{[1,3,5\text{-}C_6H_3(CH_3)_3]Mo[(CH_3)_2PC_2H_4P(CH_3)_2]N\}_2$, the methyl substituents are on noneclipsed ring carbons. The electronically favored structure is not found, presumably due to minimization of close contacts between the phosphine–methyl groups and the methyl groups on the arene. In both structures, the arene methyl groups are displaced out of the arene plane away from the metal. Carbon–carbon bond lengths within the arene ligand appear to be equal.

General structural features of this class of compounds are as follows: (1) Ring C–C bonds of arene ligands are only slightly longer than ring C–C bonds of the free arene molecules.[38,43,44] (2) M–C(ring) bond lengths are ~2.23 Å for arene–Cr complexes and range from 2.16 to 2.39 Å for arene–M complexes involving second-row transition metals. These bond lengths are somewhat longer than those found in the bis(arene) sandwich compounds. M–C(ring) lengths in the $M(\eta^6\text{-arene})_2$ complexes are all in the 2.08–2.20-Å range (with the exception of the 20-electron complex, $Co[\eta^6\text{-}C_6(CH_3)_6]_2^+PF_6^-$). (3) Distances between the metal atom and the center of gravity of the arene ring are ~1.73 Å for chromium complexes and range from 1.67 to 1.92 Å for complexes involving second-row transition-metal atoms. The $M\text{-}C_6$(grav) distances for $M(\eta^6\text{-arene})_2$ complexes, all based on first-row metal atoms, are generally shorter, ranging from 1.53 to 1.67 Å (except for $Co[\eta^6\text{-}C_6(CH_3)_6]^+PF_6^-$). (4) There is a small degree of bond alternation observed for staggered, **20**, but not eclipsed, **21**, structures. The C–C bonds that are eclipsed by M–L bonds in **20** are slightly longer than those in the staggered set. (5) In benzene or hexasubstituted benzene–ML_3 complexes generally conformation **20** is found; however, since the rotational barrier along the metal–arene axis is very low, eclipsed or intermediate geometries are possible.

D. Monosubstituted Arene Ligands

$(\eta^6\text{-}C_6H_5S)ML_3$ structures may possess one of three idealized conformations. In the first geometry, **22**,



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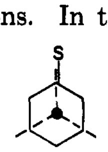

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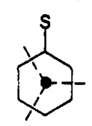

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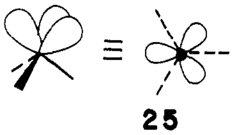
which is denoted as E, three ring carbons and the three ligands, L, are eclipsed and the substituent S resides on one of the noneclipsed ring carbon atoms. In conformation EE, **23**, the ML_3 core eclipses ring carbons, but in this case S is also eclipsed by one M–L bond. Finally, a staggered orientation, S, **24**, may also be found. As mentioned previously, there is an electronic driving force behind a conformational preference for **22** or **23**. There are a number of ways to view it.[36,51,52] An expedient departure point is to start with $Cr(CO)_3$, or for that matter, any $d^6\text{-}ML_3$ fragment. Within a hybridization model,[9b] the ML_3 group will have three M–L bonding orbitals that are filled and three empty hybrids. These will be directed in an octahedral arrangement; therefore, the empty hybrids are localized in regions of space that stagger the M–L bonds. This is shown from a top and side view in **25**. There are also three nonbonding, filled orbitals. They are analogous to the t_{2g} set of an octahedron. A localized representation of them, top and side views, is shown in **26**. So there are two electronically distinct interpenetrating trios on the $d^6\text{-}ML_3$ group. The ML_3 group will orient itself so that **25** is pointed toward regions of high electron density and **26** toward regions of low electron density in the arene ring. An electron-donor substituent on the arene will produce a charge distribution on the arene ring as shown in **27**.[36] The EE conformation, **28**, points the empty trio, **25**, toward the electron-rich ortho and para positions and the filled trio, **26**, toward the electron-deficient ipso position and the meta carbon atoms. $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$[53] and $(\eta^6\text{-}C_6H_5OCH_3)Cr(CO)_3\cdot 1,3,5\text{-}C_6H_3(NO_2)_3$[51] are representatives of this pattern. An electron-acceptor substituent will polarize electron density in an opposite manner with respect to **27**. Consequently, the E orientation, **29**, is the electronically preferred one. $(\eta^6\text{-}C_6H_5CO_2CH_3)Cr(CO)_3$[52,54] is one such example. It is easy to see that making the electron donor stronger will increase the polarization



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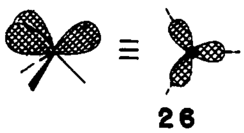

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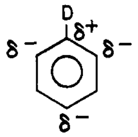

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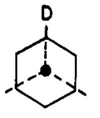

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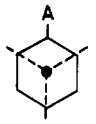

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in **27** and increase the rotational barrier. An extended Hückel calculation on (aniline)$Cr(CO)_3$ gave a rotational barrier of 1.3 kcal/mol with the EE conformation as the most stable one. This is still a relatively small potential, and, therefore, crystal packing effects as well as steric factors can override these electronic effects, particularly for weak donors or acceptors. $[\eta^6\text{-}C_6H_5CH[C(CH_3)_3]_2]Cr(CO)_3$[55] is an obvious complex in which steric factors can be stereochemically dominant. The predicted conformation is EE, but because of contacts between the very bulky alkyl group and carbonyl ligands, the $Cr(CO)_3$ group is rotated by 44° from this geometry. Another example is $[(OC)_3Cr(\eta^6\text{-}C_6H_5)]_2$.[56] Aside from this unique case, most of the structural data in Table V for the mono- as well as the di- and trisubstituted benzene ligands follow the electronically predicted patterns. Part of the reason for the concern about equilibrium conformations of arene–$Cr(CO)_3$ complexes has to do with nucleophilic and electrophilic attack on the coordinated arene ring. There is good experimental and theoretical evidence[57] that the conformation of the $Cr(CO)_3$ group can determine the regioselectivity of attack on the arene ring. The directionality of trios **25** and **26** themselves perturb the electron density on the arene ring for eclipsed (E or EE) structures. This may be an even stronger effect than that of some substituents on the arene ring.

In all of the structures summarized in Table V except for $[\eta^6\text{-}C_6H_5CH[C(CH_3)_3]_2]Cr(CO)_3$[55] and $[\eta^6\text{-}C_6H_5N(C_2H_5)_2]Cr(CO)_3$,[58] the arene ligand is planar. In each of these exceptions, the aromatic ligand is folded slightly with C-1 and C-4 being displaced out of the plane of the other four ring carbon atoms away from the metal atom. None of the structures summarized in Table V show systematic ring C–C bond length variations. The M–C(ring) bond lengths are all in the same range of 2.18–2.24 Å for the chromium complexes, except for one very long M–C(ring) distance in $[\eta^6\text{-}C_6H_5N(C_2H_5)_2]Cr(CO)_3$,[58] while the M–C(ring) bond lengths vary from 2.28 to 2.43 Å for the complexes involving second-row transition metals. Distances between the metal atom and the center of gravity of the arene ring range from 1.67 to 1.74 Å for the chromium complexes and from 1.78 to 1.92 Å for complexes involving second-row transition metals. Frequently, the substituent, S, is displaced out of the arene plane away from the metal atom. The most spectacular displacement occurs in $[\eta^6\text{-}C_6H_5CH[C(CH_3)_3]_2]Cr(CO)_3$ in which the α-carbon atom of the bulky substituent is displaced 0.41 Å from the mean plane of the arene.[55] In two cases, $[\eta^6\text{-}C_6H_5CO_2CH_3]Cr(CO)_2CS$[59] and $[\eta^6\text{-}C_6H_5CO_2CH_3]Cr(CO)_2PF_3$,[60] the α-carbon atom of the substituent group is displaced out of the arene plane *toward* the metal atom.

E. Disubstituted and Unsymmetrically Trisubstituted Arene Ligands

A variety of orientations are possible for η^6-arene–ML_3 compounds possessing disubstituted arene ligands. The various possibilities for ortho, meta, and para substitution are outlined in Figure 4. Most of the compounds that have been studied to date contain ortho-substituted arene ligands. Within this group, two of the three possible orientations (see Figure 4) have been observed, the E orientation in which three ring carbon atoms and the three ligands, L, are eclipsed and the S orientation in which the ring carbon atoms are staggered with respect to the ligands, L, and an M–L bond does not project onto the C_1–C_2 arene bond. Among the ortho-substituted-arene–ML_3 structures that exhibit the E orientation (see Table VI), the more electron-donating substituent is eclipsed while the more electron-withdrawing substituent is not eclipsed, as would be expected, based on the electronic arguments of the last section. In $[\eta^6\text{-}o\text{-}C_6H_4(OCH_3)(COCH_3)]Cr(CO)_3$, for example, the electron-donating group, OCH_3, is eclipsed and the electron-withdrawing group, $COCH_3$, is not.[61] If S_1 and S_2 have identical, or very similar, electronic characteristics, then the S conformation appears to be more favorable than the SS orientation.

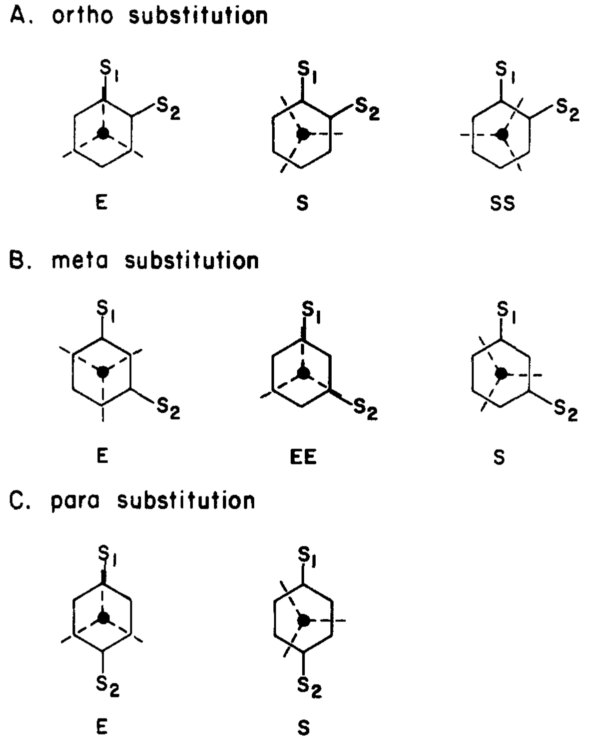


Figure 4. Conformational possibilities for disubstituted η^6-arene–ML_3 complexes.

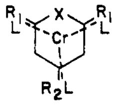
Frequently, the α atom of the eclipsed substituent is displaced out of the arene plane away from the metal atom while the α atom of the noneclipsed substituent is displaced toward the metal atom. This is the case in $[\eta^6\text{-}o\text{-}C_6H_4(OCH_3)(COCH_3)]Cr(CO)_3$, where the oxygen atom of OCH_3 is 0.56 Å above the plane and away from the chromium atom, whereas the α-carbon atom of $COCH_3$ is 0.141 Å below the plane and toward the chromium atom. However, in one case, $(\eta^6\text{-}o\text{-}C_6H_4CH_3)[C(OH)(C_2H_5)(C_6H_5)]Cr(CO)_3$, both substituents are displaced away from the metal atom,[62] and in another case, $[\eta^6\text{-}o\text{-}C_6H_4(OH)(COCH_3)]Cr(CO)_3$, both are displaced toward the metal atom.[61] Only one meta-substituted-arene–ML_3 structure and three para-substituted-arene–ML_3 structures have been reported. In each case, the S orientation is observed, in which the ring carbon atoms are staggered with respect to the ligands, L. In one of the para-substituted cases, both S_1 and S_2 are electron-donating alkyl groups. An intermediate geometry (S) is then assumed. The other case, $[\eta^6\text{-}p\text{-}C_6H_4[C(CH_3)_3](CO_2H)]Cr(CO)_3$,[63] is interesting because it contains substituents of opposite electronic parity. The preferred conformation should be E (see Figure 4c), with $S_1 = C(CH_3)_3$ and $S_2 = CO_2H$. However, this would involve close contacts between one methyl carbon of the *tert*-butyl group and the eclipsing carbonyl. Instead a staggered, S, conformation is found.

The arene rings in most of the disubstituted-arene–ML_3 structures are planar, but two of the para-disubstituted complexes, [2.2]paracyclophane–$Cr(CO)_3$[64] and [η^6-p-$C_6H_4(CH_3)(CH(CH_3)_2)$]$RuCl_2P(CH_3)(C_6H_5)_2$,[46] possess boat-shaped rings. In each case, the two substituted ring carbon atoms are bent out of the plane of the other four carbon atoms away from the metal atom. In [2.2]paracyclophane–$Cr(CO)_3$, however, this bending is no greater than in the parent cyclophane molecule.[64]

General features of the structures summarized in Table VI include the following: (1) Systematic alternations in ring C–C bond lengths are usually not observed. C–C bond length alternation has been claimed in [2.2]paracyclophane–$Cr(CO)_3$ (1.398 (8) Å for three short bonds vs. 1.417 (6) Å for the three long bonds), but the uncertainty in these bond lengths is quite large.[64] (2) The metal–ring carbon bond lengths show little variation; all, except the two long M–C(ring) bonds in [2.2]paracyclophane–$Cr(CO)_3$, are in the 2.20–2.26-Å range. (3) The metal–ring center of gravity distances likewise show little variation; all are in the 1.70–1.76-Å range.

Only one complex containing an unsymmetrically trisubstituted benzene ligand, [η^6-1,2,3-$C_6H_3(OCH_3)_3$]-$Cr(CO)_3$,[58] has been investigated structurally. This complex adopts an eclipsed configuration in which the Cr–CO bonds eclipse two of the electron-donating CH_3O substituents, as expected from the preceding analysis. The C_6-arene ring is nonplanar; it has an inverted boat shape whereby two para carbons are bent slightly toward the Cr atom.

There are a few heterocyclic arene–ML_3 complexes that are related to the compounds discussed in this and the previous section. The structures[65–67] where a more electronegative atom than C has replaced a C–H group all exist in the conformation given by **30**. One of the empty hybrids in **25** is then pointed at the electron-rich X atom and meta carbons.[36] The borabenzene–Mn-$(CO)_3$ complex, **31**,[68] has the opposite orientation; here the electron donors, **26**, are pointed toward the electron-deficient B and meta C atoms (consistently in the crystalline state for the sandwich complex Cr(2,6-lutidine)$_2$ there are two molecules in the unit cell that differ from each other by the relative orientation of the azine rings[69]). In all these examples, the heteroatom is essentially coplanar with respect to the C_5 unit. There is one exceptional complex, hexaethylborazine–$Cr(CO)_3$.[70] The borazine ring is puckered into a chair form such that all three Cr–N distances are shorter than the three Cr–B bonds. The conformation of the Cr-$(CO)_3$ group is such that the carbonyl ligands eclipse the boron atoms.



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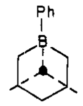

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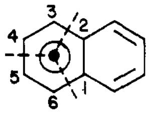
a) $R_1 = R_2 = Me, X = N, L = CO$
b) $R_1 = Me, R_2 = H, X = N, L = CO$
c) $R_1 = R_2 = H, X = N, L = NC$-$\underline{t}Bu$
d) $R_1 = R_2 = Ph, X = P, L = CO$

F. Condensed Arene Ligands

All condensed aromatic ligands are minimally ortho disubstituted because of the connected aromatic ring system. As discussed above, the ML_3 fragment can adopt three orientations (Figure 4a). All of the structures listed in Table VII, except one, are based on a naphthalene–$Cr(CO)_3$ unit. In other words, a butadiene fragment is ortho fused onto the arene–$Cr(CO)_3$ system. All but one possess the S orientation, **32**. The exception is biphenylene–$Cr(CO)_3$[71] in which the SS conformation, **33**, is found. There is an electronic reason for the conformational change, which has its origins in the attractive and repulsive interactions between the Cr-$(CO)_3$ orbitals and the uncomplexed polyene π orbitals.[71]



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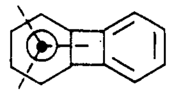
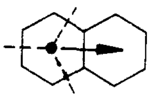


33

Perhaps the most interesting stereochemical feature of this series of compounds is the slippage of the ML_3 fragment toward the four unsubstituted carbon atoms of the arene ring and away from the two ring junction carbon atoms. This slippage results in the distance between the chromium atom and the four unsubstituted ring carbon aroms being as much as 0.1 Å shorter than the distance between the chromium atom and the two ring junction carbon atoms. M–C(ring, unsubstituted) bond lengths range from 2.19 to 2.23 Å while M–C(ring junction) bond lengths range from 2.24 to 2.33 Å). Since all the coordinated C–C distances are approximately equal in these compounds, an η^6 geometry would be one where the projection of the Cr atom onto the plane of the C_6 ring would fall on and bisect the C_3–C_6 axis (see **32**). For triphenylene–$Cr(CO)_3$, which is typical of the naphthalene-based complexes, the projection of the chromium atom is displaced by 0.03 Å from the C_3–C_6 axis toward the C_4–C_5 bond. In biphenylene–$Cr(CO)_3$ this is somewhat larger—0.05 Å. Octamethylnaphthalene and octamethylnaphthalene–$Cr(CO)_3$ experience significant deviations from planarity due to steric interactions of the methyl groups such that comparison of these electron-rich molecules with other condensed arene–$Cr(CO)_3$ species is not possible.[77b] It has been suggested that since the ring junction carbon atoms are π bonded to the three other carbon atoms, they cannot π interact with the chromium atom as effectively as the other four ring carbons.[72,73] Alternatively, this slippage can be viewed as arising from a retention of the maximal aromaticity in the uncomplexed ring. Aromaticity of the uncomplexed ring can be maximally retained by forcing the Cr–C_1,C_2 bonding to become weaker. This is very similar to what happens in several η^4-benzocyclobutadiene–$Fe(CO)_3$ derivatives.[74] Here, too, the $Fe(CO)_3$ group shifts away from the ring junction toward η^2-coordination. There is another way to view the slippage in these complexes, and this perspective will be useful in considering some dynamic features of arene complexes. Consider slipping the $Cr(CO)_3$ group from one ring to the other in naphthalene–$Cr(CO)_3$. The least-motion pathway, shown by the solid line in **34**, passes through a transition state where the projection of the Cr atom bisects the C_1–C_2 bond.



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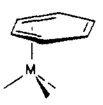
At this point, the $Cr(CO)_3$ group loses essentially all bonding to the naphthalene ring. The least-motion path is symmetry forbidden.[75] It requires approximately 35 kcal/mol from extended Hückel calculations to attain this geometry. On the other hand, shifting the $Cr(CO)_3$ group in the opposite direction to an η^2 point over the C_4–C_5 bond requires 25 kcal/mol. The lower potential for this motion is a consequence of the fact that some bonding is retained between the Cr and naphthalene at η^2. Therefore, because of the very high potential encountered by the movement indicated in **34**, the ground-state minimum is shifted in the opposite direction. We shall return to this point shortly in connection with the issue of arene–ligand exchange in arene–metal complexes.

In most cases, the complexed condensed arene ring remains planar, although slight deviations from planarity have been observed in η^6-naphthalene–$Cr(CO)_3$,[76] η^6-naphthalene–$Cr[P(OC_6H_5)_3](CO)_2$,[77] and η^6-phenanthrene–$Cr(CO)_3$.[73] In each case, the two ring carbon atoms adjacent to the ring junction carbon atoms are displaced toward the chromium atom while the two remaining ring carbon atoms are displaced away from the chromium atom. Frequently, the α-carbon atoms of the two ortho substituent groups (i.e., the α-carbon atoms of the connected ring) are slightly displaced out of the mean plane of the complexed arene ring away from the chromium atom.

Among condensed-arene–ML_3 structures containing arenes with three connected aromatic rings (e.g., phenanthrene and anthracene), end rings are complexed in preference to central rings.[73,77–80] This is what would be expected considering the least disruption of aromaticity in the benzenoid rings by a $Cr(CO)_3$ group.[81]

G. Arene Exchange

The mechanism of arene exchange in η^6-arene–ML_3 complexes has not been established fully despite extensive investigation.[82] Arene exchange between free arene and an η^6-arene–metal(d^6)L_3 complex does not occur readily unless a donor solvent like an ether or a ketone is present. In the following discussion, this donor solvent-assisted arene exchange process will be *the* process in which electronic factors will be assessed *for* their effect on reaction pathway. Mechanistically, a reasonable intuitive scenario would start with an η^6 to η^4 dissociation of the coordinated arene. The coordinately unsaturated complex then could be attacked by an external (solvent) ligand. This intermediate in turn would move to η^2-coordination and pick up a second ligand. Finally, the η^2-arene–$ML_3L'_2$ complex would eliminate the arene. Although there has not been a comprehensive theoretical study of this reaction, there are a number of key features in the electronic requirements of the reaction that can be unambiguously identified. Obviously, a major issue is the nature of the first elementary step in the reaction sequence. An associative mechanism (or an interchange mechanism of associative intimate character) for the attack of an external ligand on η^6-benzene–ML_3 would seem unlikely. Actually, previous calculations[57] have shown that the direct attack of a nucleophile at the metal for η^6-benzene–$Cr(CO)_3$ is highly repulsive; there is a girdle of electron density around the Cr atom, and this comes from the t_{2g}-like set of orbitals, $2a_1$ and e_2, shown in Figure 3. Mechanistically more plausible would be a dissociative mechanism (D or I_d) outlined above, in which the ML_3 group migrates from an η^6 to an η^4 geometry, **35**. An extended Hückel calculation[83] indicated that this excursion requires approximately 10 kcal/mol.



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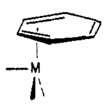

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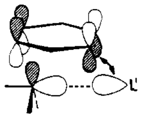

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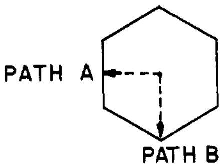
The η^4 complex, **35**, is expected to be geometrically different than the examples discussed in sections IID and VII. Established η^4 structures are known only for d^8, 18-electron complexes, and in these the uncomplexed C–C unit lies significantly out of the plane of the other four carbon atoms for the reasons discussed in section IIC. However, for **35**, there are two electrons less, and because of this, the driving force behind the ring puckering in d^8 complexes is not present in the d^6 species. An additional 15 kcal/mol is required to bend the C–C unit 25° away from the metal. So it is likely that the arene ring will remain planar (the condensed arene structures in this section provide good evidence of this point since the $Cr(CO)_3$ group is slipped toward η^4). There also must be a distortion of the ML_3 group to accept the incoming donor solvent, and a reasonable possibility is shown in **36**. For this distortion there is, in molecular orbital terms, one component of the antibonding yz–benzene-π interaction that goes down in energy. The dominant interaction between the complex and the incoming nucleophile will be between this low-lying LUMO and the lone-pair HOMO of the nucleophile as shown in **37**. Maximal overlap between the empty metal d orbital and the filled lone pair on L′ will occur when L′ follows a path that is parallel with respect to the benzene ligand plane. Not only is there unfavorable steric repulsion between L′ and the uncomplexed portion of the benzene ring, but also as indicated by the arrow in **37** there is antibonding introduced between the lone pair on L′ and the uncomplexed benzene π portion. Rotating ML_3 by 180° and allowing L′ to attack from the other side of the complex do not improve the energetics. Basically, the same problems prevail. If L′ comes in at a more acute angle than that in **37**, then it will face strong repulsions with the metal "t_{2g}" set. Therefore, there should be a sizable activation energy for attacking the η^4 complex that should be sensitive to steric effects induced by substituents on the arene ring.

The basic problem with the pathway outlined above is that the arene ring remains planar. Interestingly, the potential barrier for bending the uncomplexed portion of the arene ring becomes less when the ML_3 group is shifted to a position whereby the metal has a much lower coordination number. For example, in η^2-arene–ML_3, bending of the "butadiene" portion of the ring out of the plane away from the metal by 15° is actually favored. However, this η^6 to η^2 conversion is calculated to require 35 kcal/mol (for comparison, the energy required to go from η^6 to **36** is 27 kcal/mol). A compromise situation would be to have the ML_3 unit slip to an η^3 geometry. This coordination geometry was discussed in section IID. The calculated energy for shifting benzene–$Cr(CO)_3$ to this point is 20 kcal/mol, and it requires 6 kcal/mol to bend the uncomplexed allyl unit away from the metal by 25°. Therefore, there seem to be two general possibilities for the arene exchange reaction. Initial substitution by a solvent molecule could occur at some point along the η^6–η^4–η^2 slipping pathway, illustrated in 38 as path A. We would favor this to occur at some point along latter stages of reaction. The alternative, path B in 38, has ML_3 transversing an η^6–η^3–η^1 domain. Extended Hückel calculations have been carried out on a large number of bicyclic and tricyclic polyene–ML_n complexes (ML_n = $M(CO)_3$, MCp).[75] Potential energy surfaces were constructed for slipping ML_n within the periphery of the polyene ring. In general, it was found that shifting ML_n toward a carbon atom (analogous to path B) was energetically more favorable than a path that leads over a C–C bond. There are repulsions between metal-centered filled orbitals and the σ orbitals of the polyene that are minimized for the η^3–η^1 transit in comparison to the η^4–η^2 path. Willeford and co-workers[82c] have determined the activation parameters for exchange of benzene–, *p*-xylene–, and mesitylene–$Cr(CO)_3$ by hexamethylbenzene in cyclohexanone. Surprisingly, $\Delta H^\ddagger$ drops from 29.6 ± 1.0 kcal/mol for benzene–$Cr(CO)_3$ to 25.7 ± 1.0 for the mesitylene complex whereas the arene binding energy of mesitylene *appears* to be higher than that of benzene, 46 ± 3 vs. 42 ± 3 kcal/mol.[84] The lower enthalpy of activation for exchange for the better donor arene ligand (although the binding energy is apparently higher) seems to be most consistent with path B (assuming the first step to be the rate-determining one). Here, two electron-donating methyl groups would help to stabilize an electron-deficient η^3-arene–chromium tricarbonyl intermediate. The entropy of activation becomes large and negative along this series ranging from −4 ± 3 eu for benzene–$Cr(CO)_3$ to −18 ± 2 eu for mesitylene–$Cr(CO)_3$. Naphthalene–$Cr(CO)_3$ undergoes the arene exchange reaction far more readily than benzene–$Cr(CO)_3$.[82c] Extended Hückel calculations on naphthalene–$Cr(CO)_3$ show that it requires 24 kcal/mol to attain the most stable η^2 geometry (over the C_4–C_5 bond—see 32) and 17 kcal/mol to attain an η^3 geometry (the corresponding values for benzene–$Cr(CO)_3$ are 35 and 20 kcal/mol, respectively). A determination of the arene exchange activation parameters for complexes with arene ligands having different substituents and different substitution patterns may help to differentiate the mechanistic possibilities. For example, extended Hückel calculations[83] on naphthalene– and pyrene–chromium tricarbonyl show that there is a lower potential required for slipping $Cr(CO)_3$ along path B in 39 for the pyrene complex. On the other hand, it requires less energy to attain an η^2 geometry, path A, in 39, for naphthalene–chromium tricarbonyl.



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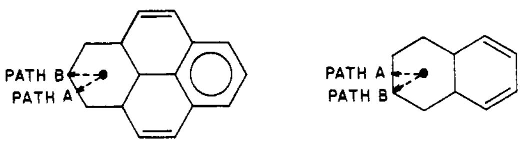

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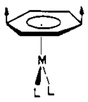
IV. η^6-Arene–ML_2 Complexes

Presented in Table VIII are the structural characteristics of the ten η^6-arene–ML_2 compounds that have been examined by X-ray crystallography. With one exception, the compounds possess idealized C_{2v} point symmetry, with the plane of the arene ring and that of the ML_2 subunit intersecting with a dihedral angle of 90 ± 10°. The exception is $\{(\eta^6\text{-}C_6D_6)Rh[1,2\text{-}[(C_6H_5)_2PCH_2]_2\text{-c-}C_4H_6]^+\}$,[85] in which the ML_2 plane is bent and slightly slipped toward one edge of the arene; it is perhaps unrealistic to place this structure in any idealized structural class.

The averages of the carbon–carbon bond lengths of all the coordinated arenes are close to 1.40 Å. While significant or systematic variations in these bond lengths, similar to those observed in other coordinated aromatic ligands,[86] do not occur, the majority of the arene rings depart significantly from coplanarity. There are two limiting conformations for η^6-arene–ML_2. Both have a nonplanar folded arene ligand, but each are directly bonded to different sides of the folded arene ligand. In conformation 40 the ML_2 group eclipses two C–C bonds. The two para carbons, which form a vector normal to the plane of ML_2, are bent out of the plane of the other four carbons, away from the metal, as shown by the arrows in 40. The last four structures listed in Table VIII exhibit this conformation. In the alternative orientation, 41, the ML_2 group eclipses two carbon atoms. Here the four noneclipsed carbon atoms move out of the plane, away from the metal, as indicated in 41; the first three entries in Table VIII have this conformation. A structurally equivalent way to view the generation of this conformation from a planar η^6-arene–ML_2 of C_{2v} symmetry (and this "perspective" is used in Table VIII) is that the two eclipsed carbon atoms move out of the plane of the other four, toward the metal.



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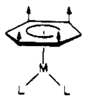

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These displacements observed for arene–ML_2 complexes are interesting because they must have electronic rather than steric origin. Those carbon atoms furthest removed from the auxiliary ligands are bending away from the metal. The electronic basis for this effect has been developed[87,88] by interacting the valence orbitals of an ML_2 group with the π levels of benzene. The approach we take here is slightly different. The orbitals of a d^8-metal–benzene fragment (see Figure 2) are interacted with the donor lone-pairs of two ligands, L, as shown in Figure 5; the symmetry labels are those for the C_{2v} symmetry. On the right are the in-phase (a_1) and out-of-phase (b_2) combinations of the lone pairs.

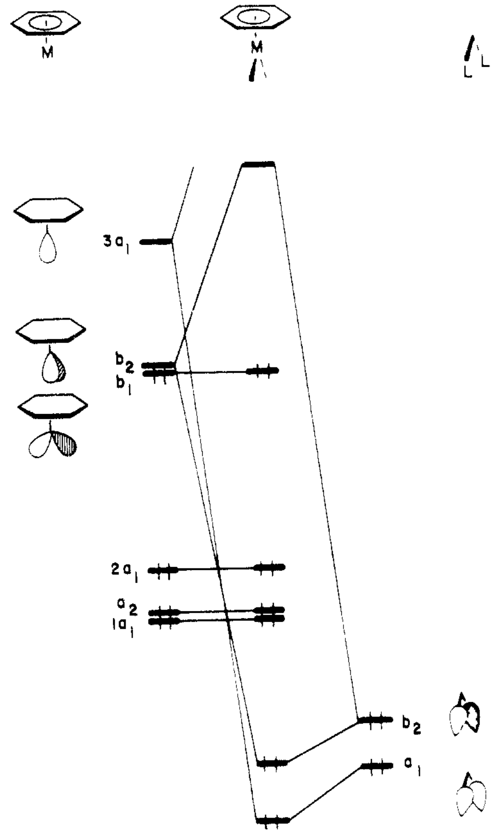


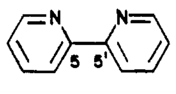
Figure 5. Construction of the valence orbitals of benzene–ML_2 from a benzene-d^8–M fragment and L_2, where L is any 2-electron donor.

The a_1 combination interacts most extensively with the $3a_1$ benzene–M fragment orbital. The b_2 combination must interact with the b_2 component of the $2e_1$ set. Both molecular bonding orbitals are occupied and their antibonding analogues are vacant. All other fragment orbitals of benzene–M are nonbonding. Notice that one of these nonbonding orbitals, the b_1 component of $2e_1$, lies at high energy. The composition of this orbital was discussed in section IIIB; it is primary metal *yz antibonding* with respect to a benzene π orbital—see the lower drawings in **16** and **17**. The most significant antibonding interaction between the metal atom and the arene carbon atoms is that between two para carbon atoms in the plane of the paper. This antibonding interaction can be diminished and b_1 stabilized by the displacement indicated in **40**.

Now we consider the alternative conformation, **41**. In **41**, the in-phase lone-pair combination is still of a_1 symmetry but the out-of-phase combination becomes b_1. Therefore, it interacts with the b_1 component of $2e_1$ (see Figure 5), and now b_2 is left nonbonding. The upper drawings of **16** and **17** show that this orbital is antibonding between the metal and four benzene carbon atoms on either side of the plane of the paper. Thus, the displacement indicated in **41** will be stabilizing.

Strong support for these theoretical explanations is found in two complexes that have a planar arene ring. The puckering of the arene ring depends on the occupation of the b_1 or b_2 components of $2e_1$. In the 17-electron complex $(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2$[89] there will be only 1 electron in this nonbonding orbital. Consequently, a good portion of the driving force behind the distortion is lost. The ring is planar within experimental error. In the 18-electron nickel congener,[89] two para carbons move out of the metal plane by 0.06 Å. One should also expect that the metal–C_4 distance decreases upon depopulation of b_1 (for conformation **40**). This does occur: the Ni–C_4 distance is 1.68 and 1.69 Å for the two compounds in Table VIII, and in the corresponding cobalt complex it decreases to 1.62 Å.

Another method to depopulate the nonbonding b_1 (or b_2) molecular orbital in 18-electron benzene–ML_2 systems is by incorporating strong π-acceptor orbitals on the auxiliary ligands that are perpendicular to the ML_2 plane. A recent example that nicely illustrates this is $(\eta^6\text{-}C_6H_5CH_3)Fe(bpy)$.[90] The 2,2′-bipyridine ligand, **42**, behaves as a strong π electron-withdrawing group in this complex presumably by way of the LUMO, **43**. Not only is the arene ligand planar in this complex, but it also has the shortest M–C_4 distance (1.545 Å). The Fe–N distance of 1.90 Å is one of the shortest reported. The C_5–$C_{5'}$ distance is also contracted by 0.07 Å in comparison to the uncomplexed bipyridine. Notice in **43** that there is bonding between C_5 and $C_{5'}$ so that occupation of this orbital should decrease the C_5–$C_{5'}$ distance. $[\eta^6\text{-}C_6(CH_3)_6]Ru(\eta^4\text{-}1,3\text{-}C_8H_8)$[91] also is a system where the η^4-1,3-C_8H_8 ligand has a low-lying acceptor orbital. In this case, its construction is topologically equivalent to the LUMO of butadiene. Notice that the M–C_4 distance is significantly shorter than those of the other second transition metal row d^8 analogues. The arene carbon atom that lies over the open face of the "butadienoid" linkage is displaced from the mean plane of the other five carbon atoms.



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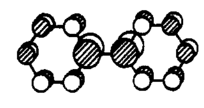

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The arene exchange reaction is generally much more facile for 18-electron arene–ML_2 complexes compared to their arene–ML_3 counterparts.[5,6] The occupation of the benzene–metal antibonding b_1 (or b_2) orbital should weaken the arene–metal bond. This should facilitate a migration of the ML_2 group off the arene-C_6 centroid in comparison with the arene–ML_3 situation outlined in section IIIG where there are no arene π–metal antibonding interactions. Here again, electronic perturbations within the arene–ML_2 complex can be used to modify the exchange rate. For example, if the L groups are capable of withdrawing electron density from the arene–metal antibonding orbital, then it follows the arene exchange should require more forcing conditions. As we have previously indicated, bipyridine is one such ligand (see **43**), and $(\eta^6\text{-}C_6H_5CH_3)Fe(bpy)$ is inert at conditions where the rates of arene exchange for the isoelectronic Ni(II) complexes are high.[90]

V. η^6-Arene–ML_4 Complexes

The structures of only five η^6-arene–ML_4 complexes have been determined. Structural data for these are summarized in Table IX. In two structures, η^6-toluene–$Mo(CH_3)_2(PC_6H_5(CH_3)_2)_2$[92] and the analogous η^6-benzene complex,[92] the arene ring is boat shaped, with the two end carbon atoms displaced out of the best ring plane away from the molybdenum atom (displaced by 0.07 and 0.08 Å in the toluene complex and by 0.08

TABLE IX. η^6-Arene-ML$_4$ Structures[a]

complex	ring[b]	C-C(ring)	M-C(ring)	M-C_6-(grav)[c]	M-L	angle S-C_6 plane[d]	ref
$[\eta^6\text{-}C_6H_5CH_3]Mo(CH_3)_2[PC_6H_5(CH_3)_2]_2$	NP[e]	1.410	2.274 (13) (4 short) 2.342 (2) (2 long) 2.297 (17) (av)	1.816	2.291 (5) (C) 2.472 (5) (P)	+(C)	92
$[\eta^6\text{-}C_6H_6]Mo(CH_3)_2[PC_6H_5(CH_3)_2]_2$	NP[f]	1.41	2.27 (0.5) (4 short) 2.36 (1) (2 long) 2.30 (2) (av)	1.82	2.295 (5) (C) 2.470 (7) (P)		92
$\{(\eta^6\text{-}C_6H_5CH_3)Mo(\eta\text{-}SCH_3)_2\}_2{}^{2+}$	NP	1.38-1.45	2.28-2.42				93
$[\eta^6\text{-}C_6(CH_3)_6]Ti(Cl_2AlCl_2)_2\cdot C_6H_6$	NP	1.42	2.50 (1.5)	2.06	2.615 (5)		94
$[(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)Mo(\mu\text{-}Cl)]_2$	NP[g]	1.40	2.20 (2) (2 short) 2.32 (1.5) (4 long) 2.28 (3) (av)	1.81	2.52 (Cl) 2.24 (1) (end carbon of allyl) 2.14 (central C)		95

[a] Distances in Å. [b] P indicates planar ring; NP indicates nonplanarity. [c] Distance between metal atom and center of gravity of arene ring. [d] + indicates substituent atom, S (in parentheses), is bent away from metal; – indicates it is bent toward metal. [e] Ring is boat shaped with end carbon atoms displaced 0.07 and 0.08 Å out of best ring plane away from Mo atom. [f] Ring is boat shaped with end carbon atoms displaced 0.08 and 0.09 Å out of best ring plane away from Mo atom. [g] Ring adopts an inverted boat conformation.

and 0.09 Å in the benzene complex). In both cases, the conformation of the complex is such that the two para carbons displaced from the plane of the ring are eclipsed by trans Mo–CH_3 bonds. This nonplanarity of the arene rings has been attributed to steric repulsion between the hydrogen atoms on the methyl ligands and hydrogen atoms on the displaced arene ring carbon atoms.[92] There may well be this steric component to the distortion, but there is also thought to be an electronic component.[87] Figure 6 shows the development of the valence orbitals of an 18-electron, C_{2v}, η^6-benzene–ML$_4$ complex. The four sets of L_4 donor hybrids on the left of the figure find symmetry matches with benzene–M orbitals and are stabilized. The $2a_1$ and *one* component of e_2, of a_2 symmetry, orbitals are left nonbonding. The other component of e_2 is destabilized by the ligand $2a_1$ level. As described in section IIIB, e_2 consists of primarily metal $x^2 - y^2$ and xy with benzene π^* mixed in a bonding way. In all of the cases we treated previously, both members of e_2 are filled. Here only the xy component (a_2) is. As a consequence, there is increased bonding to the four arene carbon atoms on either side of the plane of the paper in Figure 6 and those Mo–C bond lengths become shorter than the other two.[87] The structure of $[(\eta^6\text{-}C_6H_5CH_3)Mo(SCH_3)_2]_2{}^{2+}$[93] also shows a similar distortion. Here the $2a_1$ benzene–M orbitals in each unit form a filled σ and empty σ^* bond in the dimer.

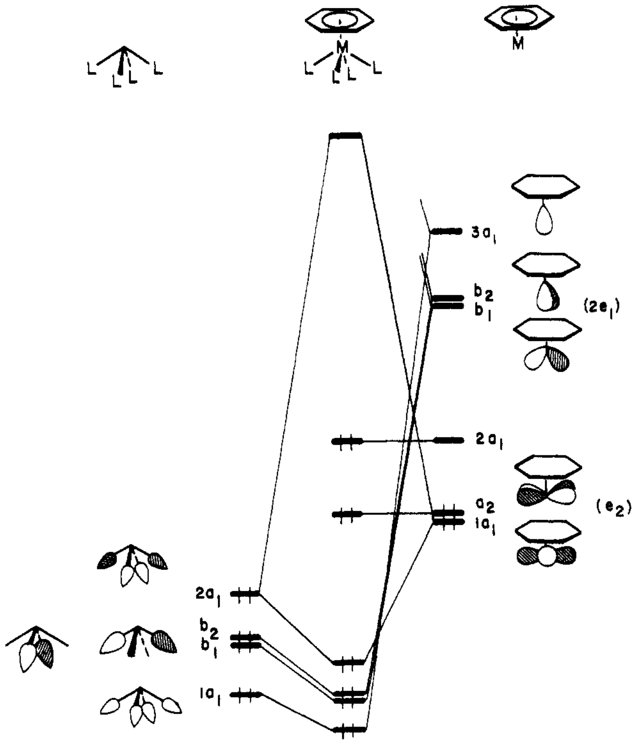


Figure 6. Orbital interaction diagram for a benzene–ML$_4$ complex.

In $[\eta^6\text{-}C_6(CH_3)_6]Ti(Cl_2AlCl_2)_2\cdot C_6H_6$,[94] the metal atom is formally d^2. In other words, there are two less electrons than shown in Figure 6. Presumably, the benzene–metal $2a_1$ (z^2) orbital is empty. The conformation of the molecule also appears to have the ML$_4$ unit rotated by 45° from that shown in Figure 6. Now most of the δ bonding will occur between the metal atom and the two para carbon atoms in the plane of the paper. Accordingly, these bonds should be shorter than the other four, i.e., the arene should exist in an inverted boat conformation. In fact, the two Ti–C bonds at an average of 2.46 (1) Å are slightly shorter than the average of the other four—2.52 (1) Å. In $[\eta^6\text{-}C_6H_6\text{-}\eta^3\text{-}C_3H_5\text{-}Mo\text{-}\mu\text{-}Cl]_2$,[95] there is also substantial variation in the Mo–C(ring) distances. They range from 2.18 (1) Å to 2.36 (1) Å. The ring here is decidedly puckered into an inverted boat conformation with two para carbon atoms bent closer to the Mo atom. It is difficult to judge whether this is due to the conformation of the ML$_4$ group, as discussed above, or other factors.

No systematic variations in the C–C bond lengths around the arene ring were observed in any of these structures. Average C–C (ring) bond lengths are in the 1.40–1.42 Å range. Notice that the M–C_6(grav) distance of 2.06 Å for the Ti complex in Table IX is much longer than that for any other first-row transition metal complex.

VI. η^6-Arene–ML$_6$ Complexes

Nominal nine-coordination would prevail in η^6-arene–ML$_6$ structures. The class has potential size and scope but presently is represented by a single structure, $(\eta^6\text{-}C_6H_6)U(\eta^2\text{-}Cl_2AlCl_2)_3$.[96] Two chlorine atoms of each tetrachloroaluminate ion are bonded to the uranium atom, and these six chlorine atom positions approximately define five of the six vertices of a pentagonal bipyramid with the C_6 centroid of the benzene ring at the seventh (axial) site of the pentagonal bipyramid—hence from a geometric point of view in defining a coordination polyhedron, the structure is more readily represented as a seven-coordinate species. Unfortunately, the position of the carbon atoms of the benzene ring could not be accurately assessed in the crystallographic determination. The ring appeared to be coplanar (to within 0.2 Å), and the U–C distance is 2.91 (1) Å, a value to be compared with U–C distances of 2.65 and 2.74 Å in $(\eta^5\text{-}C_5H_5)_3UCl$ and $(\eta^8\text{-}C_8H_8)_2U$, respectively.

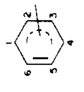
VII. Mononuclear and Nonsandwich Metal Complexes with η^4-Arene Ligands

A number of mononuclear and nonsandwich metal complexes for the η^4-arene ligands have been reported. The structural details for metal–η^4-arene interactions in these complexes are listed in Table X. The C_6 ring C–C distances and the M–C distances are very similar to those for metal–η^4-arene interactions in sandwich structures (Table II), although these comparisons can be made only for the second-row metals since no first-row metal sandwich complex with an η^4-arene ligand has been reported. Within the set of three iron structures of η^4-arene–Fe(CO)$_3$ form listed in Table X, the C–C and M–C distances are very similar. Dihedral angles generated by the folding of the η^4-arene ligand may vary between 32 and 48°. The electronic sources of this distortion are exactly analogous to those presented for the d^8-bis(benzene)–M examples in section IID. It is interesting that 19- and 20-electron sandwich complexes of the first transition-metal series favor the η^6 mode of bonding with the additional one or two electrons residing in metal–benzene antibonding orbitals. The potential 20-electron Fe(CO)$_3$ complexes instead distort to η^4. For the reasons outlined in section IID, these species will have relatively high activation barriers for ring-whizzing.[83,97]

VIII. η^3-, η^2-, and η^1-Arene–Metal Complexes

Five arene–ML_2 complexes, crystallographically characterized, have arene ligands that can be viewed as monoolefinic (η^2) or allylic (η^3) units bound to the metal atom. In these complexes, the arene ring parameters in the complexes diverge substantially from those of the free arenes (Table XI).[98] The coordination of the arene ring to the ML_2 subunit results in C–C bond length alternations and loss of planarity of the C_6 fragment such that the resonance delocalization of electron density present in the uncomplexed arene must be significantly perturbed. Hückel molecular orbital calculations suggest that arene coordination and concomitant reorganization result in as much as a 75% loss of resonance energy.[99] It should be emphasized that (a) the resonance energy of the perfluoroarenes that are η^2 ligands in $[\eta^2\text{-}C_6(CF_3)_6]Pt[P(C_2H_5)_3]_2$,[100] **44**, and $\{\eta^2\text{-}C_6[1,2{:}3,4{:}5,6\text{-}(C_2F_4)_3]\}Pt[P(C_6H_5)_3]_2$,[101] **45**, is probably considerably less than the value of 40 kcal/mol usually cited for benzene[102] and (b) p orbital "π" interaction is not fully lost until the two p orbitals in question are

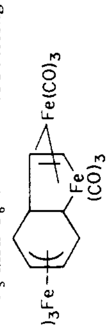
TABLE X. Mononuclear Metal Complexes with η^4-Arene Ligands



complex	C_1–C_2 and C_3–C_4[a]	C_2–C_3[a]	C_5–C_6[a]	C_1–C_6 and C_4–C_5[a]	M–C_1(C_4)[a]	M–C_2(C_3)[a]	δ,[b] deg	ref
$(C_9H_7F_6O_2)Rh[\eta^4\text{-}C_6(CF_3)_6]$[c]	1.49 (1)	1.40	1.38 (2)	1.48 (3)	2.12 (2)	2.12 (2)	42	*d*
$Fe(CO)_3[\eta^4\text{-}1,2\text{-}C_6(CF_3)_2(CH_3)_4]$	1.46 (1)	1.41 (1)	1.35 (1)	1.50 (1)	2.11 (1)	2.07 (1)	43	*e*
$Fe(CO)_3[\eta^4\text{-}3,\alpha\text{-}CH_3C_6H_4\text{—}C(CH_3){=}CH_2\text{-}Fe(CO)_3]$	1.43 (1)	1.402 (4)	1.428 (4)[g]	1.48 (1)	2.152 (4)	2.05 (1)	34.3	*f*
$Fe(CO)_3[\eta^4\text{-}1,1',1''\text{-tricarbonyl-1-ferraindene-}Fe(CO)_3]$[h]	1.43 (2)	1.38 (2)	1.39 (2)[g]	1.45 (2)	2.17 (1)	2.05 (2)	32.5	*f*
$TaCl[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2(\eta^4\text{-naphthalene})$	1.44 (1)	1.416 (7)	1.406 (7)	1.47 (1)	2.39 (1)	2.25 (2)	43	*i*

[a] Distances in Å. [b] Dihedral angle formed by folding of the arene ligand at C_1 and C_4. [c] The $C_9H_7F_6O_2$ ligand is tridentate and resulted from the reaction of coordinated acetylacetonate with $CF_3C{\equiv}CCF_3$. [d] Barlex, D. M.; Evans, J. A.; Kemmitt, R. D. W.; Russel, D. R. *J. Chem. Soc. Chem. Commun.* **1971**, 331. [e] Bond, A.; Bottrill, M.; Green, M.; Welch, A. J. *J. Chem. Soc. Dalton Trans.* **1977**, 2372. [f] Herbstein, F. H.; Reisner, M. G. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3304. [g] The second Fe(CO)$_3$ group is coordinated to the C_5 and C_6 centers accounting for the relatively large value.

[h]



[i] Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101* 611.

TABLE XI. η^1-, η^2-, and η^3-Arene-ML$_2$ Complexes

complex	M-C[a,c]	C-C[a,d]	ring band[b,e]	M-L[a] (av)	ref
$[\eta^2\text{-}C_6(CF_3)_6]Pt[P(C_2H_5)_3]_2$	2.14 (2)	1.51 (3)	NP	2.31 (2)	100
$\{\eta^2\text{-}C_6[1,2\text{-}3,4\text{-}5,6\text{-}(C_2F_4)_3]\}Pt[P(C_6H_5)_3]_2$	2.06 (2)	1.52 (2)	129	2.31 (1)	101
$(\eta^2\text{-}C_{14}H_{10})Ni[P(C_6H_{11})_3]_2$	2.03 (3)	1.422 (6)		2.234 (7)	99
$\{(\eta^3\text{-}C_{13}H_8OC_2H_5)Pt[P(C_6H_5)_3]_2{}^+\}$	2.23 (7)		149	2.288 (8)	105

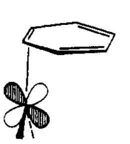
[a] Distances in Å. [b] Angle in degrees. [c] Average of two (η^2) or three (η^3) bond distances of carbon coordinated to metal. [d] Bond distance between carbons which are coordinated in the metal. [e] This is the dihedral angle between the plane of the C_6 ring and the plane of the coordinated carbons and their substituents. NP signifies that the two sets of atoms are not planar.

TABLE XII. Polynuclear Metal Complexes with an η^6-Arene Ligand Bound to a Single Metal Atom

complex	C-C[a]	M-C[b]	M-C_6(grav)[c]	ring planarity	C_6-S angle[d]	ref
$(C_6H_5)CCo_3(CO)_6[\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3]$	1.41 (1)	2.14 (3)	1.61	P		*e*
$Ru_4(CO)_9(\eta^6\text{-}C_6H_6)(C_6H_8)$	1.41 (2)	2.24 (2)	1.74	P		*f*
$Ru_6C(CO)_{14}[\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3]$		2.24				*g*
$Co_4(CO)_9(\eta^6\text{-}C_6H_6)$	1.39 (2)	2.15 (2)	1.603 (2)	P		*h*
$Co_4(CO)_9[\eta^6\text{-}C_6H_4(CH_3)_2]$[i]	1.39 (2)	2.16 (3)	1.64 (1)	P		*h*
$\{Nb_3Cl_6[\eta^6\text{-}C_6(CH_3)_6]_3{}^+\}(Cl^-)$[j]		2-2.53 (3) 2-2.34 (3) 2-2.58 (3)		?		*j, k*
$\{Nb_3Cl_6[\eta^6\text{-}C_6(CH_3)_6]_3{}^{2+}\}(TCNQ^{2-})$[l]	1.447 (7)	2-2.28 4-2.48		NP		*m*
$\{Mo_2(\mu\text{-}SCH_3)_4(\eta^6\text{-}C_6H_5CH_3)_2{}^{2+}\}$	1.38-1.45 (1)	2.28-2.416 (3)		NP (9.6°)		93
$[closo\text{-}2,4\text{-}(CH_3)_2\text{-}2,4\text{-}C_2B_9H_9]Fe[\eta^6\text{-}C_6H_5(CH_3)]$		2.116				*n*
$\{[Ru(\eta^6\text{-}C_6H_6)(OH)]_4\}(SO_4)_2\cdot 12H_2O$	1.395 (10)	2.151 (8)	1.622 (8)		–	*o*

[a] Mean aromatic C–C distance in Å. [b] Mean aromatic C to metal atom distance in Å. [c] Distance in Å from the metal atom to the center of gravity of the six aromatic carbon atoms. [d] + if substituent is bent away from the metal atom and – if bent toward the metal atom. [e] Dellaca, R. J.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1855. [f] Aime, S.; Milone, L.; Osella, D.; Vaglio, G. A.; Valle, M. *Inorg. Chim. Acta* **1979**, *34*, 49. [g] Mason, R.; Robinson, W. R. *J. Chem. Soc., Chem. Commun.* **1968**, 468. [h] Bird, P. H.; Fraser, A. R. *J. Organomet. Chem.* **1974**, *73*, 103. [i] 1:1 mixture of *o*-xylene and *p*-xylene. [j] Disordered. [k] Churchill, M. R.; Chang, S. W.-Y. *J. Chem. Soc., Chem. Commun.* **1974**, 248. [l] TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane. [m] Goldberg, S. Z.; Spivack, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Miller, J. S.; Abkowitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 110. [n] Garcia, M. P.; Green, M.; Stone, F. G. A.; Sommerville, R. G.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 871. [o] Gould, R. O.; Jones, C. L.; Robertson, D. R.; Tochter, D. A.; Stephenson, T. A. *J. Organomet. Chem.* **1982**, *226*, 199.

orthogonal. In terms of the molecular orbital scheme developed in Figure 5, both members of the antibonding metal–arene $2e_1$ set are now filled for these d^{10} complexes. In one member, **46**, the metal d component loses all interaction with the benzene π system and becomes localized on the metal. The other member of $2e_1$ also loses its metal d–benzene π antibonding interaction. In this case, as the ML_2 unit approaches an arene edge, metal d orbitals overlap with a benzene π^* orbital as shown in **47**. Therefore, both members of $2e_1$ are stabilized by distorting to η^2.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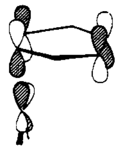
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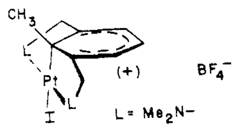
The C_6 ring in **44** exhibits the most apparent deviations from planarity and changes in C–C bond length. Free hexakis(trifluoromethyl)benzene is slightly nonplanar.[103] In the complex, the effect of the metal atom on the ring's structural parameters is to enhance the nonplanarity of the ring and produce a "long–short–long" pattern of carbon–carbon ring bond distances. These lengths beginning with the bond between the two carbons coordinated to platinum are 1.51 (3), 1.50 (3), 1.36 (3), 1.48 (3), 1.36 (3), and 1.48 (3) Å, to be compared with the uncomplexed arene average bond distance of 1.406 Å.[103] Lengthening of carbon–carbon double bonds upon coordination to transition metals is a general observation.[104] The value of 1.51 (3) Å reported for **44** lies within the range of values found for halide-substituted monoolefins bound to platinum,[100] and the other distances around the ring in **44** correspond closely to those expected for a 1,3-butadiene fragment bound to the coordinated olefin by carbon–carbon single bonds of 1.50 (2) and 1.48 (3) Å. Although the C_6 ring in **45** displays the same variational pattern of bond lengths as in **44**, the arene remains much more nearly planar. Steric factors may largely determine the degree of departure from planarity in the arene ligand.[101] For the coordination of condensed arenes as η^2 or η^3 ligands to ML_2 subunits, Hückel calculations do seem to be a reliable method of predicting which of the possible isomers will be observed.[99] Thus, anthracene in $(\eta^2\text{-}C_{14}H_{10})Ni[P(C_6H_{11})_3]_2$[99] and 1-ethoxyphenalenium cation in $\{(\eta^3\text{-}C_{13}H_8OC_2H_5)Pt[P(C_6H_5)_3]_2{}^+\}$[105] preferentially coordinate to the metal such that the remaining uncomplexed carbon atoms can be described as 2-vinylnaphthalene and 1-ethoxynaphthalene and these have the highest resonance energy of the possible compounds derived from anthracene and 1-ethoxyphenalenium cation by removal of two or three adjacent carbon atoms, respectively. Forms **44** and **45** have a very low activation energy for ring-whizzing.[106] Calculations[83] indicate that the transition state is a zwitterionic η^3 species, analogous to the phenalenium–Pt$(PPh_3)_2{}^+$ complex in Table XI.

There is one example of an η^1-benzene complex.[107] The molecular framework is illustrated in **48**. The local coordination around Pt is very close to square planar,



48

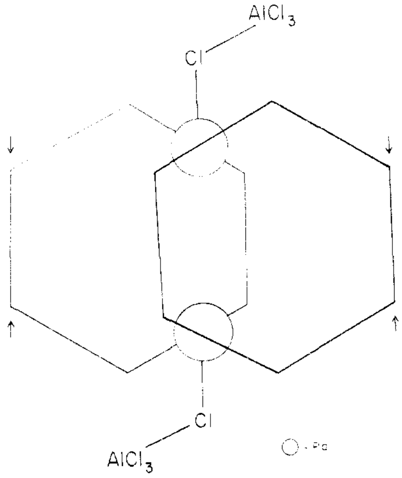
with a Pt–C distance of 2.18 Å. The two C–C bond lengths to the coordinated carbon are slightly longer (1.46 Å, av) than the other four (1.40 Å, av). The coordinated carbon remains trigonal.

IX. Polynuclear Metal Complexes with Arene Ligands

Within this group, the largest class has η^6-arene ligands bound to a single metal atom. Major structural parameters associated with the arene ligands in these complexes are summarized in Table XII. For most complexes, the arene C_6 ring is planar and the C–C, M–C, and M–C_6 center of gravity distances are very similar to those established for comparable mononuclear metal–η^6-arene complexes. In two $Nb_3[\eta^6\text{-}C_6(CH_3)_6]$ complexes, the arene ligand is folded at the C_1 to C_4 vector away from the metal. The reasons for the arene folding in these complexes and the direction are not apparent.

The remaining examples of arene complexation with a metal center in polynuclear metal compounds are rather special cases; the majority of these have an arene ligand that is also directly bound to a metal atom through a metal–carbon σ bond or indirectly through a metal σ bond and atom on an arene substituent group. Truly exceptional are the two palladium complexes in which benzene molecules bridge-bond to the two palladium atoms—*the only reported examples in which an arene molecule bonds to more than one metal atom.*

Reaction of $PdCl_2$ with aluminum metal and aluminum(III) chloride in refluxing benzene produced two dinuclear palladium complexes: $Pd_2(AlCl_4)_2(C_6H_6)_2$ and $Pd_2(Al_2Cl_7)_2(C_6H_6)_2$. Both were investigated by X-ray crystallography, although the latter suffered from crystalline disorder.[108,109] In the tetrachloroaluminate complex, the basic geometry is shown in projection, **49**.



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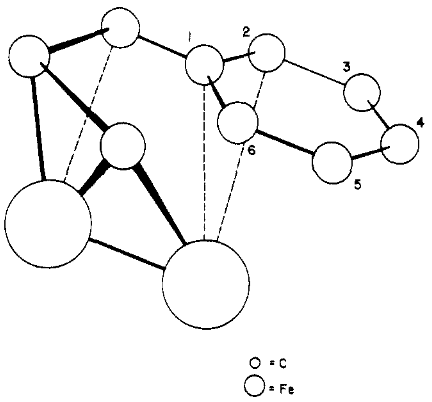
Each benzene molecule appears to be bound as a conjugated diene; in fact, the benzene rings are folded (7°) and two carbon atoms of each ring are bent away from the two palladium atoms (these carbon atoms are identified by arrows in **49**). There was no statistically significant variation in the C_6 ring C–C bond distances; the mean value was 1.40 (4) Å. Short Pd–C bonding distances were 2.37 and 2.27 Å for the "diene interactions". In the $Al_2Cl_7^-$ complex, the basic geometry of the complex was very similar to the $AlCl_4^-$ complex, but disorder, despite the low-temperature crystallographic study,[109] precludes any unambiguous stereochemical conclusions about the electronic character of the arene bonding to the two palladium atoms—apparently the barrier of benzene rotation with respect to the Pd–Pd bond is relatively small.

Triphenylcyclopropene reacts with $Fe_2(CO)_9$ to produce among other products $[(C_6H_5)_3C_3]HFe_2(CO)_6$[110] in which one iron atom of the $Fe_2(CO)_6$ unit is η^3-allyl bonded to the C_3 unit and the second iron atom σ bonded to a terminal allylic C_3 carbon unit. The other terminal allylic carbon atom's phenyl substituent is π bonded to the second iron atom through the C_1 and C_2 phenyl carbon atoms, **50**, with Fe–C_1 and Fe–C_2 distances of 2.403 (4) Å. In $HRu_2(CO)_3[P(OC_6H_4)(OC_6H_5)_2]_2[OP(OC_6H_5)_2]$,[111] one of the two orthometalated $P(OC_6H_4)(OC_6H_5)_2$ ligands has the C_2 and C_3 (C_6H_4) carbon atoms within potential bonding distance [2.33 (4) and 2.59 (4) Å] of the other ruthenium atom. However, C–H hydrogen atom positions were not established—the possibility of primary C–H–Rh multicenter bonding interactions is an alternative to the η^2-arene–Ru bonding representations; full details of the crystallographic study have not been presented.



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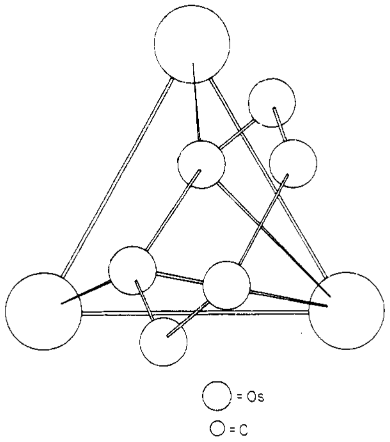
Another type of arene ligand in cluster chemistry are the benzene groups in triosmium carbonyl clusters whereby a C_6H_4 unit is bonded through the two unsubstituted carbon atoms to all three osmium atoms, as in **51**, for complexes like $Os_3(CO)_7[P(C_6H_5)_3]_2(C_6H_4)$,[112] $HOs_3(CO)_7[\mu\text{-}P(C_6H_5)_2][P(C_6H_5)_3](C_6H_4)$,[113] and $HOs_3(\mu\text{-}SCH_3)(CO)_9(C_6H_4)$.[113b] In structures like these, the benzyne ligand has a planar C_6 framework, and the intersection of the C_6 and the Os_3 planes generates angles of ~70°. No systematic alternation of C–C bond distances in the benzene ring has been reported in most of these clusters; there is still little departure from a mean 1.42-Å C–C distance; however, the benzyne ligand in $Os_3(CO)_9(\mu_3\text{-}PC_2H_5)(C_6H_4)$[113c] has C(H)–C(H) distances of 1.39 Å and an apparently unique C–C distance of 1.53 (5) Å. Because of the high uncertainty in the distance parameters, it is not prudent to comment on this apparent difference between the benzyne ligand in this cluster and those in the oth-



51

er[112,113a,b] related clusters. The C_6–Os_3 interplanar angle is 58.9° in the $C_2H_5POs_3$ cluster.

X. Arene-Metal Surface Chemistry

Structural and stereochemical features for arene molecules chemisorbed on metal surfaces cannot be precisely assessed given the present limitations in surface techniques of diffraction and spectroscopy. Nevertheless, the composite information from low-energy electron diffraction, photoelectron spectroscopy, high-resolution electron energy loss spectroscopy, theoretical calculations, and chemical studies[114-121] indicates that benzene is chemisorbed in a plane parallel to the surface plane for atomically flat surfaces like Ni(111), Ni(100), Pt(111), and Pt(100). The data are consistent with an expected π bonding. Since the metal surfaces are excellent donors, the benzene π^*–metal interaction is probably more extensive than in molecular metal–benzene complexes. For this intuitively plausible configuration, the registry between the surface metal atoms and the benzene C_6 centroid cannot be unambiguously ascertained. For example, some[117] have suggested that the C_6 centroid is centered over a single nickel atom for Ni(111)–C_6H_6, and others have proposed[114] that there are two "phases" for Ni(111)–C_6H_6—one in which the C_6 centroid is over a single nickel atom and the other in which the centroid lies over a threefold site.

Toluene chemistry on Ni(100) and Ni(111) is very different from that of benzene.[119] Because a π-bonded toluene molecule on these planes places a methyl hydrogen atom close to surface metal atoms, methyl C–H bond breaking ensues at low temperatures to generate presumably as a subsequent state, a π-bound benzyl radical.

Surface chemistry of other arenes such as naphthalene have been studied, but not in a comprehensive diffraction, spectroscopic, and chemical context.[122]

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Note Added in Proof. Recent crystallographic studies of arene–metal complexes of special note are the following: (1) The crystal structure of a 16-electron M(η^6-arene)$_2$ complex has been completed. In Ti(C_6H_6)$_2$,[123] the C_6 rings are planar, the Ti–C distances are in the range 2.22–2.25 (1) Å, and the Ti–C_6 (center of gravity) separation is 1.736 Å. The rings are eclipsed as required by the crystallographic symmetry. (2) In $\{(CH_3)_2Sn(C_6H_5\text{-}\eta^6)_2[Cr(CO)_3]_2\}$, the $Cr(CO)_3$ are η^6-bonded to the phenyl groups of $(CH_3)_2Sn(C_6H_5)_2$. There is nothing exceptional about the angle or distance parameters.[124] (3) Related to (η^5-C_5H_5)Fe(η^6-fluorenyl) is $(OC)_3Mn$(η^6-fluorenyl), recently structurally defined by an X-ray diffraction study.[125] This manganese derivative is closer to a limiting case of an η^5-cyclohexadienyl–metal interaction than is the iron complex discussed earlier. (4) A very interesting η^2-arene–metal complex is $[\mu_2\text{-}\eta^3\text{-}C(C_6H_5)\text{-}C(C_6H_5)\text{-}C(COOC_2H_5)(C_6H_5\text{-}\eta^2)]\text{-}Fe_2(CO)_6$,[126] but unfortunately the precision of the crystallographic determination was too low to allow objective comment about distance and angle features of the η^2-arene–Fe interaction. (5) A quite complex arene–metal structure has been reported[127] for a cluster species, $Ru_4(CO)_7(\mu\text{-}CO)_2$(indenyl)(dihydridoindenyl), in which the indenyl ligand is bound through the C_5 ring in an η^5 fashion to one ruthenium atom and the four nonbridged C_6 ring carbon atoms are bonded to two ruthenium atoms such that two are η^2-bonded to one ruthenium and two are η^2-bonded to the other. Unfortunately, the precision of this determination was low.

XI. References

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