

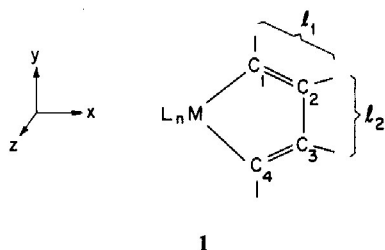
DELOCALIZATION IN METALLOCYCLES

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ABSTRACT. — The known structures of d^0 , d^6 , d^8 $L_nM(C_4R_4)$ metallocycles show bond length alternation in the carbon chain. In principle the d^6 and d^8 complexes among these could form delocalized or "aromatic" rings. The reasons for the apparent absence of bond length equalization, one manifestation of such delocalization, are discussed. The analysis leads to a set of orbital criteria for maximizing delocalization, and in an extension to some speculations concerning the possible stability of mononuclear $L_nM(CR)_x$, $x=3, 5, 6$.

Transition metal metallocycles of the general type **1**, metallocyclopentadienyls, are common products in reactions of transition metal complexes with acetylenes¹. For a wide range of metals and ligands (**2-10**, Table I) the structure determinations of such compounds show, with some exceptions, bond lengths consistent with localized double bonds²⁻⁸.



Under certain conditions such compounds might have been thought of as delocalized or aromatic systems. The basic feature of the aromatic state, as nebulously defined and as heuristically useful as it is⁹, is achievement of a π sextet (in a Hückel topology) or alternatively, substantial backbonding from the metal d -orbitals into the π^* orbitals of the C_4R_4 chain. One consequence of such delocalization should be equalization of l_1 and l_2 . Hence the "null question" that prompted this study: Why do d^6 and d^8 metallocycles,

in which d -orbitals are available for such backbonding, show little or no apparent delocalization? The d^0 systems, in which there are no obvious filled d -orbitals, show C=C bond distances similar to or even longer than in the d^6 and d^8 complexes. For purposes of this discussion, a "localized system" has alternating short-long-short carbon-carbon bonds in the C_4R_4 chain and a delocalized system will be taken to have nearly equal C-C bond lengths. There is, of course, no firm division between the two; butadiene, the prototype "localized" system, has $l_1=1.34$, $l_2=1.48$ ¹⁰.

With this question in mind the approach to be taken here is natural. We partition the metallocycle into two pieces, one consisting of the C_4R_4 chain, and the other the metal-ligands fragment. In the calculations the C_4R_4 moiety is modeled by C_4H_4 and similar simplifications are made to the metal fragments. The extended Hückel method, with parameters listed in the Appendix, is used throughout. Since the Hückel method fails miserably in reproducing bond lengths, we will use standardized geometries for the metallocyclic rings and use bonding trends and orbital occupations as the indicators of "delocalization".

First, consider the $Cp_2Ti(C_4R_4)$ complex. Figure 1 shows the construction of this molecule from the Cp_2Ti^{2+} fragment, studied in depth previously¹¹, and a $C_4H_4^{2-}$ unit. Two of the titanium-fragment d -orbitals, $2a_1$ and b_1 , both nominally empty, form σ -bonds with the carbon lone-pairs, and $1a_1$ is left as a fairly low-lying LUMO. None of the valence d -orbitals

Table I. — Structural data on some metallocycles.

Compound	d^n ^a	l_1 [ave] ^b	l_2^c	Reference
2 RhCl (SbPh ₃) ₂ (C ₄ (CF ₃) ₄)	6	1.35	1.39	2 a
3 RhCl (PPh ₃) ₂ (C ₂₄ H ₁₄ O ₂)	6	1.35	1.45	3
4 RhCl (H ₂ O) (As (CH ₃) ₂) ₂ (C ₄ (CF ₃) ₄)	6	1.33	1.43	2 b
5 (C ₅ H ₅)Co (PPh ₃) (C ₄ (C ₆ F ₅) ₄)	6	1.33	1.47	4 a
6 (C ₅ H ₅)Rh (PPh ₃) (C ₄ (C ₆ F ₅) ₄)	6	1.35	1.46	4 b
7 (C ₅ H ₅) ₂ Ti (C ₄ Ph ₄)	0	1.37	1.50	5
8 (C ₅ H ₅) ₂ Hf (C ₄ Ph ₄)	0	1.38	1.51	5
9 (η^5 -C ₅ H ₄ PPh ₃)Pd (C ₄ (COOCH ₃) ₄)	8	1.38	1.44	6
10 (norbornadiene)Pd (C ₄ (COOCH ₃) ₄)	8	1.34	1.48	7

^a Number of d -electrons, counting C_4R_4 as doubly anionic. ^b Average of C_1-C_2 and C_3-C_4 distances (see **1**). ^c C_2-C_3 distance, rounded to nearest 0.01 Å.

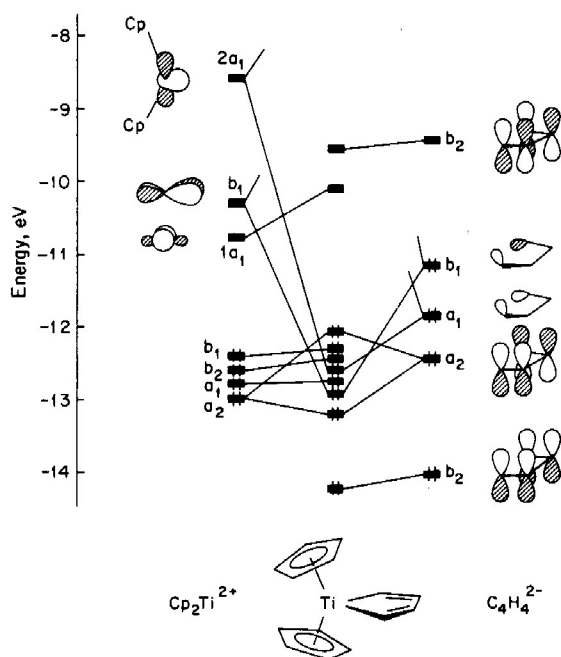
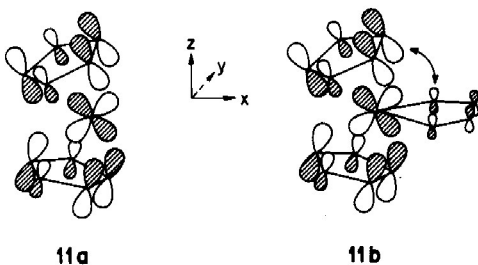


Figure 1. — Construction of $\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)$ from $\text{Cp}_2\text{Ti}^{2+}$ and $\text{C}_4\text{H}_4^{2-}$ fragments. $1 a_1$, b_1 , and $2 a_1$ are the fragment orbitals discussed in reference ¹¹, here presented in a different perspective.

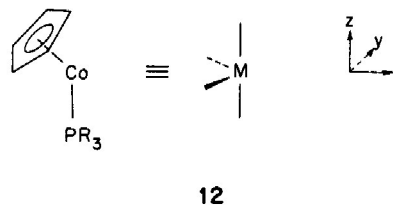
of the Cp_2Ti fragment has the proper symmetry to interact with the π -system of C_4H_4 , and from Figure 1 there is no obvious perturbation of the 4-electron localized dienic C_4H_4 chain.

The fragment-based population analysis, however, reveals some occupation (0.09 electrons; rigorous definition in the Appendix) of the $\pi_{b_2}^*$ $\text{C}_4\text{H}_4^{2-}$ orbital, the LUMO of the π -system. This can be traced to a filled $\text{Cp}_2\text{Ti}^{2+}$ fragment orbital of b_2 symmetry, **11a**, stabilizing itself by bonding with, and thereby partially occupying, $\pi_{b_2}^*$. This orbital, **11a**, is largely confined to the Cp rings of the Cp_2Ti fragment, with only 19% d_{xz} contribution, but still has some overlap with $\pi_{b_2}^*$. The total overlap integral $\langle \text{frag. } b_2 \text{ orbital} | \pi_{b_2}^* \rangle$ is 0.079. The d -orbital component of the fragment b_2 orbital contributes 0.053 to this overlap integral, with the rest coming from a direct through-space interaction between the carbons of the Cp ring and the $\text{C}_4\text{H}_4^{2-}$ fragment, **11b**. Some slight evidence for such an attractive interaction can be found in the crystal structure. The angle, $\text{Cp}-\text{Ti}-\text{Cp}$, is 134° in the metallocyclic structure ⁵, while in Cp_2TiCl_2 the angle is 131° ¹². So slight a difference could easily be



due to any number of other reasons, but if the substituents on the metallocyclic carbons were less bulky than the phenyl groups actually present, the $\text{Cp}-\text{Ti}-\text{Cp}$ angle could be even larger.

The complex $\text{CpCo}(\text{PH}_3)(\text{C}_4\text{H}_4)$, a model for a d^6 system, **5**, is similarly formed from $\text{CpCo}(\text{PH}_3)^{2+}$ and $\text{C}_4\text{H}_4^{2-}$ fragments in Figure 2. The $\text{CpCo}(\text{PH}_3)^{2+}$ fragment closely resembles a d^6 , ML_4 , quasi-octahedral fragment **12**, where the Cp ring spans three coordination sites. The two empty



valence orbitals of the fragment (see Fig. 2) are ideally situated to form σ -bonds with the $\text{C}_4\text{H}_4^{2-}$ lone pair orbitals. Like the titanium molecule, there are no immediately-obvious strong interactions involving the C_4H_4 π -type orbitals. However, the fragment population analysis shows a slight occupation (0.10 electron) of the $\pi_{b_2}^*$ orbital of the $\text{C}_4\text{H}_4^{2-}$ portion, resulting from a bonding interaction with a filled $\text{CpCo}(\text{PH}_3)^{2+}$ fragment orbital. This fragment orbital is largely (84%) d_{xz} , and the total overlap integral $\langle \text{frag. } b_2 | \pi_{b_2}^* \rangle$ is 0.087.

Surprisingly, both the occupation of $\pi_{b_2}^*$ and the metal-fragment to $\pi_{b_2}^*$ overlap integral are virtually identical in the $\text{CpCo}(\text{PH}_3)(\text{C}_4\text{H}_4)$ and $\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)$ complexes. The near-identity is a fortuitous coincidence of parameter choices, but it is not unreasonable that the overlap and occupation

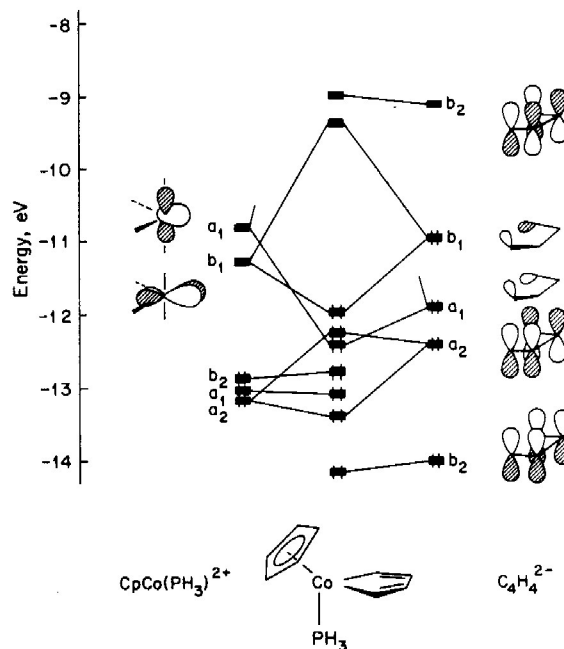


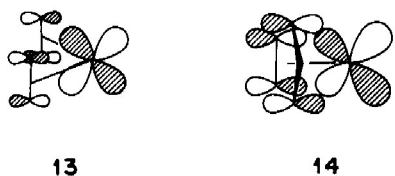
Figure 2. — Construction of $\text{CpCo}(\text{PH}_3)(\text{C}_4\text{H}_4)$ from its constituent fragments. Orbitals are labeled according to the C_{2v} symmetry of the quasi-octahedral complex.

should be similar in the two systems. In the cobalt complex the occupation arises from backbonding of a filled quasi-octahedral " t_{2g} " d -orbital into the π^* . It is perhaps smaller than expected because the d -orbital has poor overlap with the π^* -orbital, in turn because of the larger exponent used for the cobalt d -orbitals (relative to Ti). In the Ti complex the occupation arises from a filled d -Cp bonding fragment orbital which has no analogue in the quasi-octahedral Co fragment. The overlap is larger than might be expected because the less-contracted Ti d -orbital has better direct overlap with $\pi_{b_2}^*$, than the "harder" Co: $\langle d_{xz} | \pi_{b_2}^* \rangle$ is 0.135 for Ti, 0.059 for Co. Also, in the Ti fragment there is the above-mentioned direct participation by the Cp orbitals. In the Co fragment, the Cp ring orbitals are nearly non-bonding to the d_{xz} orbital and contribute little to the fragment-fragment overlap.

Results very similar to those in the Co complex were obtained from calculations on a model octahedral rhodium complex, $(\text{CO})_2\text{Cl}_2\text{Rh}(\text{C}_4\text{H}_4)^-$. Here, occupation of the $\pi_{b_2}^*$ was 0.11 electrons.

The two d^8 metallocycles, **9** and **10**, show an interesting contrast. Calculating $(\text{ethylene})_2\text{Co}(\text{C}_4\text{H}_4)^-$, a model for **10** (cobalt was used to avoid the introduction of yet another set of parameters), gives a very small occupation of $\pi_{b_2}^*$ (0.03 electrons). $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_4\text{H}_4)^{2-}$, a model for **9**, has an occupation of $\pi_{b_2}^*$ of 0.17 electrons. As the Table shows, **9** is definitely indicated—in terms of bond length equalization—to be more delocalized than **10**. The calculated "large" population of $\pi_{b_2}^*$ is therefore consistent with the structural data. It can be traced back to a fundamental difference in the nature of the metal fragments in the two compounds.

In $(\text{ethylene})_2\text{Co}(\text{C}_4\text{H}_4)^-$ the filled b_2 orbital of the metal fragment, $(\text{ethylene})_2\text{Co}^+$, is largely d_{xz} , and is at very low energy due to some backbonding into the terminal ethylene ligands, **13**. Interaction with, and occupation of, $\pi_{b_2}^*$ of the $\text{C}_4\text{H}_4^{2-}$ fragment is therefore minimal. $(\eta^5\text{-CpCo})$ has a filled b_2 orbital, again largely d_{xz} , which is ca. 1.5 eV higher in energy, because it is repelled by the terminal Cp ring. Further, as a result of this repulsion, metal p_z hybridizes the b_2 orbital away from the Cp towards the incoming $\text{C}_4\text{H}_4^{2-}$ fragment, as indicated schematically in **14**. Both the higher energy and the favorable hybridization enhance the bonding of this fragment b_2 orbital with $\pi_{b_2}^*$.



Tilting the Cp ring off the (pseudo) two-fold axis and bringing in a phosphine changes the cobalt fragment into the quasi-octahedral fragment considered earlier. During this process the d_{xz} orbital loses most of its antibonding with the Cp ring, and its hybridization. Consequently, it interacts less with $\pi_{b_2}^*$ of C_4H_4 , and the resulting metallocycle returns to a "localized" bonding system.

We digress here to consider in more detail the factors which determine the bond lengths in the $\text{C}_4\text{H}_4^{2-}$ unit. This topic has been treated exhaustively in the context of non-metallic heterocyclic compounds¹³. By computing a small potential surface on this fragment, where the bond lengths

Table II. — Approximate change in energy of C_4H_4 orbitals with change in l_1 and l_2 .

Orbital ^a	$(\partial E)/(\partial l_1)^b$	$(\partial E)/(\partial l_2)^b$
π_{b_2}	+1.75	+1.25
π_{a_2}	+2.0	-1.0
$\pi_{b_2}^*$	-4.5	+1.0
n_{a_1}	-2.5	-0.5
n_{b_1}	-0.75	0.0

^a These orbitals are sketched in Figure 1. ^b Units (eV/Å).

l_1 and l_2 were independently varied, we found an approximation to the rate of change of one-electron energy of each C_4H_4 orbital with l_1 and l_2 . This is shown in Table II.

As expected, $\pi_{b_2}^*$ favors lengthening l_1 and shortening l_2 , i. e. the energy of this orbital falls as l_1 increases and rises as l_2 increases, and occupation of it will tend to delocalize the bonding in the C_4H_4 unit¹³. This is the orbital upon which the preceding discussion has been based. To provide some reference values for comparison, the calculated occupation of this $\pi_{b_2}^*$ C_4H_4 fragment orbital in cyclopentadiene is 0.09 electrons; cyclopentadienyl anion, 0.88 electrons; and pyrrole, 0.43 electrons. Structural parameters for these heterocycles are $l_1=1.34$, $l_2=1.47$ for cyclopentadiene¹⁴; $l_1=1.38$, $l_2=1.42$ for pyrrole¹⁵; $l_1=1.36$, $l_2=1.43$ for furan¹⁶; $l_1=1.37$, $l_2=1.42$ for thiophene¹⁷; and $l_1=1.34$, $l_2=1.44$ in substituted phospholes¹⁸. Much of this data is from microwave spectroscopy, and disagrees noticeably with available crystal structures: $l_1=1.32 \pm 0.05$, $l_2=1.44$ for cyclopentadiene¹⁹; $l_1=1.32$, $l_2=1.43$ for furan²⁰.

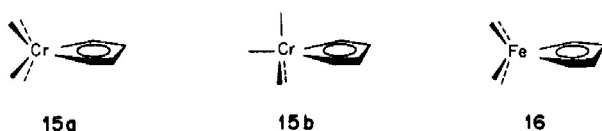
While occupation of $\pi_{b_2}^*$ provides a convenient qualitative indicator of delocalization, and is frequently used as such, Table II shows that the bond lengths are quite sensitive to other orbitals as well. The carbon " sp^2 lone pair" orbitals, by virtue of being delocalized in the C_4H_4 chain, are both stabilized by lengthening l_1 . By a σ -effect, then, the more "carbanionic" the nature of the metallocycle, the more "delocalized" the resulting structure.

Yet another orbital which is important is the π_{a_2} orbital. Vacating it also has the effect of lengthening l_1 and shortening l_2 . If, however, this orbital overlaps significantly with a filled metal-fragment orbital, there is no deoccupation of π_{a_2} . In calculations which include overlap explicitly this filled orbital-filled orbital interaction may even reinforce the trend of short l_1 , long l_2 over that preferred by the isolated π_{a_2} orbital. The analogy here is to a 6-electron Möbius π -system with localized double bonds²¹. Here is another factor in causing the observed localized structures. In all the complexes there is a filled metal-fragment orbital of a_2 symmetry, a "non-bonding" d_{yz} orbital in the d^6 - d^8 cases and a Cp- d_{yz} bonding orbital in the Cp_2Ti system, which has an overlap integral $\langle \text{frag. } a_2 | \pi_{a_2} \rangle$ virtually identical to that of the metal-fragment b_2 orbital with $\pi_{b_2}^*$. This is reasonable, since metal b_2 (d_{xz}) and a_2 (d_{yz}) orbitals both have identical overlap with symmetry-adapted combination of carbon p_z orbitals when the C—metal—C angle is 90° ^{13, 22}. Compound **9** is an exception in that the b_2 - b_2 overlap is enhanced by hybridization.

What then might be the requirements for a metallocycle that would show more delocalized bonding? The previous analysis suggests the following: 1. The metal fragment should

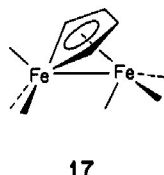
provide empty b_1 , a_1 orbitals capable of σ -bonding with the $C_4R_4^{2-}$ unit. 2. Also a filled orbital of b_2 symmetry, preferably with good overlap with $\pi_{b_2}^*$ of $C_4R_4^{2-}$, must be present. 3. Finally, we wish the metal fragment to have an empty orbital of a_2 symmetry.

The existing compounds satisfy the first requirement; the second is partially satisfied, the overlap being poor except perhaps in **9**. Condition 3 is not met in any of the known complexes. A metal possesses only one a_2 orbital; in any quasi-octahedral, square-planar, or tetrahedral molecule (or fragment) this a_2 d -orbital is nonbonding and therefore lowlying and filled in a low-spin 18-electron complex. Some possible complexes which do satisfy condition 3 are shown in **15** where the Cr is present as Cr(II), d^4 . Such molecules are unprecedented, probably for good reason, but a fortunate choice of chelating ligands might permit their isolation. Molecule **16** could be considered a trigonal-



prismatic d^6 complex, stabilized relative to the octahedron by the accepting b_2 orbital²³. Since octahedral d^6 metallocycles are known (see Table I), **16** is apparently not the favored ground-state, but may be accessible as an intermediate.

All three conditions are beautifully met by the binuclear sawhorse $Fe_2(CO)_6^{2+}$ fragment in the low symmetry of the known binuclear metallocycles, **17**²⁴. Empty orbitals suitable for σ -bonding and for stabilization (hence deoccupation) of π_{a_2} , and a filled orbital with good overlap with $\pi_{b_2}^*$, are provided by the fragment, and the structures invariably show delocalized bonding with nearly equal C-C bond lengths. Typical values for l_1 are $1.39 \pm .02$ Å, for l_2 $1.42 \pm .01$ Å.



The 5-coordinate d^6 rhodiocycles, **2** and **3**, present several points of interest^{25, 26}. A trigonal-bipyramidal d^6 complex would be expected to have a half-filled e -level and be a triplet, or Jahn-Teller unstable²⁷. The nature of the $C_4R_4^{2-}$ ligand prevents a first-order Jahn-Teller effect from operating. This is the result of two factors: 1. The ligand is a potent σ donor and effectively breaks the degeneracy of the xy , x^2-y^2 set. 2. The symmetry breaking is reinforced by the relatively small bite angle of the ligand. The workings of both factors are shown schematically in Figure 3.

We still find a fairly low HOMO-LUMO gap in the undistorted C_{2v} complex (ca. 1.5 eV) which suggests a second-order Jahn-Teller distortion²⁸ of $a_1 \times b_1 = B_1$ symmetry. Such a distortion could manifest itself in unequal C-Rh

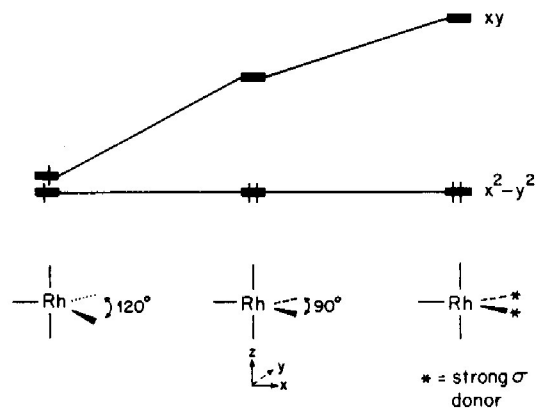
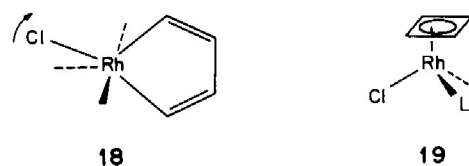


Figure 3. — The perturbation of the upper e set of an ML_3 trigonal bipyramidal complex by a change in angle between two equatorial ligands (middle) and an improvement in their σ -donor capability (right).

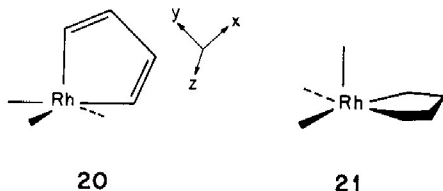
bond lengths; another possible distortion is an angular deformation, **18**, which we calculate to be slightly stabilizing. The RhL_3 portion in the xy plane is Y-shaped in the C_{2v} complex, and distortion **18** is towards a T. The latter has been found in other studies to be slightly more stable in coordinatively unsaturated ML_3 complexes²⁹. The crystal structure does show distortions from C_{2v} symmetry^{2a}.



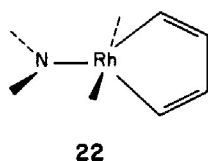
An interesting feature of the structure of **2** is an unusually short C_2-C_3 bond, l_2 . We find no difference between this molecule and the coordinatively-saturated rhodiocycles (**4**, **6** in Table I) in the π -trends (other authors²⁵ reach different conclusions), although there are some σ -bond differences³⁰. No good reason for the short l_2 occurs to us, except perhaps the following: the CF_3 groups might exert a powerful perturbation on the C_4R_4 system, relative to the more innocuous substituents in the other complexes; or, the Jahn-Teller distortion may be permitting large vibrational motions or even a disorder in the crystal. The published crystal data, however, do not support this second possibility^{2a}, and the differences between **2** and **4** (Table I) raise doubts about the first. The other pentacoordinate rhodiocycle, **3**, has a longer C_2-C_3 bond³, but has an extended π -system which may also be interacting with this bond. The structure is also of poorer quality than that of **2**.

Even the existence of these molecules is somewhat of a surprise. Why, for instance, do they not adopt the structure **19**, analogous to $Fe(CO)_3$ (cyclobutadiene) complexes? Probably because there is no facile pathway for its formation: Closing the ring at C_1 , C_4 and simultaneously forming the π -complex is symmetry-forbidden in most reaction paths retaining a mirror plane between C_1 , C_4 . It would be interesting see what these molecules do when photolyzed.

A five-coordinate d^6 complex might be expected^{27, 31} to adopt a square-pyramidal structure **20** or **21**. **20** is a continuation of the distortion to the T, discussed earlier. It is not observed, however, because the Cl bears a donor of



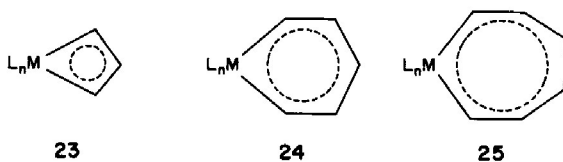
π -symmetry, p_y . In C_{2v} or near- C_{2v} structures, for instance the trigonal bipyramid of Figure 3, this p orbital overlaps with an empty d orbital, d_{xy} (the LUMO), and gives some partial double-bond character to the Rh-Cl bond. The crystal structures show a shorter Rh-Cl distance in the 5-coordinate complex than in the 6-coordinate complex. In the square pyramid **20** said p orbital, now $1/\sqrt{2}(p_x + p_y)$, overlaps with the filled d -orbital $x^2 - y^2$ in a four-electron destabilizing interaction. Replacing the Cl with a ligand lacking π -donor capability should enhance the T distortion **18**, possibly to the square pyramid **20**. A single-faced π -donor, e. g. amido, should prefer a near- C_{2v} geometry with the π -donor in the xy plane, **22**, despite the apparent steric awkwardness of this orientation. In a d^8 trigonal bipyramidal complex, a π -donor would seek an axial site, but if equatorial it would orient its donor-capability along the axis, perpendicular to the equatorial plane²⁷.



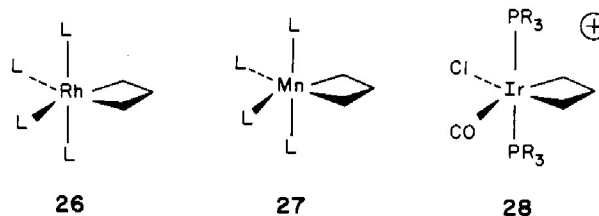
The other square-pyramid **21** is an unlikely structure, one reason being that it also has a small HOMO-LUMO gap, in model calculations even smaller than the C_{2v} "trigonal bipyramidal" complex. The analogy between ML_3 and CH_3^+ ³² suggests that **21** should resemble $C_5H_5^+$, and a near-degenerate HOMO-LUMO pair is expected.

Extensions

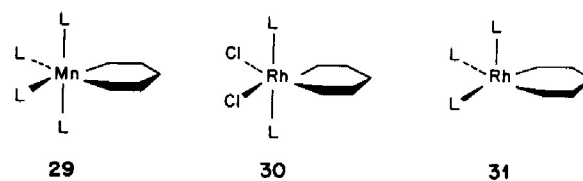
Interactions between a metal and delocalized π -systems constitute a vast area of inorganic chemistry, encompassing such ligands as porphyrins and other macrocycles, bipyridines, dithiolates, and acetylacetonates. This discussion will be limited to a very brief consideration of what might be done to stabilize other metallocycles, **23-25**. Some of these compounds are of obvious interest as possible intermediates in the Reppe reaction^{33, 34} and the Pd (II)-induced oligomerization of acetylenes studied by Maitlis *et al.*^{35, 36}.



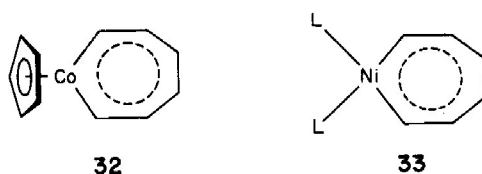
In the 3-carbon metallocycle, treating the C_3R_3 fragment as having three extra electrons (i. e. $C_3R_3^{3-}$) gives a fragment isoelectronic with $C_4R_4^{2-}$ but with a filled a_2 π -orbital at much higher energy. d^6 or d^8 3-carbon metallocycles which are analogous to the known 4-carbon metallocycles, such as **26**, will have repulsion between the already high-lying π - a_2 orbital and the a_2d_{yz} orbital and are not likely to be stable (L is a neutral two-electron donor). Removing two electrons, probably from the C_3R_3 a_2 orbital, gives more promising-looking compounds, e. g. **27**, **28**; **28** is actually a known compound³⁷. There are several complexes known of ring-opened C_3R_3 bridging a binuclear³⁸ unit.



The five-carbon metallocycle **24** (metallobenzene) presents another problem. No longer is π , such a nuisance; the filled π orbital is rather low-lying, and there is an accessible empty a_2 orbital. If treated as singly anionic, the $C_5R_5^-$ unit wants a metal fragment with empty orbitals of a_1 , b_1 symmetry for σ -bonding, and a filled b_2 for backbonding into the lowest π^* . Now octahedral complexes of the type **29** or **30** are acceptable, and should show some delocalization and aromatic character in the C-C bond lengths. Another possibility is the square-pyramidal d^8 complex **31**. Since the $C_5R_5^-$ unit has a very low-lying LUMO (b_2), it will be a ferocious π -acceptor, perhaps better described as a mild oxidant. Thus complexes like **29** or **30** would be more stable if the other ligands around the metal were not also acceptors but donors instead. Likewise, π -donor substituents on the carbon chain, especially *ortho* and *para* to the metal, should help stabilize the system. Compounds with two more electrons might exist if both the metal and carbon chain, again at the *ortho* and *para* positions, carry π -acceptors.



Mononuclear metallocycloheptatrienes **25** are not likely to be very stable, since *cis*-reductive elimination of benzene from d^6 complexes can be a symmetry-allowed and (probably) thermodynamically-favorable reaction³⁹; nor are they likely to be planar⁴⁰. If planar, and treated as doubly-anionic, the $C_6R_6^{2-}$ portion wants, as usual, empty a_1 and b_1 metal-fragment orbitals for σ -bonding. The HOMO of the π -system is b_2 , the LUMO a_2 , so an ideal match would be with a metal fragment having empty b_1 , b_2 and filled a_2 d orbitals. One such fragment is the conical η^3 -CpCo²⁺, suggesting **32** as a possibly isolable molecule. Reactions of CpCo(CO)₂



with acetylenes have given a variety of products^{4, 36, 41}, including the cobaltole (four-carbon metallocycle) considered earlier, but not apparently **32**. Another possibility is **33**, the empty p_z orbital on the metal serving as the b_2 acceptor.

The stability of several of these structures is greatly enhanced by coordination to a binuclear rather than a mononuclear metal fragment. The factors at work are similar to those discussed above for the ferrole, but the detailed analysis of the electronic structure of the lovely $M_2L_n(CR)_y$ molecules recently synthesized by the Stone⁴² and Wilke⁴³ groups⁴⁴ must remain for the future.

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Appendix

The computational parameters for the extended Hückel calculations⁴⁵ were taken from earlier work⁴⁶, and are listed in Table III. A modified Wolfsberg-Helmholz formula⁴⁷ was used throughout. The following geometries were used (distance in Å). In titanium metallocycles, $Ti-C_1=2.15$, $l_1=1.37$, $l_2=1.4455$, $C_1-Ti-C_4=80.2^\circ$, $Ti-C_{Cp}=2.384$, $(C-C)_{Cp}=1.411$, $C-H=1.1$, $Cp-Ti-Cp=134.5^\circ$; in rhodium metallocycles, $Rh-C_1=2.02$, $l_1=1.33$, $l_2=1.42$, $C_1-Rh-C_4=80.2^\circ$, $Rh-C_{CO}=1.82$, $C-O=1.18$, $Rh-Cl=2.38$, $C-H=1.1$; in cobalt metallocycles, $Co-C_1=2.0$, $l_1=1.33$, $l_2=1.4562$, $C_1-Co-C_2=82.4^\circ$, $Co-C_{Cp}=2.124$, $(C-C)_{Cp}=1.43$, $Co-P=2.234$, $P-H=1.414$, $H-P-H=93.3^\circ$, $(C-H)_{Cp}=1.1$, $Co-C_{C_2H_4}=2.1092$, $(C-C)_{C_2H_4}=1.34$, $(C-H)_{C_2H_4}=1.07$, $C-C-H=120^\circ$, $H-C-H=113.548^\circ$.

Fragment orbital populations are defined in equation (1),

$$P_{\mu\mu} = 2 \sum_{\alpha} C_{\mu\alpha} \sum_{\nu} S_{\mu\nu} C_{\nu\alpha} \quad (1)$$

where α runs over all (doubly-occupied) molecular orbitals, and ν runs over all fragment orbitals⁴⁸. Both μ, ν refer to a basis set of fragment orbitals in which overlaps (S) and wave function coefficients (C) are expressed. Defined in this manner, the fragment orbital population $P_{\mu\mu}$ is dimensionless, but in the text a unit of "electrons" is assigned.

Table III. — Extended Hückel parameters.

Orbital	H_{ii} , eV	Exponents ^a	
		ζ_1	ζ_2
H 1s	-13.6	1.3	
C 2s	-21.4	1.625	
C 2p	-11.4	1.625	
O 2s	-32.3	2.275	
O 2p	-14.8	2.275	
P 3s	-18.6	1.60	
P 3p	-14.0	1.60	
Cl 3s	-30.0	2.033	
Cl 3p	-15.0	2.033	
Ti 4s	- 8.97	1.075	
Ti 4p	- 5.44	0.675	
Ti 3d	-10.81	4.55 (0.420 6)	1.40 (0.783 9)
Co 4s	- 9.21	2.0	
Co 4p	- 5.29	2.0	
Co 3d	-13.18	5.55 (0.568 0)	2.10 (0.606 0)
Rh 5s	- 8.09	2.135	
Rh 5p	- 4.57	2.10	
Rh 4d	-12.50	5.54 (0.582 3)	2.40 (0.640 5)

^a Two Slater exponents are listed for d -orbitals, each followed by its coefficient in a double zeta representation.

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