and results we report elsewhere[11] suggest that species which may formally involve the +2 uranium oxidation state such as B and 11 are mechanistically plausible entities. This question is presently under further investigation.

To place these results in perspective, it is also important to note that the properties of the bis(pentamethylcyclopentadienyl)uranium(III) complexes are similar to those of bis(cyclopentadienyl)titanium(III) complexes,[41] both in terms of redox behavior and coordination chemistry. The structural and stoichiometric similarities to the coordination chemistry of bis(cyclopentadienyl)lanthanide(III) complexes should also be noted.[4a,36,40]

**Acknowledgment.** We thank the National Science Foundation (Grant CHE8009060, T.J.M.) for support of this work. We thank Professor R. G. Finke for information in advance of publication.

**Registry No. 2**, 71794-95-1; **3**, 79448-93-4; **4**, 71763-75-2; **5**, 71763-76-3; **6**, 79448-94-5; **7**, 79448-95-6; **8**, 71763-77-4; **9**, 71762-98-6; **10**, 71763-62-7; **11**, 79448-96-7; **12**, 79448-97-8; $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$, 68963-88-2; $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$, 67506-91-6; $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$, 67506-89-2; $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$, 67588-76-5.

**Supplementary Material Available:** Crystal structure analysis report, a table of anisotropic thermal parameters for nonhydrogen atoms (Table II), and a listing of observed and calculated structure factors from the final cycle of least-squares refinement for $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ (37 pages). Ordering information is given on any current masthead page.

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# Piano-Stool Complexes of the $CpML_4$ Type

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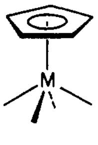
$CpML_4$ complexes apparently occur only in the four-legged piano-stool geometry. The electronic structure of this class of compounds is explored, with emphasis on geometrical distortions, the orientational preferences of single-faced $\pi$-donor and -acceptor ligands. An analysis of the electronic structure of a sterically encumbered alternative geometry, a Cp-capped trigonal bipyramid or 3:3:1 structure, leads to some criteria for stabilizing this type. Axial substituents which are good $\sigma$ and $\pi$ donors, yet small in size, are required. An explanation of the cis specificity of photochemical substitution in $CpML_4$ complexes is provided in terms of the geometry of the $CpML_3$ intermediates and the directionality of the vacant orbitals thereof.

The cyclopentadienyl ligand is the emblem of modern organometallic chemistry. In one structural type we often see two, and more rarely three or four Cp's surrounding a metal atom. In another common materialization the Cp ring binds to it a metal and an associated set of from zero to five ligands. These are the ubiquitous $CpML_n$ complexes, and one of them, $CpML_4$, 1, is the subject of this work.



1

A "four-legged piano-stool" geometry is the paradigm for $CpML_4$ complexes of group 5B and 6B transition metals.[1] Several dozen X-ray structures give a good picture of this class. All $CpML_4$ complexes whose solid-state structures are known are conveniently described as square pyramids,[2-5] with the Cp at the apex. Pseudo-five-coordination evokes immediately an entire complex of ideas on the nonrigidity of the five-coordinate type. At the same time it is clear that the $Cp^-$ ligand is the electronic equivalent of three simple Lewis bases. So $CpML_4$ complexes are electronically in the seven-coordinate manifold. Indeed nearly all known to date are $d^4$, adhering to the 18-electron rule.[6] The tension generated by the seemingly conflicting perspectives of steric pseudo-five-coordination and electronic seven-coordination is part of what makes these complexes interesting.

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(1) For a review, see: Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1–37.

(2) $CpM(CO)_4$: (a) Wilford, J. B.; Whitla, A.; Powell, H. M. *J. Organomet. Chem.* **1967**, *8*, 495–502. (b) Baird, H. W.; Dahl, L. F., mentioned in: Doedens, R. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2576–2581.

(3) $CpM(CO)_3L$: (a) Salnikova, T. N.; Andrianov, V. G.; Struchkov, Yu. T. *Koord. Khim.* **1976**, *2*, 707–711. (b) Rajaram, J.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 1313–1317. (c) Deutscher, J.; Fadel, S.; Ziegler, M. *Angew. Chem.* **1977**, *89*, 746. (d) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6326–6327. (e) St. Denis, J.; Butler, W.; Glick, M. P.; Oliver, J. P. *Ibid.* **1974**, *96*, 5427–5436. (f) Mickiewicz, M. M.; Raston, C. L.; White, A. H.; Wild, S. B. *Aust. J. Chem.* **1977**, *30*, 1685–1691. (g) O'Connor, J. E.; Corey, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 3930–3931. (h) Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1945–1949. (i) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213–1220. (j) Bennett, M. J.; Mason, R. *Proc. Chem. Soc., London* **1963**, 273. Bird, P. H.; Churchill, M. R. *Inorg. Chem.* **1968**, *7*, 349–356. (l) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1969**, 1309–1321. (m) Chaiwasie, S.; Fenn, R. H. *Acta Crystallogr., Sect. B* **1968**, *24*, 525–529. (n) Mawby, A.; Pringle, G. E. *J. Inorg. Nucl. Chem.* **1972**, *34*, 525–530. (o) Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 920–924. (p) Albright, M. J.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1978**, *161*, 221–231. (q) Semion, V. A.; Chapovskii, Yu. A.; Struchkov, Yu. T.; Nesmeyanov, A. N. *Chem. Commun.* **1968**, 666–667. Semion, V. A.; Struchkov, Yu, T. *Zh. Strukt. Khim.* **1968**, *9*, 1046–1054. (r) St. Denis, J. R.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1–16. (s) Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1969**, 8–15. (t) Bir'yukov, B. P.; Struchkov, Yu. T.; Anisimov, K. N.; Kolobova, N. E.; Beschastnov, A. S. *Chem. Commun.* **1968**, 667–668. Bir'yukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 655–664. (u) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197–2202.

(4) $[CpM(CO)_3]_2$: (a) Adams, R. D.; Brice, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6594–6602. (b) Adams, R. D.; Collins, D. E.; Cotton, F. A. *Ibid.* **1974**, *96*, 749–754; *Inorg. Chem.* **1974**, *13*, 1086–1090. (c) Wilson, F. C.; Shoemaker, D. P. *Naturwissenschaften* **1956**, *43*, 57–58. (d) See also: Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192–197.

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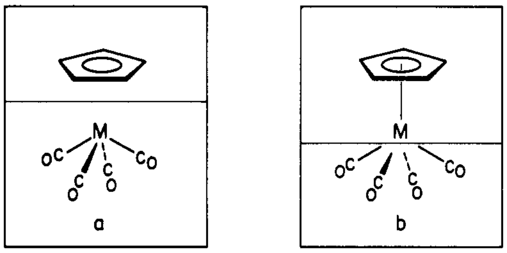
In the present article we describe the basic features of the electronic structure of the piano-stool complexes, their geometry, and some aspects of their reactivity. The analysis relies on molecular orbital calculations of the extended Hückel type with parameters detailed in the Appendix, supported by symmetry arguments.

## $CpM(CO)_4$

$CpML_4$ complexes with four identical L groups are a convenient starting point. For L = CO, M = V, Nb, Ta, these are indeed known molecules. The crystal structure of $CpV(CO)_4$ has been published,[2a] and some structural information is available for $CpNb(CO)_4$.[2b] The complexes possess an almost perfect piano-stool geometry. The Cp ring is $\eta^5$ and is disordered in the case of V in the solid state.[2a] The OC–M–Ct (*C*en*t*er of cyclopentadienyl) angle $\alpha$ is 119.5° for M = V, 121.7° for M = Nb. The highest possible symmetry for the entire complex is $C_s$, yet the $M(CO)_4$ fragment is practically of $C_{4v}$ symmetry.

A fragment analysis of the bonding, an approach we have found useful,[7] can be made in two ways. Either we interact Cp with $V(CO)_4$, **2a**, or CpV with four carbonyls, **2b**.



**2**

There are advantages to each—the former allows us to discuss the coordination of the Cp ring and barriers to internal rotation; the latter makes clear the role of the carbonyls and prepares the way for the analysis of other ligands. So both partitioning schemes will be implemented. A similar analysis, in the context of interpreting the photoelectron spectra of $CpML_4$ complexes, has been published by J. C. Green and co-workers.[8]

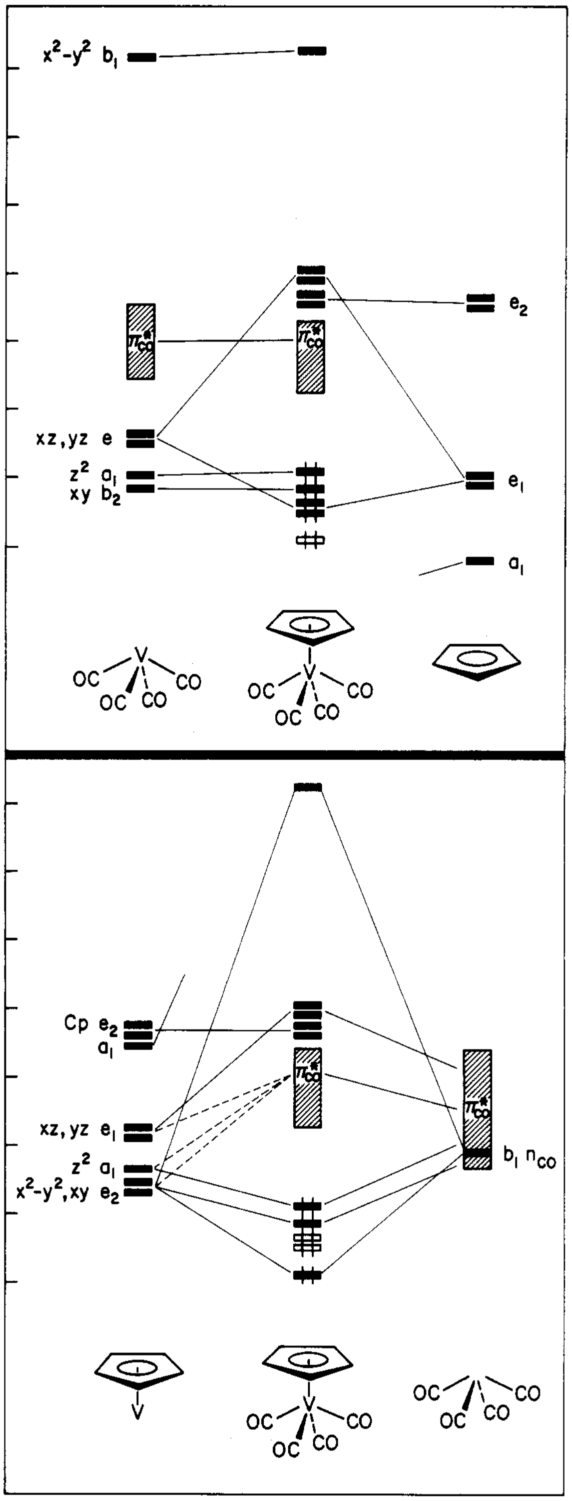


**Figure 1.** Two ways of forming the orbitals of $CpV(CO)_4$. The lined block represents a group of carbonyl $\pi^*$ orbitals. The level bars not filled in represent orbitals of the composite molecule whose parentage is not in those fragment orbitals shown. For each case the origin of those levels may be deduced by inspecting the other interaction diagram. Dashed lines imply weak contributions.

The orbitals of the fragments involved (Figure 1), MCp, $M(CO)_4$, are well-known.[9] MCp has a $t_{2g}$ set below, $a_1$ +

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(5) $CpM(CO)_2LL'$: (a) Bush, M. A.; Hardy, A. D. V.; Manojlovic-Muir, Lj.; Sim, G. A. *J. Chem. Soc. A* **1971**, 1003–1009. (b) Reisner, G. M.; Bernal, I.; Brunner, H.; Muschiol, M.; Stebrecht, B. *J. Chem. Soc., Chem. Commun.* **1978**, 691–692. (c) Aleksandrov, G. G.; Struchkov, Yu. T.; Makarov, Yu. V. *Zh. Strukt. Khim.* **1973**, *14*, 98–102. (d) Ginzburg, A. G.; Bokyi, N. G.; Yanovsky, A. I.; Struchkov, Yu. T.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1977**, *136*, 45–55. (e) Smith, R. A.; Bennett, M. J. *Acta Crystallogr., Sect. B* **1977**, *33*, 1113–1117, 1118–1122. (f) Reisner, M. G.; Bernal, I.; Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1977**, *137*, 329–347. (g) Churchill, M. R.; Chang, S. W.-Y. *Inorg. Chem.* **1975**, *14*, 98–105. (h) Sim, G. A.; Sime, J. G.; Woodhouse, D. I.; Knox, G. R. *Acta Crystallogr., Sect. B* **1979**, *35*, 2403–2406, 2406–2408. (i) Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1061–1067. Chan, L. Y. Y.; Dean, W. K.; Graham, W. A. G. *Ibid.* **1977**, *16*, 1067–1071. (j) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30–32. (k) Back, W.; Danzer, W.; Liu, A. T.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 495–496. (l) Brotherton, P. D.; Raston, C. L.; White, A. H.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1193–1195. (m) Bernal, I.; LaPlaca, S. J.; Korp, J.; Brunner, H.; Herrmann, W. A. *Inorg. Chem.* **1978**, *17*, 382–388. (n) Churchill, M. R.; Fennessey, J. P. *Ibid.* **1968**, *7*, 953–959. (o) Fenn, R. H.; Cross, J. H. *J. Chem. Soc. A* **1971**, 3312. (p) Hardy, A. D. U.; Sim., G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1900–1903. (q) Jones, G. A.; Guggenberger, L. J. *Acta Crystallogr., Sect. B* **1975**, *31*, 900–902. (r) Knox, J. R.; Prout, C. K. *Ibid.* **1969**, *25*, 1952–1958. (s) LaPlaca, S. J.; Bernal, I.; Brunner, H.; Hermann, W. A. *Angew. Chem.* **1975**, *87*, 379. (t) An interesting $(C_5Me_5)Ta(CPh)Cl(PMe_3)_2$ structure is reported by: Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171–176. (u) Rehder, D.; Müller, I.; Kopf, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1013–1017.

(6) The exceptions known to us include the following. $CpTiX_2(dtc)$: Coutts, R. S. P.; Waites, P. C. *J. Organomet. Chem.* **1975**, *84*, 47–52. Various 14 electron Ta alkyl complexes: Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.

(7) Hoffmann, R. *Science (Washington, D.C.)* **1981**, *211*, 995–1002, and references therein.

(8) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37–112. Green, J. C.; Jackson, S. E. *J. Chem. Soc., Dalton Trans.* **1976**, 1698–1702.

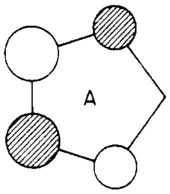
$e_2$ in the local $C_{5v}$ symmetry, and at higher energy three delocalized combinations of $a_1 + e_1$ symmetry corresponding to three hybrids pointing away from the Cp. $M(CO)_4$, slightly pyramidal, has four mainly d orbitals at low energy, $a_1 + b_2 + e$ in local $C_{4v}$ symmetry, and one $x^2 - y^2$, $b_1$, much higher. The local symmetry is high, but the total symmetry of the molecule is low. As the composite molecule is assembled it is useful to think of the axial pseudosymmetry, for this reveals the strength of the various interactions. The correlations among $C_{5v}$, $C_{4v}$, and axial pseudosymmetry are obvious:

| $C_{5v}$ | axial pseudosymmetry | $C_{4v}$ |
|---|---|---|
| $a_1$ | $\sigma$ | $a_1$ |
| $e_1$ | $\pi$ | e |
| $e_2$ | $\delta$ | $b_1,b_2$ |

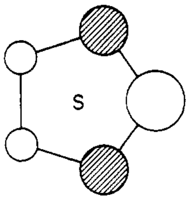
Consider first fragmentation **2a**. The binding of $ML_4$ with Cp follows the typical pattern of cyclopentadienyl complexes. There is strong $\pi$ bonding between $ML_4$ $\pi$-$(xz,yz)$ and Cp $\pi(e_1)$. This destabilizes the metal $xz,yz$ set and effectively sets the hallmark of electronic seven-coordination, only two low-lying orbitals ($z^2$ and $xy$). One might have thought the $z^2$ would be destabilized by the cyclopentadienyl $a_1$ in-phase $\pi$ combination. But it is not—the $\pi$-orbital lobes probe the region of the $z^2$ nodal surface. $\delta$-type interactions with Cp $e_2$ are small.

In the internal rotation around the P–M axis an undistorted fourfold rotor is pitted against a fivefold one. The resulting 20-fold barrier cannot be large. In our calculations it is less than 1 cal/mol.[10a] Crystal-site symmetries will, of course, provide sufficient packing asymmetries so as to increase this barrier, but we doubt if it will ever exceed a couple of kcal/mol in the crystal. It is thus no wonder that the Cp ring in the Cp $V(CO)_4$ structure is disordered.[2a]

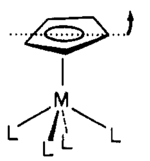
In many piano-stool complexes a slight tilting of the Cp ring from a plane perpendicular to the Ct–M axis is observed.[3i] We find a source for the tilting only in the $\delta$ interactions. **3** and **4** show the two components of the Cp $e_2$ set, chosen as symmetric (S) or antisymmetric (A) with respect to the horizontal mirror plane. One of these interacts with the single occupied $ML_4$ $\delta$-type orbital, $b_2$. Which $e_2$ component overlaps with $b_2$ depends on the $ML_4$–Cp orientation. Let us call **5**, where one carbon of the Cp is directly above a carbonyl "eclipsed", and **6**, 45° (but readily also ±9°, ±27° ...) of torsion away from it, "staggered". In **5** the interaction is between $b_2$ and A; in **6** it is between $b_2$ and S. Since a two-electron binding interaction is under discussion, the molecule will seek to maximize overlap. This can be achieved by a tilt in the direction shown in **5** and **6**, not that the effect is expected to be large, for the primary bonding to the Cp is through $\sigma$ and $\pi$ interactions. In $CpV(CO)_4$ we calculate a tipping of the ring by 0.8° for either conformation, in the expected direction.



**3**

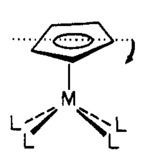


**4**



eclipsed

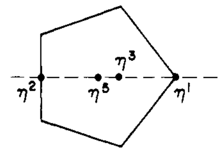
**5**



staggered

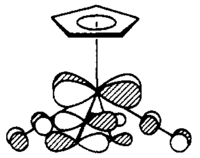
**6**

How much energy does it cost for the $V(CO)_4$ to shift away from pentahapto coordination? An analysis along the lines of our previous study of haptotropic shifts[10b] shows that maximum binding is, as expected, available at the $\eta^5$ position (see **7**). It costs 0.38 eV to slip off to $\eta^3$, 0.98 eV to $\eta^2$, and 1.22 eV to $\eta^1$. No adjustment in $ML_4$ rotor geometry with slipping was allowed.

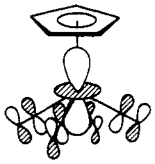


**7**

Let us now return to the other fragmentation mode, **2b**, CpM + 4L, in Figure 1. The carbonyl lone pairs are of $a_1 + b_1 + e$ symmetry, and their total of eight $\pi^*$ orbitals transform as $a_1 + a_2 + b_1 + b_2 + 2e$. Only one of the carbonyl lone pairs, the highest lying $b_1$ combination, is shown at right in Figure 1, bottom. The other, lower-lying, combinations are not drawn. The lone pair e combination interacts with CpM $xz$, $yz$, and $a_1$ hybrid, and the $b_1$ with one component of the $e_2$ set. So one forms four M–CO $\sigma$ bonds. The two remaining primarily metal d orbitals, $z^2$ and $xy$, are stabilized by $\pi$ bonding with the carbonyls. This is shown schematically in **8** and **9**. and since these orbitals are important in the sequel, more precisely in contour diagram form in Figure 2. Note that the $\pi$ bonding in the $z^2$ oribtal is achieved only as the Ct–M–CO angle departs from 90°. This $\pi$ bonding is partially responsible for the pyramidalization of the four legs of the stool.



**8**



**9**

Another molecular orbital calculation on $CpML_4$ and $CpML_3L'$ complexes is reported by Schmidt and Rehder.[11]

## The 3:3:1 or Capped Trigonal Bipyramid Alternative

This is another high symmetry possiblity for $CpML_4$ structures, one that appears[12] not to be made use of in

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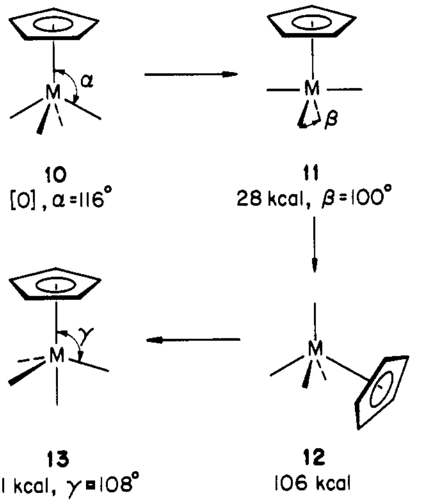
(9) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. (b) Elian, M.; Chen, M. M.-L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148–1155. (c) Burdett, J. K. "Molecular Shapes"; Wiley-Interscience: New York, 1980.

(10) (a) For a general analysis of rotational barriers in polyenyl and cyclopolyenyl–$ML_4$ complexes, see: Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812–3821. (b) Nguyen, Trong Anh; Elian, M.; Hoffmann, R. *Ibid.* **1978**, *100*, 110–116.

(11) Schmidt, H.; Rehder, D. *Transition Met. Chem.* (*Weinheim, Ger.*) **1980**, *5*, 214–220.

ground-state structures. It consists of a $C_{3v}$ LML$_3$′ fragment coupled to a Cp ring. One way to reach this structure is to enter the pseudo-five-coordination mode of thinking and to consider the Berry pseudorotation[13] sequence **10** → **11** → **12** → **13**. **13** is the structure we have in mind—a Cp occupying the axial site of a trigonal bipyramid. For three molecules in this sequence some angular optimzation was attempted. The optimum angles and relative energies are shown below the structures. Least justice was done to the low-symmetry structure **12**, where we assumed that all axial–V-basal ligand (Ct for cyclopentadienyl) angles were 116°.



**10**
[0], α=116°

**11**
28 kcal, β=100°

**12**
106 kcal

**13**
21 kcal, γ=108°

The piano-stool structure **1** (or **10**), electronically a 3:4 seven-coordinate molecule, is the most stable point on this piece of a pseudorotation surface. Next in energy, and apparently caught in its own local well, is **13**, the Cp-capped trigonal bipyramid. From an electronic point of view, this is a 3:3:1 seven-coordinate molecule, a capped octahedron, or capped trigonal prism.

In our previous theoretical analysis of seven-coordination[14] we found ≤7 kcal/mol separating all the possible polytopes of a d$^4$ M(CO)$_7$. It is natural that when three carbonyls are replaced by a cyclopentadienyl that the situation will change. First, seven-coordinate molecules are inherently in steric difficulties, and the equilibrium geometries are very likely to be influenced by a delicate balance of steric effects.[14,15] Second, there are electronic substituent site preferences which will come into play when three good acceptors are removed.

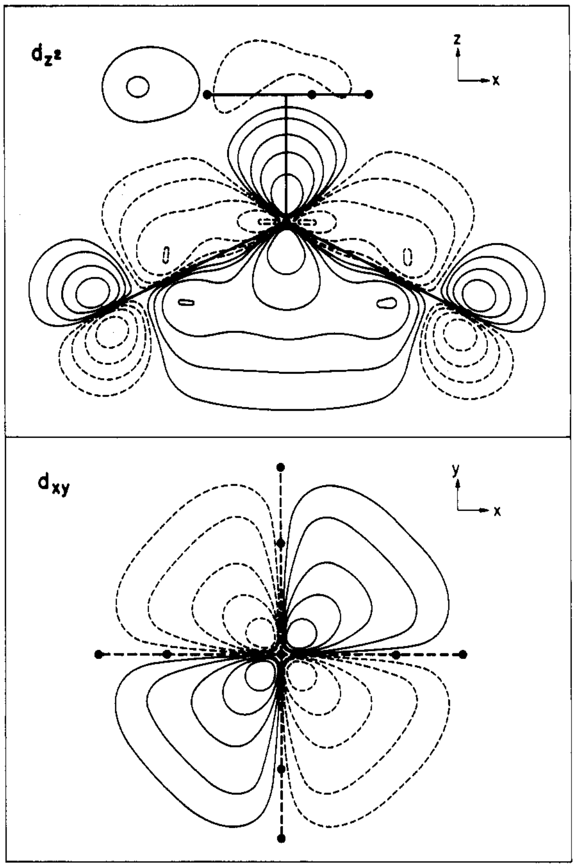


**Figure 2.** The two occupied d type orbitals of CpV(CO)$_4$. The $z^2$ is shown in the $xz$ plane, the $xy$ in the $xy$ plane. The contour values of $\psi$ are ±0.2, 0.1, 0.055, 0.025, and 0.01.

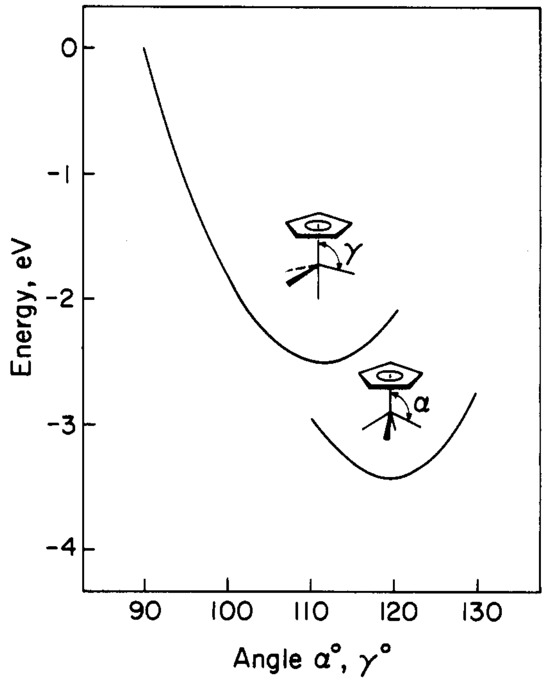


**Figure 3.** Energies of 3:3:1 and piano-stool geometries of CpVH$_4$$^{4-}$. The energy-scale markings are in eV relative to an arbitrary energy zero.

It is easy to see how the steric and electronic factors could so conspire as to destabilize **11**–**13** relative to **10**. But let us examine **13** in more detail. It appears to be in a local energy minimum with respect to Berry pseudorotations. Those are not the only interconversion modes imaginable, so it may still be that there is a pathway all downhill in energy from **13** to **1**. But we think it is worthwhile to think about stabilizing this so-for-unobserved geometrical type.

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(12) There is a dispute in the literature concerning the structure of CpV(CO)$_3$H$^-$: Puttfarcken and Rehder (Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1980**, *185*, 219–230) suggest a 3:3:1 structure while Kinney et al. (Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635–637, 7902–7915), who first reported the synthesis and properties of this anion, argue for a piano-stool structure.

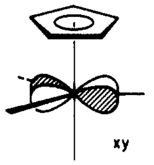
(13) In the context of transformations of CpML$_4$ complexes, the pseudorotation possibility has been suggested and studied in detail before: (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1969**, *91*, 1550–1551. (b) Faller, J. W.; Anderson, A. S.; Chen, C.-C. *Chem. Commun.* **1969**, 719–720. *J. Organomet. Chem.* **1969**, *17*, P7–P9. (c) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–5860. (d) Faller, J. W.; Anderson, A. S.; Jakubowski, A. *J. Organomet. Chem.* **1971**, *21*, C47–52. (e) Kalck, P., Poilblanc, R. *Ibid.* **1969**, *19*, 115–121. Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *Ibid.* **1970**, *24*, 445–452. (f) Pfeiffer, E.; Vrieze, K.; McCleverty, J. A. *Ibid.* **1979**, *174*, 183–189. (g) Brunner, H.; Herrmann, W. A. *Chem. Ber.* **1973**, *106*, 632–639; *J. Organomet. Chem.* **1974**, *74*, 423–429. (h) Wright, G.; Mawby, R. J. *Ibid.* **1971**, *29*, C29–30.

(14) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511–522.

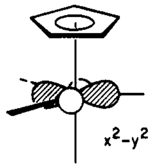
(15) (a) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67. (b) Kepert, D. L. *Ibid.* **1979**, *25*, 41–144.

First let us try to dissect out the steric and electronic differences between 1 and 13. We have already noted the optimized geometries for $CpV(CO)_4$ alternatives. The angle $180° - \gamma$ between the axial and equatorial carbonyls is small, 72°, and this might be taken as a sign of steric trouble in that structure—the equatorial carbonyls trying to escape close contacts with the cyclopentadienyl ring but bumping into the axial carbonyl. If that is so, the steric strictures might be relieved for a smaller ligand. Figure 3 shows how the total strictures varies with indicated angle in the piano-stool and 3:3:1 structures for a model $CpVH_4^{4-}$. The optimum $\alpha$ and $\gamma$ are both greater than in the carbonyl case. This is consistent with the smaller bulk of the hydride. But the difference of 21 kcal/mol between the optimum structures is about the same, making us think that the differential is primarily electronic.

The electronic structure of the 3:3:1 form can be obtained again in two ways, from CpM + 4L or from $C_{3v}$ $ML_4$ + Cp. We will not present the analyses in detail here. Once again there is a nice closed-shell structure for a $d^4$ complex with a substantial gap between the filled and unfilled levels. The two highest occupied levels are of $\delta$ pseudosymmetry, concentrated metal $xy$ and $x^2 - y^2$. These orbitals are drawn in 14 and 15.

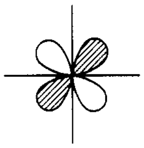


**14**

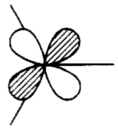


**15**

The $x^2 - y^2$ orbital of the 3:3:1 structure is at about the same energy as the $z^2$ of the piano stool, but the $xy$ orbitals of the two geometries differ in energy, that of the piano stool being more stable. Here then is the electronic difference between the two structures. The two orbitals are drawn schematically in a top view along the Cp–M axis in 16 and 17. They are the same orbital, but the ligand field around it differs. In 16 the equatorial ligands lie in the nodal planes of $xy$, and it is not affected by them. In 17 the ligand set interacts with $xy$. The ligand orbital that does the mixing is one component of the e set formed from the ligand $\sigma$ orbitals. The e set of a $\pi$ pseudosymmetry, the $xy$ of $\delta$ pseudosymmetry. So the interaction is not optimal, but it is sufficient to destablize the $xy$ in the 3:3:1 form by ~0.5 eV and so produce the preference for the piano stool.

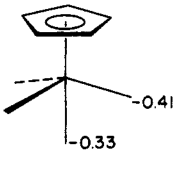


**16**



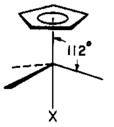
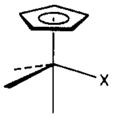
**17**

What can one do to overcome this inherent bias for the piano-stool geometry? The charge distribution on the hydrides in $CpVH_4^{4-}$ is given in 18. The axial ligand is more positive. This implies that a less electronegative ligand, a good $\sigma$ donor, will enter preferentially there. This was confirmed by calculations changing the Coulomb integral of the ligand in question, as the first entries in Table I show.



**18**

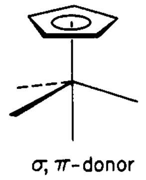
Table I. Relative Energies of Some Substituted 3:3:1 Structures

| |  |  |
|---|---|---|
| substituent | relative energy,[a] kcal/mol | relative energy,[a] kcal/mol |
| H | 21 | 21 |
| "$\sigma$ acceptor"[b] | 25 | 21 |
| "$\sigma$ donor"[c] | 18 | 22 |
| Cl | 46 | 22 |
| CO | 33 | 19 |

[a] Relative to piano-stool structure with $\alpha$ = 120°. [b] Hydrogen orbital with $H_{ii}$ −15.0, 1.4 eV lower than normal H. [c] Hydrogen orbital with $H_{ii}$ −12.2, 1.4 eV higher than normal H.

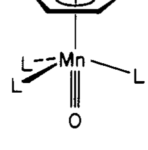
An argument for a $\pi$ effect is also easily made. The $xy$ and $z^2$ orbitals in the piano-stool geometry are coupled in $\pi$ interactions with every leg of the stool. This was made explicit in 8 and 9. The 3:3:1 geometry is different. The unique axial ligand cannot engage in $\pi$ bonding with the $\delta$ pseudosymmetry filled d orbitals on the metal. Thus if there are any $\pi$ donors in the metal–ligand set they should enter that site and decrease the preference for the piano-stool structure.

The substituent pattern then that is most favorable for the 3:3:1 geometry is a single substituent that is both a good $\sigma$ donor and a good $\pi$ donor, 19. Table I reveals, however, that an axial halide actually destabilizes the 3:3:1 structure. We can trace the problem to a steric source—the axial site is uncommonly congested. The computed result, that Cl has a greater resistance to being placed into the axial position, agrees with the pattern of activation energies observed by Faller and co-workers.[13]

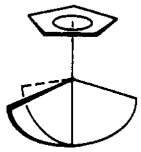


**19**

We would not give up on trying to design a stable 3:1:1 structure. An axial oxo or thio ligand, 20, is an interesting possibility. Steric problems might be solved by a tripod ligand, 21, though the three arms had better be small.



**20**



**21**

A perceptive referee, noting the tracing of the barrier to the $xy$ and $x^2 - y^2$ orbitals of $\delta$ symmetry, has suggested that the 3:3:1 structure might be stabilized by a capping

**Table II. Some Optimized Angular Parameters of the Molecular Geometry of $CpMo(CO)_3CH_3$ in Conformation 22**

| angle[a] | computed angle, deg | observed angle,[b] deg |
|---|---|---|
| Ct-Mo-$C_1$ | 105 | 110 |
| Ct-Mo-$C_4$ | 110 | 118 |
| Ct-Mo-$C_2$($C_3$) | 124 | 127 |
| Mo-Ct-$C_5$ | 92 | 92 |
| between planes Ct-Mo-$C_1$ and Ct-Mo-$C_2C_3$ | 84 | 84 |

[a] The atom numbering follows structure 22. [b] Reference 31.

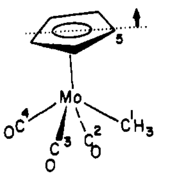
ligand with lower energy vacant orbitals of δ symmetry, e.g., $\eta^6$-arene or $\eta^7$-cycloheptatrienyl. A model calculation on $(C_7H_7)VH_4^{2-}$ indeed confirms this. The 21 kcal/mol difference of the Cp case is reduced to 20 kcal/mol if the $C_7H_7$ ring is moved down so the C–V distance is the same as in the $C_5H_5$ complex and 15 kcal/mol if the $C_7H_7$ ring is kept at the same "elevation" as the $C_5H_5$.

## $CpM(CO)_3L$ and the Conformational Preferences of π-Bonded Ligands

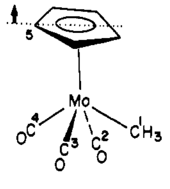
For this category many crystal structures are available. Some are for relatively simple ligands, L = $C_2H_5$, $C_3H_7$, $CH_3$ ($\eta^5$-azulene instead of Cp), $CH_2COOH$, Cl, I ($\eta^5$-indenyl instead of Cp), ZnBr, HgCl, $C_6H_5$, $Ga(CH_3)_2$, $AuPPh_3$.[3] The last three are with W, the others Mo. Several structures with more complex L, most with Mo as the metal, have been published.[3] A particularly interesting class are the $[CpM(CO)_3]_2$ dimers with M = Cr, Mo, W.[4]

The geometrical facts concerning these molecules are simple.[1,3] The $CpM(CO)_3L$ moiety generally possesses an approximate mirror plane through M. The usual value of the trans OC–M–L angle is 125–133° (higher border favored), trans OC–M–CO is 105–117° (lower value favored), and cis OC–M–CO is 74–80° (lower border favored). The Cp ring is tilted by several degrees. The best π-acceptor ligand seems to be beneath the middle of a Cp CC bond.[3a,c,g]

To see how the extended Hückel calculation would do at reproducing these geometrical distortions, we took $CpMo(CO)_3CH_3$ and optimized five angular degrees of freedom. The optimization was repeated for two conformations, 22 and 23, with distances taken from the structure of $CpMo(CO)_3(C_2H_5)$.[3g] The results are shown in Table II.



22



23

Agreement between computed and observed structures is reasonably good. Our calculations favor conformation 22 over 23 by 0.4 kcal/mol, and this only when all five angular parameters are allowed to relax. The barrier is now no longer 20-fold but 5-fold. It remains small. This is in agreement with the observed fluxionality of the Cp ring in NMR experiments for any $CpM(CO)_2LL'$ complex.[1]

Note that the two planes of the $M(CO)_3L$ fragment in $CpM(CO)_3CH_3$ become distinguished from each other. Thus the trans OC–M–$CH_3$ angle (calcd) is 135°, while the trans OC–M–CO angle is 112°. This kind of asymmetry, which could be viewed as an excursion along a Berry pseudorotation coordinate, is typical of the known structures.

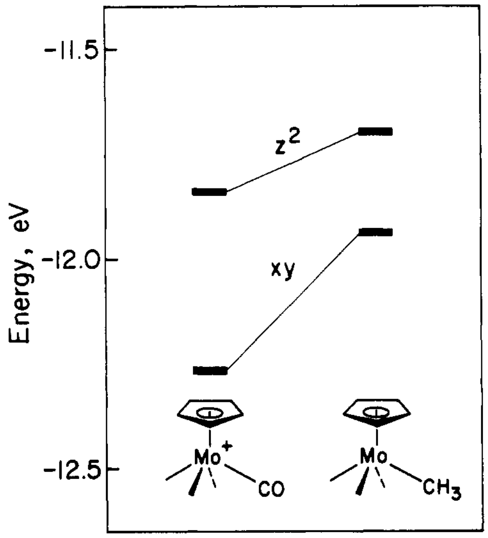
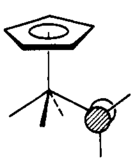


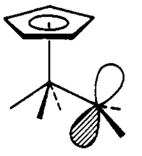
**Figure 4.** A comparison of the two d block levels of piano-stool geometries, each optimized, of $CpMo(CO)_3(CH)_3$ and $CpMo(CO)_4^+$.

Figure 4 shows what happens to the two occupied d block orbitals of $CpMo(CO)_3CH_3$ relative to $CpMo(CO)_4^+$. Both $z^2$ and $xy$ are destabilized upon substitution of CO by methyl. This is what one would expect given the loss of one carbonyl's π-acceptor character. Note that $xy$ is more destabilized than $z^2$, a sign of the better donor ability of $xy$. This will be important in determining the orientation of single-faced π donors or acceptors. Incidentally the published photoelectron spectra of $CpM(CO)_3(CH_3)$, M = Mo, W, agree that the two d levels are close to each other in energy.[8]

The orientation of single-faced π-donor or -acceptor substituents is always an interesting problem. The conformational question is posed by structural alternatives 24 and 25 for a carbene ligand. It can be asked for any single faced π donor or acceptor, e.g., ethylene, acetylene, amide, carbonyl, etc. Known structures in this category include L = Ph,[3q] RC=C=O,[16] RC=O,[5n] PhCOEt.[5i] Some Mo carbene complexes have also come from the recent work or Brockhart.[17]



24



25

In 24 the unique acceptor orbital will interact with $xy$; in 25 it will react with $z^2$. The interaction with $xy$ is just better, as measured by the fragment overlaps in a reasonable geometry, $\langle xy|p \text{ in } 24\rangle = 0.138$, $\langle z^2|p \text{ in } 25\rangle = 0.102$. Why is there such a differential? There is a simple trigonometric effect at work. If the Ct–Mo–$CH_2$ angle is θ, then the overlap of a probe p orbital with $xy$ is maximal at θ = 90° and goes as sin θ. The corresponding overlap with $z^2$ goes as sin 2θ and is maximal at θ = 45 and 135°.

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[16] Kreissl, F. R.; Frank, A.; Schubert, V.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632.

[17] Brookhart, M., private communication.

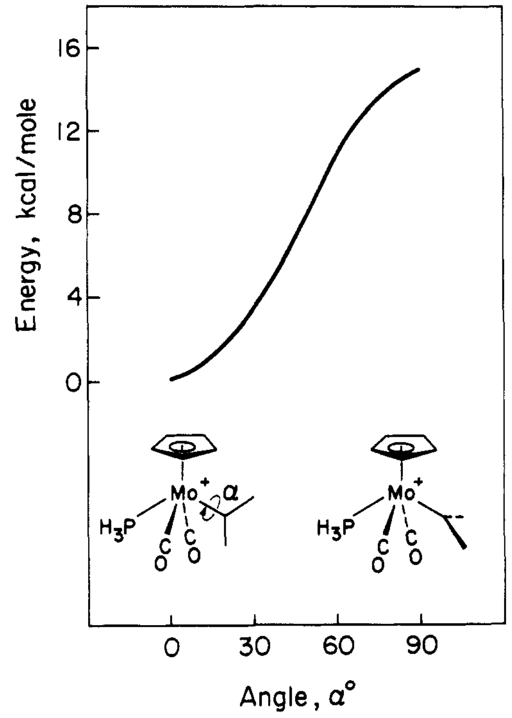
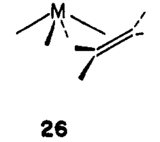


**Figure 5.** Computed energy, as a function of carbene rotation, of $CpMo(PH_3)(CO)_2CH_2^+$.

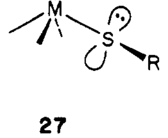
$\theta$ for the carbene structure is $\sim 114°$,[5i] so the $z^2$ overlap is diminished more from its optimal value than the $xy$ overlap.

A potential energy curve computed for $CpMo(CO)_2(PH_3)(CH_2)^+$ with a geometry based on the known $CpMo(CO)_2(GePh_3)(C(OEt)Ph)$ structure[5i] is shown in Figure 5. Conformation **24** is preferred by some 15 kcal/mol. The two carbene hydrogens in $CpMo(CO)_2(PR_3)(CH_2)^+$ are equivalent on the NMR time scale, down to −100 °C.[17] But two distinct hydrogen environments are detected at this temperature for the W analogue. Thus the "upright" equilibrium conformation **24** is confirmed. The barrier to rotation in the W complex is estimated at ca. 10 kcal/mol, and the Mo barrier must be substantially smaller.[17]

The carbene complex $CpMo(CO)_2(GePh_3)(C(OEt)Ph)$ does have conformation **24** in the solid state.[5i] Related RCO and RCCO structures[5n,16] have a similar orientation of the acceptor. The extension of conformational predictions to other $\pi$ acceptors is obvious—for instance, olefins, and acetylenes should prefer **26** for electronic reasons, while an SR or a $PR_2$ should avoid interaction with $xy$, as in **27**. All of this is subject to the strong steric constraints that must be operative in this structural type. It may well be an olefin or a thiol simply cannot follow its electronic inclinations.



**26**

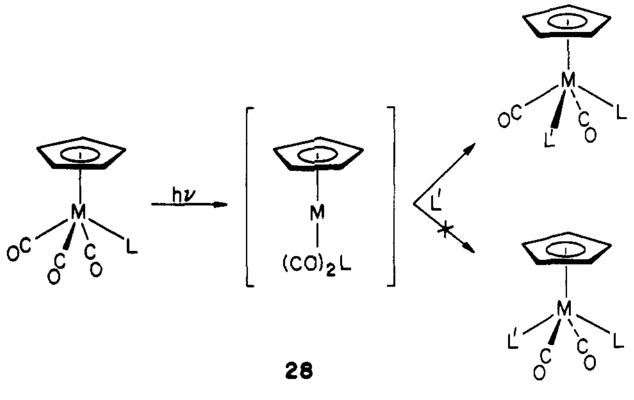


**27**

The electronic structure of $CpML_3(CH_2)$ and related complexes has also been studied by P. Hofmann.[18a]

## One Aspect of the Reactivity of Piano-Stool Complexes

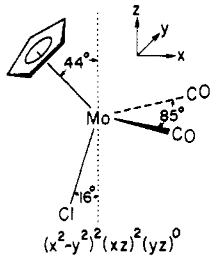
The $CpM(CO)_3L$ complexes, especially those with M = Mo, are quite reactive. The carbonyl insertion reaction and many substitution reactions have been explored.[1,19] An interesting point of difference between the thermal and photochemical substitutions[19,20] is that the latter occur stereospecifically to give *cis*-$CpMo(CO)_2LL'$, **28**.[20] The reason for this may be electronic.



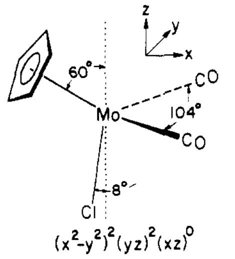
**28**

We had already noted that there are several low-lying vacant orbitals in these piano-stool complexes which are M–CO antibonding. It makes sense then that a carbonyl is dissociated in the rate-determining step of the reaction, and this has been established.[20] The resulting $CpM(CO)LL'$ is a 16-electron six-coordinate complex. Such complexes with two cis $\pi$ acceptors should depart from pseudooctahedral geometry, a situation we have discussed in some detail elsewhere.[21] A double minimum should arise, the two minima corresponding to different occupations of the d$\pi$ levels. In one minimum the OC–M–CO angle opens from 90° in the other it closes.

Taking $CpMo(CO)_2Cl$ as a model we have found both these minima. The partially optimized geometries may be seen in **29** and **30**. In our calculations the carbonyl closed isomer, **29**, is more stable by 8.7 kcal/mol. The barrier to rearrangement from **30** to **29** is small, 0.2 kcal/mol, but nonvanishing. The reasons for the isomer energy ordering may be traced along the lines of argument we presented earlier,[21] but we will not do so here.



**29**



**30**

Suppose one finds oneself in the lower energy minimum **29**. A base should attack this coordinatively unsaturated complex in a frontier-controlled manner. The LUMO of the complex is $yz$, hybridized to some extent with $xy$ and

---

(18) (a) Hofmann, P., private communication. (b) Hofmann, P. *Angew. Chem.* **1977**, *89*, 551–553.

(19) (a) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294–299. (b) Bolton, E. S.; Dekker, M.; Knox, G. R.; Robertson, C. G. *Chem. Ind. (London)* **1969**, 327–328. (c) Manning, A. R. *J. Chem. Soc. A* **1967**, 1984–1987. (d) Craig, P. J.; Green, M. *Ibid.* **1968**, 1978–1981. (e) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055–2062. *Ibid.* **1980**, *102*, 2698–2703. (f) Su, S. R.; Wojcicki, A. *Inorg. Chem.* **1975**, *14*, 89–98.

(20) Alway, D. G.; Barnett, K. W. *Ibid.* **1980**, *19*, 1533–1543.

(21) Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*.

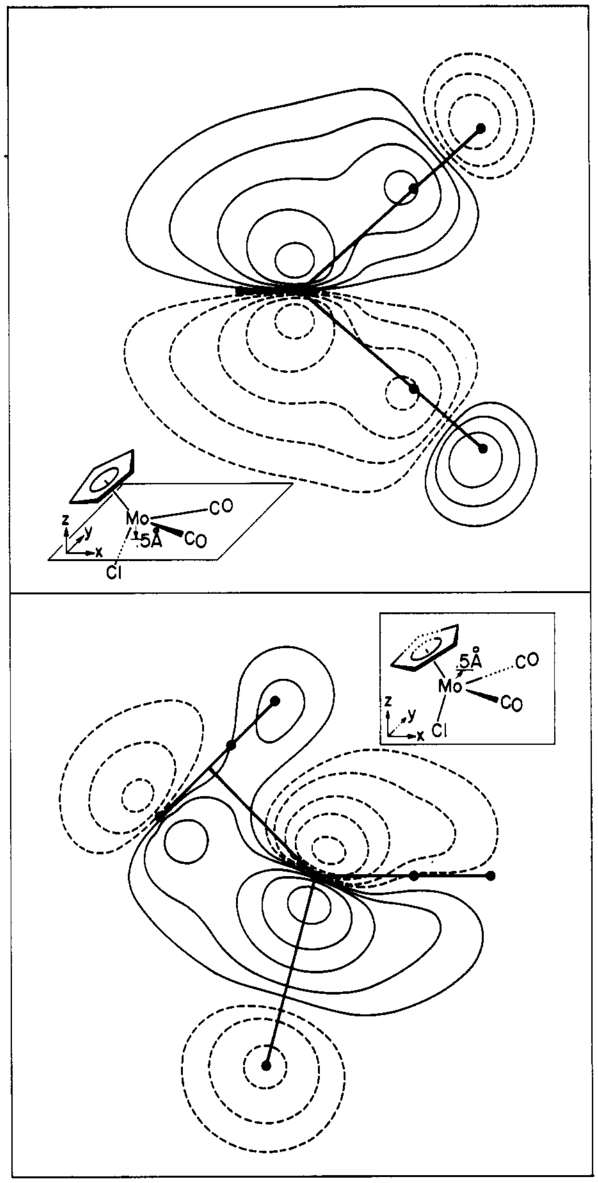


**Figure 6.** Two sections of the LUMO of the lower energy minimum of CpMo(CO)$_2$Cl, structure **29**. The contour values of $\psi$ are the same as in Figure 2.

$y$. Two cuts through this LUMO are shown in Figure 6. Use of this orbital by an approaching base affords, after some geometrical relaxation, the cis isomer.

It should be mentioned here that in general coordinatively unsaturated 16-electron CpML$_{n-1}$ complexes derived from 18-electron CpML$_n$ by loss of a ligand should "retain a memory" of their parentage and not easily relax to more symmetrical structures. This phenomenon has been traced in detail by P. Hofmann for the 16-electron CpML$_2$ case.[18b]

## CpM(CO)$_2$LL′

This is a rich class of complexes, with extensive structural information available.[5] Geometrical (cis–trans) and optical[1,13,19,22] isomerism has been studied, as well as reactivity in insertion and substitution reactions.[13] The stereochemical nonrigidity and isomerization of CpM(CO)$_2$LL′ have been analyzed in detail by Faller and coworkers[13a-d] and others.[13e-h]. There is evidence at hand for an intramolecular mechanism.[12] The fewer carbonyls there are in the molecule, the easier the reaction. For example, the NMR coalescence temperature is greater than 100 °C for CpMo(CO)$_2$LCl but −62 °C for CpMo(CO)L$_2$Cl (L = PMePh$_2$).[13c]

Table III. Calculated Energies (kcal/mol) for Some CpMo(CO)$_2$PH$_3$X Structures

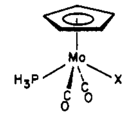
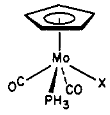
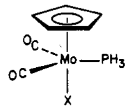
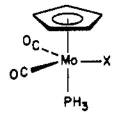
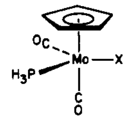
| | X = H | X = Cl |
|---|---|---|
|  | [0] | [0] |
|  | 4.3 | 2.6 |
|  | 15.4 | 34.3 |
|  | 30.8 | 37.4 |
|  | 31.6 | 29.1 |

Table IV. Parameters Used in EH Calculations

| orbital | $H_{ii}$, eV | $\zeta_1$ | $\zeta_2$ | $C_1{}^a$ | $C_2{}^a$ |
|---|---|---|---|---|---|
| V 3d | −11.00 | 4.75 | 1.70 | 0.4755 | 0.7052 |
| 4s | −8.81 | 1.30 | | | |
| 4p | −5.52 | 0.875 | | | |
| Mo 4d | −11.06 | 4.54 | 1.90 | 0.5899 | 0.5899 |
| 5s | −8.77 | 1.96 | | | |
| 5p | −5.60 | 1.90 | | | |
| Cl 3s | −30.00 | 2.033 | | | |
| 3p | −15.00 | 2.033 | | | |
| P 3s | −18.60 | 1.60 | | | |
| 3p | −14.00 | 1.60 | | | |
| C 2s | −21.40 | 1.625 | | | |
| 2p | −11.40 | 1.625 | | | |
| O 2s | −32.40 | 1.95 | | | |
| 2p | −14.80 | 1.95 | | | |
| H 1s | −13.60 | 1.30 | | | |

[a] Coefficients in double-$\zeta$ expansion.

Replacement of acceptors by donors and large groups by small ones should lessen the preference for the pseudo-square-pyramidal over the pseudo-trigonal-bipyramidal, or 3:3:1, structure. That follows from the general considerations outlined above. We thought we could add something to the discussion by detailed calculations on CpMo(CO)$_2$(PH$_3$)X, X = M, Cl. Idealized geometries were constructed partly from experimental data (for the piano-stool structures) and partly from calculations of CpM(CO)$_3$X (for a hypothetical 3:3:1 transition state).[23] Table III shows the calculated energies.

The piano-stool geometries are preferred, as expected. Within this structural type the trans isomer is more stable, by a little. In the 3:3:1 structure the placement of X apical is preferred, which we also anticipated. The calculated activation energies for cis–trans isomerization, assuming

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[23] The swing angles from the M–Cp axis were assumed as follows: in the piano-stool geometry X = 108°, CO = 124°, PH$_3$ = 108°, in the 3:3:1 structure, 105° for all ligands.

the 3:3:1 structures are transition states, are somewhat high, though the correct ordering of H and Cl barriers is obtained. It could be that the approximate computational method is at fault. We suspect that more of the discrepancy stems from the fact that our idealized 3:3:1 structures are still far from the true transition state or intermediate structures. We have not optimized these geometries nor considered more asymmetric pseudo-seven-coordinate pathways. This remains a project for the future.

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## Appendix

Our calculations were of the extended Hückel type,[24] with "weighted" $H_{ij}$'s. The parameters are listed in Table IV. The $H_{ii}$ values of V and Mo were obtained by charge iterative calculations on $CpV(CO)_4$ (experimental geometry) and $CpMo(CO)_3CH_3$ (geometry of the ethyl complex).

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# Dehydrogenation of 1,3-Cyclohexadiene by $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. Preparation, Dynamic NMR, and X-ray Crystal Structure of $[\eta^3\text{-}CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$

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The coordinately unsaturated rhodium hydride dimer, $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, effected a dehydrogenation of 1,3-cyclohexadiene to benzene. This reaction was not catalytic; the other product was ($\eta^3$-cyclohexenyl)rhodium bis(triisopropyl phosphite). In attempts to follow the 1,3-cyclohexadiene reaction along a back-reaction sequence, the chemistry of $(\eta^6\text{-arene})Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ was examined. Reaction of the benzene complex with potassium triisopropoxyborohydride gave benzene and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. Reaction of the hexamethylbenzene complex with either methyllithium or potassium triisopropoxyborohydride gave ($\eta^3$-pentamethylbenzyl)rhodium bis(triisopropyl phosphite). The latter compound was crystallographically and spectroscopically defined. NMR studies established that this molecule exists in rapid equilibrium with an excited-state form proposed to be an ($\eta^5$-benzyl)rhodium structure.

## Introduction

Synthesis and chemistry of coordinately unsaturated polynuclear transition-metal complexes represent a major focus of our research. Previously, we have described the synthesis[2,3] and the structural features[2,4–6] of $[HRhL_2]_x$ clusters and have also demonstrated the high reactivity of these polynuclear compounds to catalytic olefin and alkyne hydrogenation reactions.[3,7–9] To date, the major set of clusters studied has been the phosphite complexes, $\{HRh[P(OR)_3]_2\}_x$, particularly the dimeric species $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.

Reactivity toward donor molecules under stoichiometric conditions was high for the coordinately unsaturated hydride $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.[10,11] Nevertheless, there was significant selectivity to this reactivity. For example, the dimeric hydride reacted with 1 equiv of carbon monoxide or an acetylene to form $(\mu\text{-}H)_2(\mu\text{-}CO)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$[10] and $(\mu\text{-}H)(\mu\text{-}CR{=}CHR)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$,[9] respectively. Simple donor molecules like phosphite elicited rapid cleavage of the dimeric form to generate the saturated mononuclear $HRhL_4$ species.[3] However, olefins reacted only very slowly, if at all, with the dimer.[12] Hydrogen oxidatively added to the dimer in an extremely fast reaction to form the triply bridged dimeric hydride.[13]

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[12] These reaction rates are comparable to the rate of decomposition of the dimer in solution. Rates were very low; reaction time of days were required. Reaction products were complex and included alkanes apparently generated from the isopropyl groups in the phosphite ligands.

[13] Olefins do react with this hydride to form alkanes and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$; reaction rates are extremely high.

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