Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

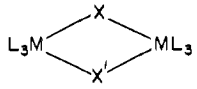
Ring Puckering and Metal–Metal Separations in One Class of Dibridged Binuclear Complexes

ALLAN R. PINHAS and ROALD HOFFMANN*

Received July 20, 1978

A recent structure of $Cp_2M_2(NO)_2$ and a comparison with other $Cp_2M_2(CO)_x(NO)_{2-x}$ structures showed that the two metal atoms and the bridging carbonyls or nitrosyls in nearly all cases lie in a single plane. However, the isolobal compound $Co_2(CO)_8$ and related structures with terminal carbonyls have the inner rhomboid puckered. The reasons for the presence or absence of the puckering deformation are traced to the slightly different symmetry properties of the frontier orbitals in the MCp or $M(CO)_3$ cases. Metal–metal bond-length differences with electron count are examined, leading to an apparent contradiction between the theory and the structural facts known for this series of compounds.

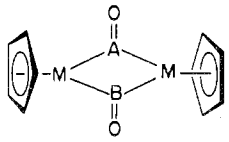
There are many dibridged binuclear complexes of type **1**,



1

with X and X′ = CO, NO, PR_2, NR_2, SR, OR, and halogen. These have proved a fertile source for experimental and theoretical studies of metal–metal interactions. In particular Dahl and co-workers have most effectively exploited bond-length changes upon oxidation or reduction to deduce the symmetry properties and bonding characteristics of the frontier molecular orbitals (MO's) of the molecules.[1]

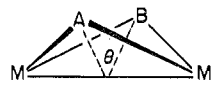
In some previous work we and others[2] have attempted to delineate the role of metal monomer geometrical preferences, the bonding opportunities offered by the bridging groups, and the direct metal–metal interactions in M_2L_6 complexes. The present work was motivated by an interesting structural observation made by Bernal and co-workers[3] in the course of a crystallographic study of $Cp_2Co_2(CO)(NO)$ and $Cp_2Co_2(NO)_2$. A comparison was made of the structures of these compounds with those previously determined for $Cp_2Fe_2(NO)_2$[4] and $Cp_2Co_2(CO)_2$.[5] These compounds all have the basic geometry **2**, and in fact three of them are isomorphic. Some geometrical parameters are compared in Table I.



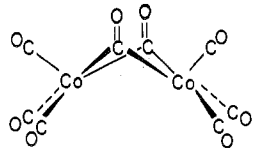
2

If an electron-counting formalism of Cp^- and NO^+ is adopted, the metal atoms have the configuration shown in the table. The 18-electron rule would imply a metal–metal double bond in the d^8–d^8 complex, a bond order of 1.5 in the d^8–d^9 complexes, and a single bond in the d^9–d^9 complexes. However, Bernal and co-workers noted that the metal–metal separation in the d^8–d^9 complexes is essentially the same as in the d^9–d^9 compounds[6] and the d^8–d^8 separation is only marginally shorter. This runs counter to the accepted notions of metal–metal bonding and the 18-electron rule and thus attracted our attention.

There is still another interesting aspect of these complexes. In all but one of the structures listed in Table I the inner MAMB rhomboid is planar; i.e., the dihedral angle between the M–A–M and M–B–M planes, θ, as defined in **3**, is 180° or close to it. The exception is $Cp_2Ni_2(CO)_2$ where both independent molecules in the asymmetric unit are puckered, with θ = 140 and 147°. If one makes the standard isolobal replacement of three carbonyls for a Cp^-, one realizes that the



3



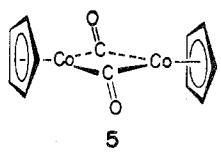
4

d^9–d^9 systems are analogous to $Co_2(CO)_8$. However, the inner rhomboid in $Co_2(CO)_8$, **4**, is not planar, but highly puckered, θ = 127°. Some of the many other complexes of type **1** are puckered and some are planar.[8] What influences the distortion of the inner rhomboid in these systems? We decided to probe this question at the same time as we analyzed the metal–metal bonding.

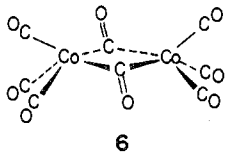
Inner-Ring Puckering

The variation in θ with d-electron count has been studied earlier by Burdett for $Fe_2(CO)_6(PR_2)_2$ complexes.[2b] A molecular orbital scheme was provided which gave puckering, its magnitude a function of R, for d^7–d^7 complexes and planarity, θ = 180°, for d^8–d^8 complexes. One might have thought that the MO scheme of Burdett could be taken over directly for the present problem, but unfortunately this is not so. As was pointed out by us earlier,[2a] the ordering of the metal orbitals depends critically on the nature of the bridging ligands. In particular it is expected to differ greatly from the donor, PR_2^-, to the π acceptor, CO or NO, case.

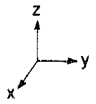
The variation in the MO schemes with the nature of the bridging ligand, the factors determining the puckering of the inner rhomboid, and the metal–metal distances are probed in this paper by means of extended-Hückel calculation. The parameters are given in the Appendix. The initial set of calculations is on $Cp_2Co_2(CO)_2^{x-}$ and $(CO)_6Co_2(CO)_2^{y-}$ with inner-ring geometries identical with that shown by one of the structures.[9] The initial geometries are shown schematically in **5** and **6**. The cyclopentadienly complexes have the rings



5



6



staggered in the observed structures. However, the barrier to Cp rotation cannot be high, and we have made them eclipsed so as to maintain the highest possible symmetry, C_{2v}, while bending. The flapping or puckering motion is studied by moving the bridging groups in the +z direction while keeping M–C distances constant.

0020-1669/79/1318-0654$01.00/0

Table I. Structural Parameters of Some $Cp_2M_2(AO)(BO)$ Complexes

molecule	config[a]	M-M, Å	M-A-M, deg	A-M-B, deg	ref
$Cp_2Fe_2(NO)_2$	d^8-d^8	2.326	82.3	97.7	4
$Cp_2Co_2(NO)$-(CO)	d^8-d^9	2.370	80.7	99.3	3
$Cp_2Co_2(CO)_2^-$	d^8-d^9	2.372	80.3	99.8	5
$Cp_2Co_2(NO)_2$	d^9-d^9	2.372	81.1	99.0	3
$Cp_2Ni_2(CO)_2$[b]	d^9-d^9	2.357	78.4	94.3	6
$(MeCp)_2Ni_2$-$(CO)_2$	d^9-d^9	2.390	79.7	100.3	6

[a] See text. [b] Average of two molecules in an asymmetric unit.

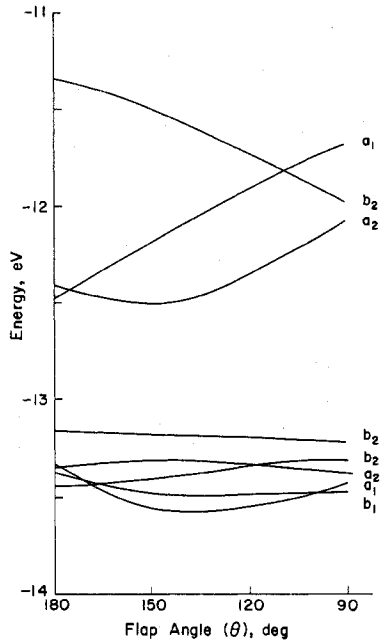


Figure 1. Walsh diagram for the bending of the bridging carbonyls out of the plane for $Co_2(CO)_8$. θ is defined in structure **3**.

For the d^9-d^9 complexes a comparison of $Co_2(CO)_8$ and $Co_2Cp_2(CO)_2^{2-}$ yields a calculated optimum flap angle of 143° for the former and 179° for the latter. Thus the former is correctly predicted to be puckered and the latter planar. To obtain an understanding of the differences we turn to the Walsh diagrams for the flapping motion, Figures 1 and 2. Both molecules contain a set of low-lying levels (below −12.5 eV) which are metal–ligand bonding or "t_{2g}" orbitals and above them a set of three important frontier orbitals of a_1, a_2, and b_2 symmetry. These become occupied as the metal exceeds a d^6-d^6 electron count. All levels are occupied in the d^9-d^9 complex.

Where do these orbitals come from? The easiest way to see them is to first form the $M_2(CO)_6$ or M_2Cp_2 unit.[2b,10] This is done schematically in Figure 3. Each $M(CO)_3$ or MCp unit has three low-lying orbitals, the remnants of the octahedral t_{2g} set and three hybrids, relatively high lying.[11] These combine to give a nest of six t_{2g} levels and six high-lying MO's. One of these, the M–M σ^* level, is too high in energy to enter into bonding. Thus five high-lying orbitals remain. These interact with the bridging carbonyl lone pairs and their π^* orbitals in such a way as to send two way up in energy and keep three down. These are the upper $a_1 + a_2 + b_2$ orbitals of Figures 1 and 2. It is here also that the difference between various bridging ligands enters. The phosphido group, lacking acceptor character, destabilizes three, not two, of the five upper orbitals, leaving only the a_1 and b_2 at accessible energy.

The three valence orbitals of $Cp_2Co_2(CO)_2^{2-}$ and $Co_2(CO)_8$ show different behavior with puckering. The b_2 orbital favors

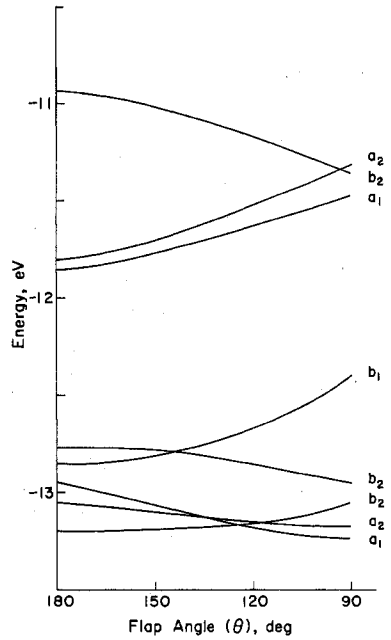


Figure 2. Walsh diagram for the bending of the bridging carbonyls out of the plane for $Cp_2Co_2(CO)_2^{2-}$. θ is defined in structure **3**.

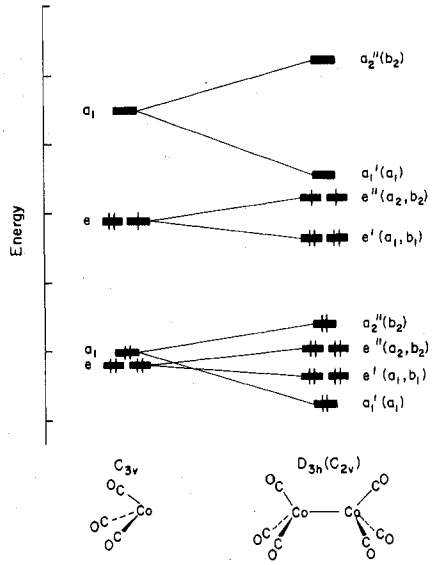
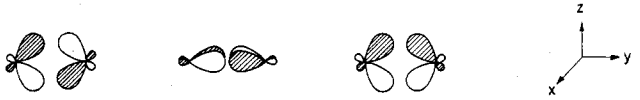


Figure 3. Schematic representation of the orbitals of $Co_2(CO)_6$ built up from those of two $Co(CO)_3$ fragments. The energy scale markings are in eV.

distortion from planarity, the a_1 orbital likes to retain a planar rhomboid, and the a_2 orbital shows a variable pattern generally favoring $\theta = 180°$, but taking an important slight dip only in the $Co_2(CO)_8$ case. These general trends are easiest understood by referring to the shapes of the orbitals, given in **7**–**9** for the Cp case, with only the metal contribution shown



7, b_2 **8**, a_2 **9**, a_1

in each. In fact the b_2 orbital cannot interact, by symmetry, with any bridging π^* orbital, while the a_2 and a_1 orbitals carry substantial contributions. This is shown from a different viewpoint, along the z axis, in **10** and **11**.

The contribution of the bridging carbonyl π^*, rather than the metal–metal bonding, dominates the slopes of the crucial

10, a_2 11, a_1

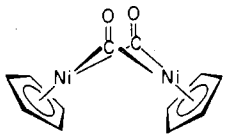
orbitals. As θ decreases from 180°, metal–bridging carbonyl bonding overlap decreases for a_1 and a_2, and so these rise in energy. The b_2 orbital has no interaction at 180°, but such interaction is turned on as θ decreases. Consequently, that orbital falls in energy.

We now return to the differences between the Cp and $(CO)_3$ terminal ligands. The three important orbitals of each are compared side by side in Figure 4. Note the top–bottom asymmetry in the carbonyl levels, especially pronounced in the a_2 and a_1 orbitals. This tilting is a consequence of the octahedral descent of the $M(CO)_3$ orbitals.[11,12] The in-pointing orbitals are, so to speak, anchored to an octahedral coordinate system "fixed" by the terminal carbonyls. This constraint is absent in the cyclopentadienyl case.

The tilting of the $M(CO)_3$ vs. MCp orbitals has a critical effect on the rotational barrier in polyene– and cyclopolyene–ML_3 systems.[12] In the present case it influences the slopes of the three orbitals in the Walsh diagrams and, most importantly, that of the a_2 orbital. The best interaction between the bridging carbonyl π^* and the metal a_2 combination in $Co_2(CO)_8$ is not at $\theta = 180°$, the planar geometry, but at a smaller θ; i.e., the bridging carbonyls rise above the plane to match the maximum in the a_2 orbital. This creates the important initial dip in the a_2 orbital energy (Figure 1). In turn this is the main factor in making the $Co_2(CO)_8$ puckered, while the inner rhomboid in $Co_2Cp_2(CO)_2^{2-}$ is planar.

In the Cp_2M_2AB series (M = Fe, Co, Ni; A and B = CO, NO), structural studies are available for d^8–d^8, d^8–d^9, and d^9–d^9 complexes. The d^9–d^9 system favors $\theta = 180°$, with one exception. Since the b_2 orbital, which is the orbital vacated as one proceeds to d^8–d^8, has its maximum energy at $\theta = 180°$ (Figures 1 and 2), if the d^9–d^9 system is planar, the d^8–d^9 and d^8–d^8 molecules should show an even greater preference for a planar geometry.

The exception referred to is the structure of $Cp_2Ni_2(CO)_2$, in which the inner rhomboid puckers and at the same time the cyclopentadienyl rings move below the MAMB plane, **12**.[6] Two other structures with mixed CpM, $M'L_3$ metal environment,[8h,i] and one with bridging isocyanides, $Cp_2Ni_2(CH_3NC)_2$,[8f] show a similar distortion.



12

The particular deformation exhibited by these structures was not examined by us earlier, since we kept the Cp center–Ni–Ni–Cp center axis linear. We proceeded to study this motion. The energy curves for ring puckering with and without Cp canting are compared in Figure 5. The potential energy varies very gently when the Cp's move to follow the puckering of the inner ring. For the d^9–d^9 Cp complexes we would conclude that it is likely that a range of geometries near the planar structure will be found as further examples are studied.

The tilting of the cyclopentadienyl rings below the MAMB plane causes the b_2, a_2, and a_1 orbitals to look no longer like those in **7**, **8**, and **9** but builds up electron density on the top side of the plane. The bridging carbonyls here, as they did in the terminal carbonyl case, rise above the plane to match this maximum and thus flapping occurs.

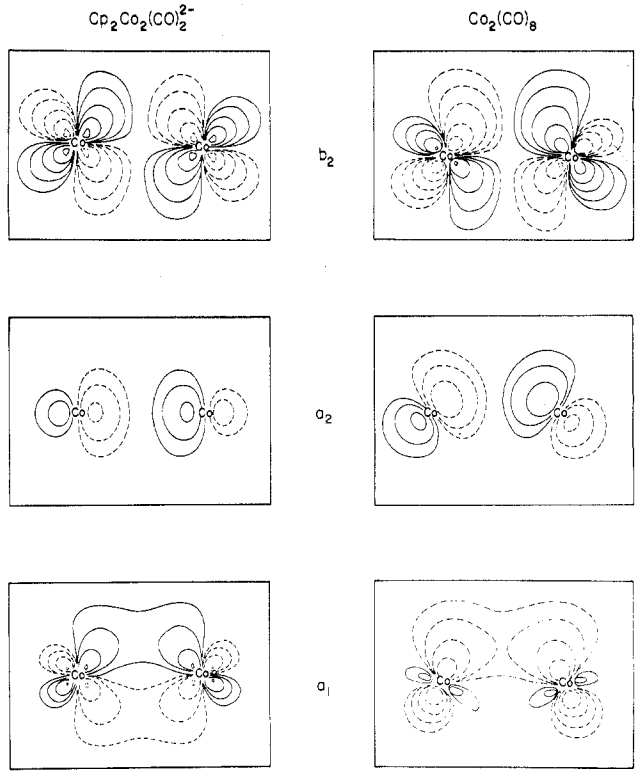


Figure 4. Contour maps of the top three occupied orbitals of $Cp_2Co_2(CO)_2^{2-}$ and $Co_2(CO)_8$, showing only cobalt contributions. The b_2 and a_1 orbitals are in the yz plane, and the a_2 orbitals are in a plane parallel to yz and 0.5 Å in the $+x$ direction. The contour levels of ψ are 0.4, 0.2, 0.1, 0.05, and 0.025, with negative values in dashed lines.

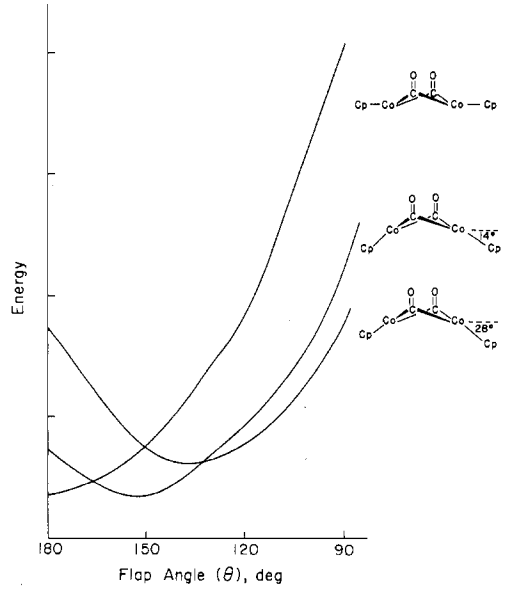


Figure 5. Total energy change for the bending of the bridging carbonyls out of the plane for $Cp_2Co_2(CO)_2^{2-}$. The cyclopentadienyl rings are canted as indicated in the structures. θ is defined in structure **3**. The energy scale markings are in eV.

Another way of viewing the above is to consider the work of Hofmann[13] which says that a $CpM(CO)_2$ fragment with 18 electrons around the metal prefers a "planar" structure[14] vs. a pyramidal one. Some of our previous work pointed to the importance of monomer geometrical preferences in determining dimer structures. In the present context one could say that, as the Cp rings move down, the bridging groups must move up to keep each monomer center locally planar. The

Table II. Calculated Metal-Metal Distances

confign	molecule	M-M, Å	molecule	M-M, Å
d^9-d^9	$Cp_2Co_2(CO)_2^{2-}$	2.42	$Cp_2Co_2(NO)_2$	2.40
d^8-d^9	$Cp_2Co_2(CO)_2^{-}$	2.37	$Cp_2Co_2(NO)_2^{+}$	2.33
d^8-d^8	$Cp_2Co_2(CO)_2$	2.29	$Cp_2Co_2(NO)_2^{2+}$	2.24

net result is a puckered dimer.

Metal–Metal Bonding

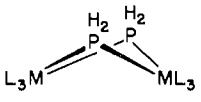
Given that we understand how the terminal ligands influence the puckering of the bridged ring, we now return to the question of the metal–metal separation. In the series of compounds in Table I both the metal and bridging ligands change. Since the metal radii are approximately equal,[15] we assume that the change in metal will not have a great effect on the geometry. Calculations were carried out on two systems, $Cp_2Co_2(CO)_2$ and $Cp_2Co_2(NO)_2^{2+}$, to see the effect of substituting the better π acceptor nitrosyl for carbonyl. In each case the Co–L–Co and L–Co–L angles were varied in such a way as to keep the inner ring planar. The optimum Co–Co separations are given in Table II.

There is some difference between the nitrosyl and carbonyl d^8–d^8 cases, and detailed examination of the orbitals shows a not unexpected variation in composition of the a_1 and a_2 orbitals. However, the b_2 orbital, which is the one responsible for any changes as one progresses from d^8–d^8 to d^9–d^9, is *identical* in the carbonyl and nitrosyl cases. This of course is a consequence of the symmetry-imposed absence of any contribution of the bridging ligands in this orbital.

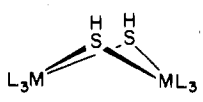
This b_2 orbital, illustrated in Figure 4, is clearly metal–metal π antibonding. How much so? The experimental structural information in Table I would indicate very little antibonding character in that MO, since the bond lengths do not vary much with electronic configuration. The theoretical calculations of Table II would have predicted a lengthening of some 0.13–0.16 Å on going from d^8–d^8 to d^9–d^9. *Unfortunately we have no explanation of the discrepancy between the calculated and observed distances.* A speculative idea is that in the d^9–d^9 dinitrosyl complex some orbitals other than the b_2, for instance those derived from the remaining nitrosyl π^* orbitals, are occupied. We see some such low-lying orbitals in the dinitrosyl calculation, but (1) if they were occupied one would expect N–O bond lengthening, which is not observed,[16] and (2) their proximity to the b_2 would make one worry whether $Cp_2Co_2(NO)_2$ might possess a high-spin ground state; however, $Cp_2Co_2(NO)_2$ is diamagnetic.[17]

Other Dibridged Binuclear Complexes

Just how critical the role of the bridging groups is may be seen in a comparison of the Walsh diagram in Figure 1 and the one in Figure 6 for $Co_2(CO)_6(PH_2)_2$, **13**. As was



13



14

mentioned above, the carbonyl bridging case has three orbitals available (a_1, a_2, b_2) for electrons above the d^6–d^6 count, whereas the phosphido analogue has but two, a_1 and b_2. The slope of the b_2 level is also reversed between the two cases. Both these facts are a consequence of the change in character of the bridging group. In the CO case the acceptor orbitals stabilize b_2 with puckering, while in the donor case of PH_2^- the b_2 orbital is destabilized by the same motion.

Our slopes are somewhat different from those of Burdett,[2b] since his motion brought the two metals closer together and ours, as described earlier, did not. This has the effect of destabilizing the b_2 orbital more and it also helps stabilize the a_1 orbital, so that his a_1 goes slightly down and ours goes slightly up in energy. In the phosphido bridged system we find that the d^8–d^8 molecules should be planar and the d^7–d^7 molecules puckered. This is in complete accord with Burdett's theoretical analysis and the available experimental results.[18]

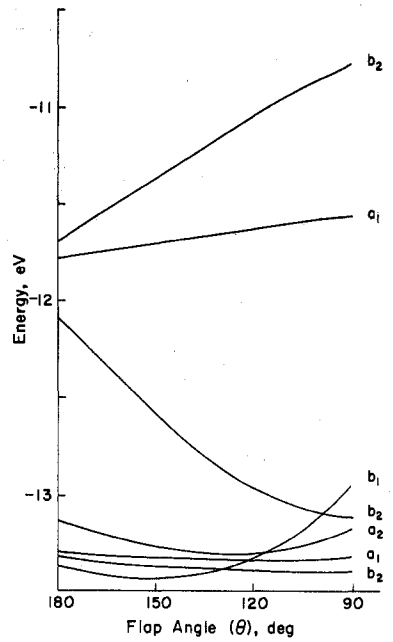


Figure 6. Walsh diagram for the bending of the bridging phosphido groups out of the plane for $Co_2(CO)_6(PH_2)_2$. θ is defined in structure **3**.

Table III. Extended-Hückel Parameters

orbital	H_{ii}, eV	exponents[a] ζ_1	ζ_2
H 1s	−13.4	1.3	
C 2s	−21.4	1.625	
2p	−11.4	1.625	
N 2s	−26.0	1.950	
2p	−13.4	1.950	
O 2s	−32.3	2.275	
2p	−14.8	2.275	
P 3s	−18.6	1.75	
3p	−14.0	1.30	
S 3s	−20.0	1.817	
3p	−13.3	1.817	
Co 4s	−9.21	2.0	
4p	−5.29	2.0	
3d	−13.18	5.55 (0.5679)	2.10 (0.6059)

[a] Two Slater exponents are listed for 3d functions. Each is followed in parentheses by the coefficients in the double-ζ expansion.

A calculation on the thiolate bridged system **14** reveals a similar situation; i.e., with terminal carbonyls d^8–d^8 is planar and d^7–d^7 puckered. However, a very interesting situation occurs here, in that we find no difference in the proclivity of the internal ring to pucker between terminal carbonyls and terminal Cp rings. This is a result of the a_2 no longer being a filled orbital. Thus, that all important dip in energy that occurred in Figure 1 is no longer present. Since the HOMO (b_2 orbital) goes up in energy for all of these molecules as θ decreases, when it is filled a planar structure is preferred and when it is empty the other orbitals dictate the amount of puckering.

Acknowledgment. Our interest in this problem was generated by the structural studies of I. Bernal, to whom we express our appreciation. We are grateful to B. E. R. Schilling and D. L. Thorn for numerous discussions, to L. F. Dahl for communicating structural information prior to publication, to J. Jorgensen for the drawings, and E. Kronman for the typing.

Our research work at Cornell was supported by the National Science Foundation through Research Grant CHE-7606099.

Appendix

The calculations were of the extended-Hückel type using parameters (see Table III) taken from previous work.[2a] A "weighted H_{ij}" formula was used in all calculations.[20] Distances not previously indicated are S–H = 1.33 Å, Co–S = 2.26 Å, P–H = 1.44 Å, Co–P = 2.16 Å, Co–N = 1.83 Å, and N–O = 1.19 Å.

Registry No. $Cp_2Co_2(CO)_2^{2-}$, 68813-14-9; $Cp_2Co_2(CO)_2^{-}$, 58543-12-7; $Cp_2Co_2(CO)_2$, 58496-39-2; $Cp_2Co_2(NO)_2$, 51862-20-5; $Cp_2Co_2(NO)_2^{+}$, 68875-56-9; $Cp_2Co_2(NO)_2^{2+}$, 68813-15-0; $Co_2(CO)_8$, 10210-68-1; $Co_2(CO)_6(PH_2)_2$, 68813-16-1.

References and Notes

(1) (a) L. F. Dahl, W. R. Costello, and R. B. King, *J. Am. Chem. Soc.*, **90**, 5422 (1966); (b) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967); (c) L. F. Dahl and C.-H. Wei, *ibid.*, **2**, 328 (1963); (d) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967); (e) B.-K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, **14**, 3103 (1975).

(2) (a) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976); (b) J. K. Burdett, *J. Chem. Soc., Dalton Trans.*, 423 (1977); (c) J. G. Norman and D. J. Gmur, *J. Am. Chem. Soc.*, **99**, 1446 (1977).

(3) I. Bernal, J. D. Korp, G. M. Reisner, and W. A. Herrmann, *J. Organomet. Chem.*, **139**, 321 (1977).

(4) J. L. Calderón, S. Fontana, E. Frauendorfer, V. W. Day, and S. D. A. Iske, *J. Organomet. Chem.*, **64**, C16 (1974).

(5) N. E. Shore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 256 (1976); **99**, 1781 (1977).

(6) L. Byers and L. F. Dahl, private communication. An earlier structure determination of $Cp_2Ni_2(CO)_2$ gave a similar Ni–Ni separation: J. P. Nice and O. S. Mills, cited in O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968).

(7) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).

(8) (a) G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 256 (1977); (b) G. G. Cash and R. C. Petterson, *ibid.*, 30 (1977); *Acta Crystallogr., Sect. B*, **33**, 2331 (1977); (c) W. Clegg, *Inorg. Chem.*, **15**, 1609 (1976); (d) E. Keller and H. Vahrenkamp, *Chem. Ber.*, **110**, 430 (1977); (e) W. Henslee and R. E. David, *Cryst. Struct. Commun.*, **1**, 403 (1972); (f) R. D. Adams, F. A. Cotton, and G. A. Rusholme, *J. Coord. Chem.*, **1**, 275 (1971); (g) N. G. Connelly, G. A. Johnson, B. A. Kelly, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 436 (1977); (h) F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1067 (1974); (i) I. L. C. Campbell and F. S. Stephens, *ibid.*, 337 (1975); (j) R. Mason, K. M. Thomas, D. F. Gill, and B. L. Shaw, *J. Organomet Chem.*, **40**, C67 (1972); (k) G. LeBorgne, D. Grandjean, R. Mathieu, and R. Poilblanc, *ibid.*, **131**, 429 (1977); (l) A. J. Carty, N. J. Taylor, H. N. Paik, W. Smith, and J. G. Yule, *J. Chem. Soc., Chem. Commun.*, 41 (1976); (m) R. Ball, M. J. Bennett, E. H. Brooks, W. A. G. Graham, J. Hoyano, and S. M. Illingworth, *ibid.*, 592 (1970); (n) R. D. Ball and D. Hall, *J. Organomet. Chem.*, **56**, 209 (1973); (o) P. M. Treichel, W. K. Dean, and J. C. Calabrese, *Inorg. Chem.*, **12**, 2908 (1973); (p) W. K. Dean and D. G. Van Derveer, *J. Organomet. Chem.*, **146**, 143 (1978); (q) Y. S. Wong, H. N. Paik, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 309 (1975); (r) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4422 (1974); (s) S. Aime, G. Gervasio, L. Milone, R. Rossetti, and P. L. Stanghellini, *J. Chem. Soc., Chem. Commun.*, **370** (1976); *J. Chem. Soc., Dalton Trans.*, 534 (1978); (t) G. P. Khare and R. J. Doedens, *Inorg. Chem.*, **15**, 86 (1976); (u) F. A. Cotton, B. E. Hanson, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, **99**, 3293 (1977); (v) E. Keller, A. Trenkle, and H. Vahrenkamp, *Chem. Ber.*, **110**, 441 (1977); (w) P. F. Lindley and O. S. Mills, *J. Chem. Soc. A*, 1279 (1969); (x) F. S. Stephens, *ibid.*, 2745 (1970); (y) F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1752, 1754 (1972); (z) A. J. Carty, G. N. Mott, N. J. Taylor, G. Ferguson, M. A. Khan, and P. J. Roberts, *J. Organomet. Chem.*, **149**, 345 (1978); (aa) A. J. Carty, G. N. Mott, N. J. Taylor, and J. E. Yule, *J. Am. Chem. Soc.*, **100**, 3051 (1978); (bb) M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *ibid.*, **100**, 3354 (1978); (cc) A. W. Edelblut, B. L. Haymore, and R. A. D. Wentworth, *ibid.*, **100**, 2250 (1978).

(9) Other geometrical parameters: Co–C in Cp ring, 2.108 Å; C–C in Cp ring, 1.399 Å; C–H, 1.09 Å; Co–CO terminal, 1.797 Å; C–O terminal, 1.168 Å; C–O bridging, 1.190 Å; Co–C–O terminal, linear; dihedral angle between MAMB and Cp ring planes, approximately 90°.

(10) (a) D. L. Thorn and R. Hoffmann, *Inorg. Chem.*, **17**, 126 (1978); (b) J. W. Lauher, M. Elian, R. H. Summerville, and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 3219 (1976).

(11) (a) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); (b) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *ibid.*, **15**, 1148 (1976).

(12) T. A. Albright, P. Hofmann, and R. Hoffmann, *J. Am. Chem. Soc.*, **99**, 7546 (1977).

(13) P. Hofmann, *Angew. Chem.*, **89**, 551 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 536 (1977).

(14) "Planar" here refers to the configuration of the two M(CO) axes and the normal from the M to the η^5-bonded Cp ring.

(15) (a) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, New York, 1960, pp 249–257. (b) B.-K. Teo, P. Eisenberger, and B. M. Kincaid, *J. Am. Chem. Soc.*, **100**, 1735 (1978).

(16) The N–O bond lengths are 1.254 Å in the d^8–d^8 complex of ref 4 and 1.187 Å (d^9–d^9) and 1.20 Å (d^8–d^9) in the complexes in ref 3.

(17) W. A. Herrmann and I. Bernal, *Angew. Chem.*, **89**, 186 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 172 (1977).

(18) See, for example, ref 1d,e and 8c.

(19) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 3179, 3489 (1962); **37**, 2872 (1962).

(20) (a) J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 3686 (1978); (b) R. Hoffmann and P. Hofmann, *ibid.*, **98**, 598 (1976).

Contribution from the Istituto di Chimica Generale dell'Università, 20133 Milano, Italy, and from the Istituto Chimico dell'Università, 62032 Camerino, Italy

Metal Derivatives of Azoles. 3.[1a] The Pyrazolato Anion (and Homologues) as a Mono- or Bidentate Ligand: Preparation and Reactivity of Tri-, Bi-, and Mononuclear Gold(I) Derivatives[1b]

GIOVANNI MINGHETTI,[2a] GUIDO BANDITELLI,[2a] and FLAVIO BONATI*[2b]

Received April 18, 1978

Stable gold(I) derivatives of several azoles, $[Au(az)]_n$, are obtained by various routes (azH = pyrazole or various 1-unsubstituted pyrazoles, benzo-1,2,3-triazole, or 1,2,4-triazole). In these compounds the az^- group acts as an exobidentate *N,N'* ligand; in several cases $n = 3$, and a trinuclear, enneaatomic ring structure is suggested. On the other hand, in the monomeric compounds $Ph_3PAu(az)$ where azH is benzotriazole or 3,5-dimethyl-4-nitropyrazole (pz'H) the azolato anion is monodentate. The compound $Ph_3PAu(pz')$ reacts with $[(CO)_2RhCl]_2$ affording $(CO)_2Rh(\mu\text{-}pz')_2Rh(CO)_2$ and with fluoboric acid or $AgBF_4$ yielding $[Ph_3PAu(\mu\text{-}pz')AuPPh_3]^+BF_4^-$, where only one exobidentate pyrazolato-*N,N'* bridges two gold atoms. The trimeric gold(I) pyrazolates, $Au_3(pz)_3$, react with iodine to give $Au_3(pz)_3I_2$, probably mixed-valence compounds, while with *sym*-trinitrobenzene an unstable 1:1 charge-transfer adduct is obtained and with iodine chloride the coordinated ligand is iodinated in the 4-position affording tris(3,5-dimethyl-4-iodopyrazolato-*N,N'*)trigold(I).

Introduction

Pyrazoles[3] are weak bases and fair nitrogen ligands thanks to the tertiary nitrogen atom. 1-Unsubstituted pyrazoles (pzH)[4] are also very weak acids. Indeed, they react with metallic potassium affording K^+pz^-,[5] with Grignard reagents, PhMgX, yielding pzMgX,[6] or with certain hydrides, such as alkali metal borohydrides, to give hydrogen and the corresponding poly(1-pyrazolyl)borate,[7,8] $M^+[(pz)_nBH_{4-n}]^-$ ($n = 2$, 3, or 4 according to the conditions employed[9]), where the pyrazolato ligands are monodentate. Other species where the

0020-1669/79/1318-0658$01.00/0