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## Transition Metal Pentacoordination

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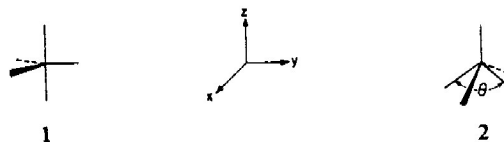
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A unified molecular orbital treatment of pentacoordinate transition metal complexes for the  $D_{3h}$  trigonal-bipyramidal and the  $C_{4v}$  square-pyramidal geometries is presented. Symmetry arguments and calculations on model compounds for which  $\pi$ -bonding effects are excluded yield basic  $\sigma$ -bonding trends. Thus the axial bond should be weaker in the trigonal bipyramid for  $d^0$ - $d^4$  and  $d^{10}$  and stronger for  $d^8$  low-spin complexes; the apical bond of a square pyramid with  $\theta < 165^\circ$  is stronger for  $d^0$ - $d^6$  and  $d^{10}$  and weaker for  $d^8$ . A similar pattern is obtained for  $\sigma$ -substituent effects: the stronger  $\sigma$  donor prefers the equatorial position of a trigonal bipyramid for  $d^0$ - $d^4$ ,  $d^{10}$  and the axial site for  $d^8$ ; in the square pyramid the preferred position for a stronger  $\sigma$  donor is apical for  $d^0$ - $d^6$  and  $d^{10}$  and basal for  $d^8$ . The substitutional preferences of substituents bearing cylindrical and single-faced  $\pi$ -donor and -acceptor orbitals are explored. The  $\pi$  interaction is greatest when the substituent is equatorial in a trigonal bipyramid, with its donor or acceptor orbital in the equatorial plane. A single-faced  $\pi$  acceptor will orient itself  $eq_\perp$  for  $d^8$ - $d^{10}$ ; a single-faced  $\pi$  donor,  $eq_\parallel$ . A cylindrical  $\pi$  acceptor will favor the equatorial site for  $d^8$ - $d^{10}$ ; a  $\pi$  donor, the axial site. In the interesting  $d^8$  case the effect of a  $\pi$  acceptor on the relative bond strengths counteracts the  $\sigma$  effect, while a donor reinforces it. In a square pyramid the extent of  $\pi$  interaction varies with the degree of pyramidality. For a nearly flat square pyramid cylindrical  $\pi$  interaction is greatest in the basal site but changes to the apical position as the pyramidality increases. In a basal site there is always more interaction in the  $ba_\parallel$  orientation.

Pentacoordinate transition metal complexes occupy a unique position in inorganic chemistry. As unstable reactive intermediates such species are commonly implicated in associative primary reactions of tetra-coordinate molecules and dissociative reactions of hexacoordinate compounds.<sup>1-3</sup> When pentacoordinate molecules are stable enough to be isolated, they confront us with a fascinating geometrical problem—the choice between trigonal bipyramid, square pyramid, and even other extreme conformations, and a generally soft potential energy surface connecting these minima.<sup>4-7</sup>

In this paper we build on our previous analysis of the bonding in pentacoordinate phosphorus<sup>8</sup> to derive a general theory of substituent effects and geometrical preferences in pentacoordinate transition metal complexes. The geometries considered in detail are the  $D_{3h}$  trigonal bipyramid, 1, and the  $C_{4v}$  square pyramid, 2. The electronic effects were modeled on  $ML_5$ , where M is a metal atom of the third transition series, L a pseudoligand carrying either s orbitals alone, when the



isolated effects of  $\sigma$  bonding were to be studied, or a full complement of s and p orbitals. The qualitative discussion of bonding effects should be valid for metal atoms in any transition series. Details of the extended Hückel calculations are given in the Appendix.

A cautionary note must be inserted here. The arguments to be presented in this paper are primarily symmetry and overlap based, with detailed calculations playing only a supportive role. Even so, the conclusions should be viewed by the reader critically, not as the last word of theory but as the working out of the consequences of one particular model. It is legitimate to question some of the foundations of the model, for instance the crucial role we will assign to hybridization with  $(n+1)p$  orbitals. And the geometrical features of transition

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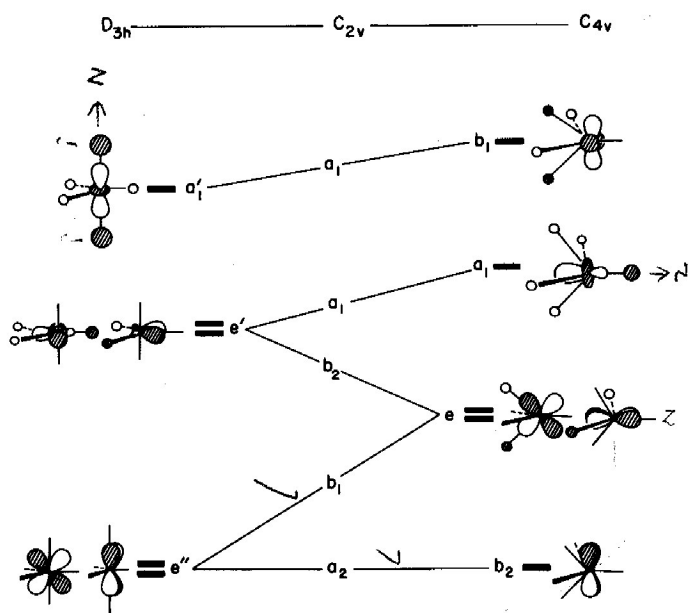
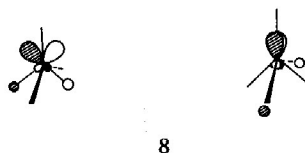


Figure 4. Wave function and energy changes along a Berry pseudorotation coordinate.

with  $\theta$ , which is done in Figure 3. The character of the levels is most clearly exhibited at  $\theta = 180^\circ$ , an octahedron minus one ligand. Just as in an octahedral complex there is a triad of levels,  $xz$ ,  $yz$ , and  $xy$ , not engaged in  $\sigma$  bonding. There is the high-lying  $x^2 - y^2$  orbital, strongly metal-basal ligand antibonding. At intermediate energy lies the  $z^2$  orbital, mainly metal-apical ligand antibonding.<sup>11</sup>

The degeneracy of the  $e$  set ( $xz$ ,  $yz$ ) and the  $b_2$  ( $xy$ ) orbital holds only at  $\theta = 180^\circ$ . At smaller  $\theta$  the  $xy$  orbital remains pure  $d$ , but the  $e$  set begins to mix in antibonding way with basal ligand orbitals.<sup>12b,c</sup> Not only is the  $e$  orbital set thus destabilized, but with significant consequences for  $\pi$  bonding the  $e$  orbitals become hybridized away from the basal ligands and toward the apical site. The effect is shown in an exaggerated manner in 8. The explanation of the hybridization



8

is the same as for the  $e'$  orbital of the trigonal bipyramid.

The  $z^2$  orbital decreases in energy with decreasing  $\theta$  for two reasons. First, the antibonding between  $z^2$  and the basal ligand orbitals is decreased, as the basal ligands move toward the nodal surface of the  $z^2$  orbital. Second, the basal-apical ligand-ligand interactions, which are antibonding, are reduced.

The equilibrium conformation of an  $ML_5$  molecule, if it is a square pyramid, will clearly depend on the number of  $d$  electrons. From Figure 3 it can be seen that  $d^6$  systems will favor a "flat" square pyramid, with  $\theta = 180^\circ$  but that the addition of more electrons will tend to distort the molecule so that  $\theta < 180^\circ$ . In our model  $d^8$   $ML_5$  the optimum  $\theta$  is  $164^\circ$ .

It is also simple to construct the correlation diagram for a Berry pseudorotation<sup>13,14</sup> which relates the  $D_{3h}$  and  $C_{4v}$  extremes by a pathway maintaining  $C_{2v}$  symmetry. This is shown in Figure 4. If the pseudorotation process is continued to another trigonal bipyramid, as was done by Eaton,<sup>14</sup> it becomes clear that the symmetry-allowed interconversions are for  $d^0$ - $d^2$  and  $d^6$ - $d^{10}$  low-spin species. As far as the preferences for  $C_{4v}$  or  $D_{3h}$  are concerned, we note that, superimposed on the slight  $d^0$  framework preference for a trigonal bipyramid,<sup>8</sup> the level trends in Figure 4 imply that  $d^3$ - $d^4$  would favor  $D_{3h}$  by still more, and  $d^5$ - $d^6$  a square pyramid (and from Figure 3 one with

$\theta = 180^\circ$ ).<sup>15</sup> For the  $d^6$  case one might expect an equilibrium between a low-spin square pyramid and a high-spin trigonal bipyramid. The situation has a direct analogy to the low-spin square-planar and high-spin tetrahedral equilibrium for  $Ni(II)$  and other  $d^8$  systems, as well as corresponding spin-state and geometry questions for cyclobutadienes and methylenes.

An interesting case in which the square-pyramidal and trigonal-bipyramidal conformers of one molecule both exist as distinct structures, at least in the solid state, is that of the low-spin  $d^7$   $Co(II)$  complexes  $Co(dpe)_2Cl^+$ .<sup>16</sup> The red modification of this complex is square pyramidal,  $Cl$  apical, while the green form is a trigonal bipyramid, with  $Cl$  equatorial. In solution the two geometries interconvert rapidly.

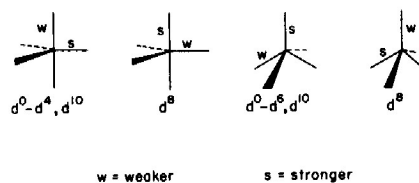
#### $\sigma$ -Bond Strengths in Pentacoordinate Complexes

The nature of the orbitals which we have derived allows an obvious inference of the effect of the number of  $d$  electrons on the  $\sigma$ -bond strength. First we confirmed that in our model  $D_{3h}$   $ML_5$  system, for  $d^0$ , the axial bonds are weaker, just as in  $PR_5$ . Orbitals 3 and 4 in the  $D_{3h}$  geometry are pure  $d$  and thus should have no effect on the bond strength. Orbitals 5 and 6, filled next in a low-spin complex, are  $M$ -equatorial  $L$  antibonding. Thus the initially stronger equatorial bonds are weakened, to the extent that in our calculation the  $d^8$  complex has stronger axial bonds. As one fills in the last two  $d$  electrons into  $z^2$ , 7, the axial bonding is again weakened, so that by  $d^{10}$  the  $d^0$  order, axial weaker than equatorial, is restored.

The  $C_{4v}$   $d^0$  case was not analyzed in great detail in our previous work on  $PR_5$ , though it was noted that for a geometry with  $\theta \approx 160^\circ$  the apical bond was stronger.<sup>8</sup> This was consistent with electron-rich multicenter bonding for the basal bonds, normal apical bonding. The introduction of  $d$  orbitals, as in our model  $ML_5$ , results in a perturbation of the system. At  $\theta = 180^\circ$  the basal bonds are slightly stronger than the apical one, but at smaller  $\theta$  the trend reverses, with the crossover coming at  $\theta \approx 165^\circ$ . Filling the  $xy$  orbital has no effect on the  $d^0$  trend. The next four electrons go into the  $e$  orbital, whose metal-ligand antibonding character depends on the pyramidity of the structure. For a flat square pyramid there is little effect, but for smaller  $\theta$  there could be a significant weakening of the basal bonds. For  $\theta = 160^\circ$ , a typical value,  $d^6$  has the basal bonds definitely weaker than the apical one.

The next orbital,  $a_1$ , is strongly  $M$ -apical  $L$  antibonding. Thus at  $d^8$  the bond strengths are reversed from the  $d^0$  case. With two more electrons in the strongly  $M$ -basal  $L$  antibonding  $x^2 - y^2$  orbital the original order is restored.<sup>17-22</sup>

We summarize the anticipated trends for the strength of the metal-ligand  $\sigma$  bonding, noting that a comparison with experiment must be postponed until we complete our analysis of  $\pi$ -bonding effects.



w = weaker      s = stronger

The cases not listed above are intermediate in their preferences. The computed overlap populations make the crossover in axial vs. equatorial bond strengths in the trigonal bipyramid at  $d^5$  and  $d^9$ , with a stronger axial bond for  $d^6$  and  $d^7$ . In the square pyramid  $d^7$  and  $d^9$  show a reduced trend for a stronger basal bond.

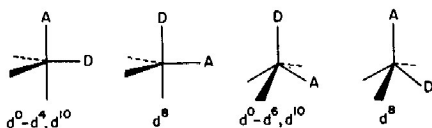
#### $\sigma$ -Substituent Effects

The detailed form of the molecular orbitals of the two coordination geometries yields in an obvious manner the preferred substitution sites for  $\sigma$  donors and acceptors. The argument is simple—it is assumed that more electronegative

ligands will preferentially enter those sites which carry an excess of electrons in the unperturbed  $ML_5$  system. The further identification of a  $\sigma$  acceptor with the more electronegative and  $\sigma$  donor with the more electropositive (or less electronegative) ligand is obvious.

Thus in  $d^0$ ,  $D_{3h}$ , the axial atoms are more negative, which follows from Rundle's simple picture of electron-rich three-center bonding. The consequent preference for electronegative substituents in the axial sites has been discussed previously.<sup>8</sup> The  $e'$  orbital (3, 4), which is filled from  $d^0$  to  $d^4$ , has no electron density on the ligands and so will not change the  $d^0$  trend. The  $e'$  orbital, 5 and 6, which is next filled, puts electron density on the equatorial atoms. At  $d^6$ , and especially at  $d^8$ , they become more negative than the axial atoms. Thus for  $d^8$   $D_{3h}$  complexes we would clearly expect a reversal of the  $d^0$  Muetterties rule, with more electronegative atoms preferring the equatorial positions. The  $z^2$  orbital, 7, has most of its electron density on the axial ligands. It reverses the trend again, so that  $d^{10}$  is like  $d^0$ . Similar arguments for the square pyramid lead again to a reversal of the  $d^0$  and  $d^{10}$  trend at  $d^8$ .

The predictions of favored sites for  $\sigma$  donors, D, and  $\sigma$  acceptors, A, can be summarized as



Extended Hückel calculations confirm our analysis. We defer a discussion of the experimental evidence for the pattern of substitution until we consider the preferences arising from  $\pi$  bonding.

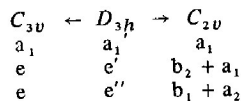
#### $\pi$ -Substituent Effects in the Trigonal Bipyramid

In this section the geometrical preference of  $\pi$ -electron donors and acceptors will be examined, independent of  $\sigma$  effects. The restrictions on interaction as a result of symmetry will be considered, coupled with calculations utilizing model donors and acceptors. A  $\pi$  donor is defined as a substituent with one or two high-lying occupied molecular orbitals of local  $\pi$  symmetry while a  $\pi$  acceptor is defined as a substituent with one or two low-lying unoccupied molecular orbitals of a  $\pi$  type.

The simplifying theoretical argument will be applied to the  $D_{3h}$  case first. Axial substitution is shown in 9 while equatorial substitution is given by 10. The molecular symmetry is

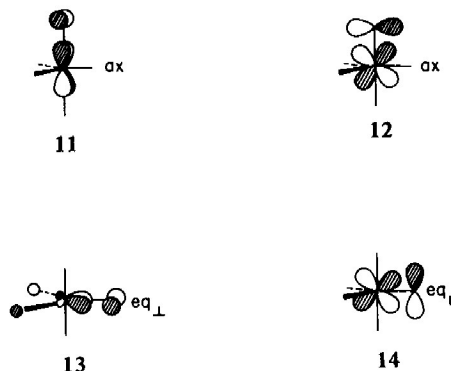


reduced from  $D_{3h}$  to  $C_{3v}$  on axial substitution and to  $C_{2v}$  on equatorial substitution. The substituent orbitals transform as  $e$  in  $C_{3v}$  and as  $b_1, b_2$  in  $C_{2v}$ . The conventional axis choice in  $C_{2v}$ , namely,  $z$  axis along  $C_2$ , is inconsistent with our original coordinate system, given next to 1, which in turn was the natural choice for an unsubstituted trigonal bipyramid. There is no good way out of this notational problem. We have retained the original  $d$  orbitals but have gone to a conventional  $C_{2v}$  axis system by redefining what was  $y$  in 1 as  $z$ , and  $z$  as  $x$ . Thus  $\sigma_h(D_{3h}) \rightarrow \sigma_v(yz)(C_{2v})$ . The important molecular orbitals of  $ML_5$  transform as indicated below



The prime consideration is whether a given donor or acceptor interacts with molecular orbitals of the  $ML_5$  skeleton more or less at a given position, rather than the extent of interaction.

For an acceptor the site with maximum interaction will be stabilizing; for a donor the interaction may be stabilizing or destabilizing. The important axial and equatorial interactions which are allowed by symmetry are shown in 11–14. In the



axial case we have made the approximation that the substituents effectively do not interact with the framework  $e$  orbital derived from  $e'$ , but only with the orbital derived from  $e''$ .

The axial interactions 11 and 12 are identical by symmetry. The equatorial interactions are labeled as  $eq_{\perp}$  (13) and  $eq_{\parallel}$  (14) according to the orientation of the substituent donor or acceptor orbital perpendicular or parallel to the threefold axis. The  $eq_{\parallel}$  interaction is identical with either of the axial ones. Thus the distinction between axial and equatorial substituents bearing a cylindrically symmetrical acceptor set (CN, CO,  $PR_3$ ...) depends on the magnitude of the  $eq_{\perp}$  interaction 13.

It was noted above that the  $D_{3h}$   $e'$  orbitals, one member of which is engaged in the interaction 13, are hybridized away from the equatorial ligands. A direct consequence of this is that the  $3d-p$   $\pi$  overlap in  $eq_{\perp}$ , 13, is significantly greater than the corresponding interactions 11, 12, and 14.

Equatorial  $\pi$  bonding is thus stronger than axial. This has been noted by others,<sup>23</sup> but it is important to be careful not to draw the inference therefrom that  $\pi$ -interacting substituents, whether donors or acceptors, will always prefer the equatorial site. Donor interaction can be destabilizing, and one must carefully examine the number of  $d$  electrons and the level scheme before reaching a particular conclusion.

Let us first consider the orientational preferences of single-faced  $\pi$  donors or acceptors. When such substituents appear in the axial site, there is no effective discrimination among possible orientations. In the equatorial site there is. Figure 5 shows an interaction diagram comparing  $eq_{\parallel}$  and  $eq_{\perp}$  orientations for single-faced donors or acceptors. In the construction of this diagram it is assumed that the energy gap denominator in a perturbation theory expression for the interaction is not dominant but that instead the magnitude of the interaction is controlled by the overlap.

For  $d^8-d^{10}$  the acceptor will clearly prefer an  $eq_{\perp}$  orientation 15. In the donor case one is filling both the donor orbital and the metal levels interacting with it. The interactions become four-electron destabilizing ones,<sup>24</sup> and conformational preferences are set by seeking out the site of least interaction. For  $d^8-d^{10}$  that is the  $eq_{\parallel}$  orientation, 16.



The analysis of cases with less than eight  $d$  electrons requires some care. One has to distinguish between instances of weak and strong  $\pi$  interaction. The situation illustrated in Figure 5 is that of weak interaction—namely, the perturbation caused by the substituent is smaller than the energy separation between

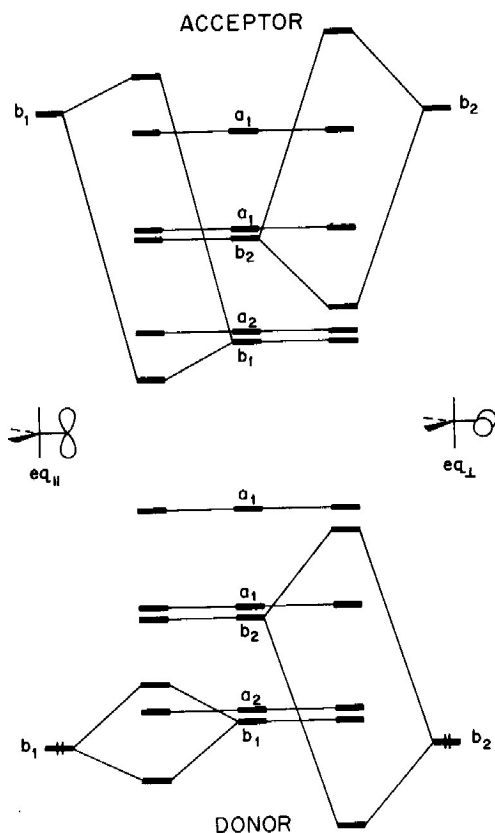


Figure 5. Interaction diagram for a weak equatorial acceptor (top) or donor (bottom). The  $eq_{\parallel}$  orientation of the single-faced  $\pi$  donor or acceptor is at the left; the  $eq_{\perp}$  orientation at the right.

$e'$  and  $e''$  set by the  $\sigma$  bonding. With strong  $\pi$  acceptors or donors the ratio of  $eq_{\parallel}$  and  $eq_{\perp}$  interactions may remain the same, but the level ordering might be like that in Figure 6. The figure is based on calculations with model donors or acceptors. Note that in the weak interaction scheme, Figure 5, one would conclude that a low-spin  $d^2$  system with an equatorial acceptor ligand would prefer  $eq_{\parallel}$ , but from the strong interaction diagram, Figure 6, one would choose  $eq_{\perp}$ . We think it is better to leave the analysis of individual cases to the reader—the diagrams are complex, but the principles required for their construction are now understood.

An especially interesting case of such an interaction is for a single ethylene ligand. The ethylene  $\pi$  orbital makes for roughly equivalent bonding in any position, but the ethylene  $\pi^*$  acceptor orbital carries the same symmetry properties as the single p orbital in **15** and **16**. It follows that a coordinated olefin will prefer an orientation such as **17** rather than **18**. This



is indeed the conformation found in a number of such structures.<sup>25-32</sup> In one complex,  $Os(CO)(NO)(C_2H_4)(PPh_3)_2^+$ , for which a structure like **17** is indicated, a barrier to olefin rotation of 9.5 kcal/mol has been deduced.<sup>33</sup> For a series of complexes  $Fe(CO)_4(\text{olefin})$  the rotational barrier would appear to be higher still.<sup>34</sup> We would predict an increase in that barrier with increasing  $\pi$ -acceptor capability of the olefin.<sup>35</sup>

To turn from ethylene to other single-faced donors or acceptors an interesting possible case of a donor orientational preference is available in the structure of dichlorotrakis(1,2-dimethylimidazole)copper(II), a  $d^9$  complex.<sup>36</sup> The structure, shown schematically below, is a trigonal bipyramid with two

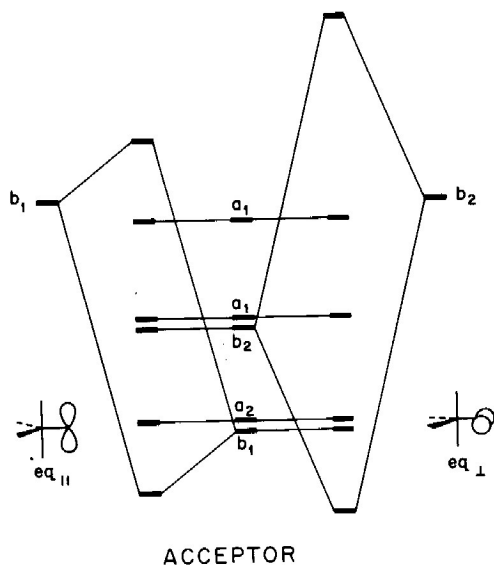
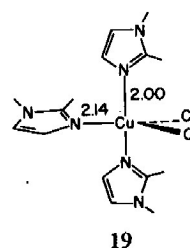
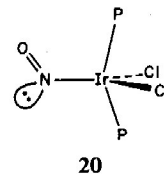


Figure 6. Interaction diagram for a strong equatorial acceptor:  $eq_{\parallel}$  at left;  $eq_{\perp}$  at right.



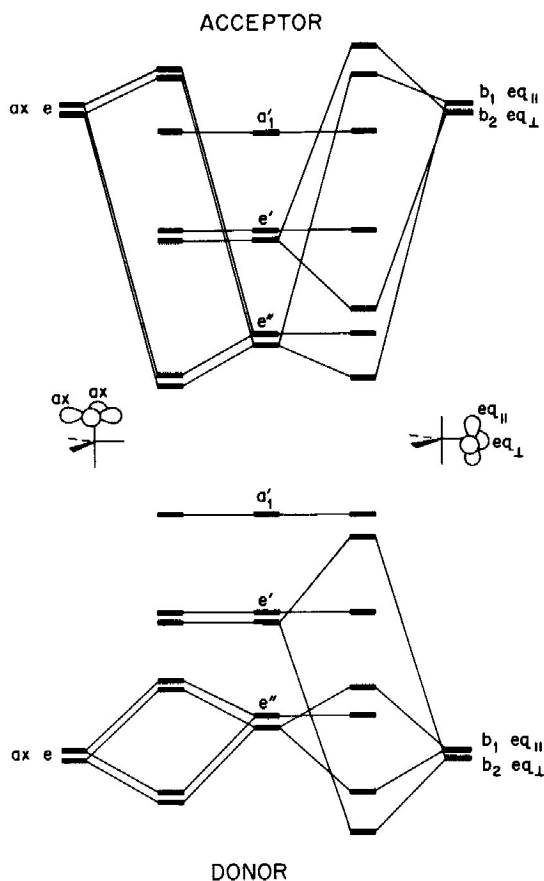
dimethylimidazole units axial and one equatorial. The orientation of the equatorial imidazole ligand is of interest. If we view it as a  $\pi$  donor, the observed orientation indeed is  $eq_{\parallel}$ . Of course it may be that steric and not electronic effects set the observed solid-state preference.

Another instance of an equatorial substituent with an orientational degree of freedom is that of a nitrosyl. The fascinating story of the pentacoordinate nitrosyls is told elsewhere.<sup>37,38</sup> In most "good" trigonal bipyramids the MNO angle is close to  $180^\circ$ . However, many of the nitrosyl structures identified as square pyramids are in fact intermediate in geometry between the two extremes. An example is  $IrCl_2(NO)(PPh_3)_2$ , with a  $PIrP$  angle of  $170^\circ$ , while  $ClIrCl$  is  $157^\circ$ .<sup>39</sup> The bent nitrosyl eclipses the  $PIrP$  axis, which better



approximates the axial locus of the trigonal bipyramid. Note that the observed bending puts the NO acceptor orbital  $eq_{\perp}$ , the donor orbital  $eq_{\parallel}$ , as expected. A similar situation occurs in  $IrI(CH_3)(NO)(PPh_3)_2$ ,<sup>40</sup> but not in  $IrX(CO)(NO)(PPh_3)_2^+$   $X = I, Cl$ .<sup>41</sup>

We proceed to an analysis of the site preferences of cylindrically symmetrical  $\pi$  donors and acceptors. The requisite information is already at hand, namely, the estimate that the ordering of interactions is  $eq_{\perp} > eq_{\parallel} = ax$ . Figure 7 shows a comparison of axial and equatorial substitution by donors and acceptors, in the weak-interaction limit. For  $d^8-d^{10}$  the conclusion follows that a  $\pi$  acceptor will favor an equatorial site; a  $\pi$  donor, an axial one. For complexes with less d electrons an evaluation of the strength of the  $\pi$  bonding must



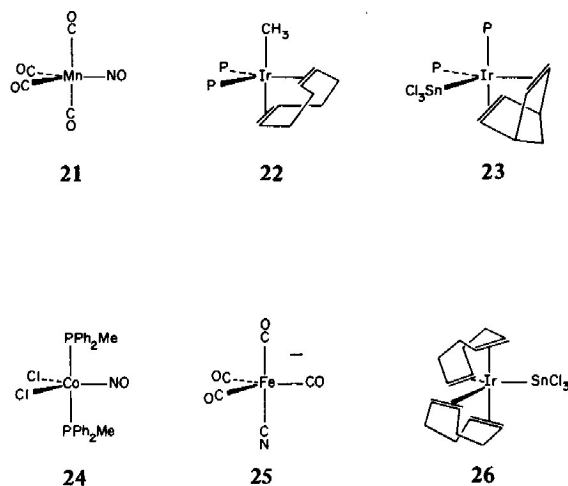
**Figure 7.** Interaction diagram for a cylindrically symmetrical  $\pi$  acceptor (top) and donor (bottom). The left side of the figure has the substituent in the axial site; the right side, in the equatorial position.

be made first, to see whether Figure 7 or another diagram, appropriate to strong  $\pi$  interaction, is suitable.

Of course the choice between substitution sites is a resultant of preferences set by both the  $\sigma$ - and  $\pi$ -donating capabilities of the ligand in question. Our conclusions often are parallel for the  $\sigma$  and  $\pi$  system (for  $d^8$  both good  $\sigma$  donors and good  $\pi$  donors will prefer the axial site). Given that many inorganic ligands understandably show opposite  $\sigma$  and  $\pi$  character, *i.e.*, are good  $\sigma$  donors and good  $\pi$  acceptors, we are often led to a hazardous evaluation of the relative strength of  $\sigma$  and  $\pi$  bonding. If we nevertheless persist we find that our conclusions receive some support, though they are not unambiguous, from existing structural and dynamic studies.

Osborn,<sup>42</sup> Churchill,<sup>43</sup> Raymond,<sup>23</sup> and their coworkers have generalized that strong  $\pi$ -acceptor ligands will tend to occupy equatorial sites in a trigonal bipyramid. This conclusion is based on crystal structures such as those of **21**,<sup>44</sup> **22**,<sup>45</sup> **23**,<sup>43</sup> **24**,<sup>46</sup> **25**,<sup>23</sup> and **26**,<sup>47</sup> as well as static and dynamic nmr studies.<sup>42,48</sup> It is also interesting to note the contrast between the phosphine positions in **22** and **23**. The methyl group, an excellent  $\sigma$  donor, appears in the axial site, in accord with our theoretical conclusion.<sup>43</sup> (py)Fe(CO)<sub>4</sub> and (pyr)Fe(CO)<sub>4</sub> have recently been characterized.<sup>49</sup> In both of these  $d^8$  compounds the nitrogen base, a poorer acceptor than CO, occupies the axial site. In Ir(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub><sup>+</sup> the better acceptors, the carbonyls, occupy the equatorial sites.<sup>50</sup> Molecular orbital calculations on several substituted Fe(CO)<sub>5</sub> derivatives have been carried out.<sup>72</sup>

The next topic to be discussed is the relative strength of axial and equatorial bonds in trigonal-bipyramidal complexes. We have already mentioned in a previous section the trends to be expected from  $\sigma$  bonding. The analysis of  $\pi$  bonding is a corollary of the energetic scheme of Figure 7 and the attached

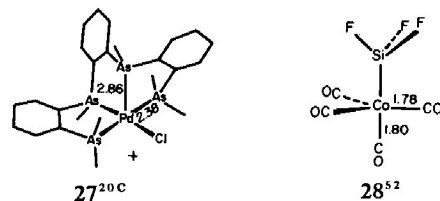


discussion. For  $d^8$ - $d^{10}$  complexes a cylindrically symmetrical  $\pi$  acceptor will strengthen the metal-ligand bond, but it will do so more when the acceptor is equatorial than when it is axial. For the corresponding  $d^8$ - $d^{10}$  donor case, the donor's four-electron destabilizing interaction will weaken both axial and equatorial bonds, but there will be differentially more weakening of the metal-ligand bond when the donor ligand is equatorial.

It will be recalled that the  $\sigma$ -bonding effect is that in  $d^8$  the axial bond is stronger and in  $d^{10}$  it is weaker. Thus in the interesting and common case of  $d^8$  complexes we have the conclusion that if the ligands are  $\pi$  donors both  $\sigma$ - and  $\pi$ -bonding effects cooperate to make for a strong or short axial bond and a weak or long equatorial bond. When the ligands are good  $\pi$  acceptors, unfortunately the  $\sigma$  and  $\pi$  effects oppose each other.

The results of (mainly) X-ray crystallographic studies of ML<sub>5</sub> systems are presented in Table I. Since there is a heavy atom in the system, the precision of the ML distances is inherently limited. Nor have we tried to analyze critically the reliability of the structure determinations. The trigonal-bipyramidal  $d^8$  cases all have  $\pi$ -acceptor ligands. The equatorial bonds are generally longer, which would be consistent with the  $\sigma$  effect dominating. It is hazardous to make anything of the small axial-equatorial bond length difference in the opposite direction in Mn(CO)<sub>5</sub><sup>-</sup>, but a carbonyl ligand on a negatively charged metal atom creates a situation of great relative acceptor strength. Perhaps the  $\pi$  effect is coming to the fore here. For  $d^{10}$  cases an outstanding exception to our expectations, noted as such by others as well,<sup>6,7,51</sup> is CdCl<sub>5</sub><sup>3-</sup>. The axial bonds should be longer than the equatorial ones, but in the available crystal structure they appear to be shorter.

There are numerous structures in which not all the ligands are identical, but nevertheless a similar ligand occurs in both equatorial and axial or apical and basal sites. These also provide a probe of our theoretical conclusions. By way of example two such structures are shown in **27** and **28**.



The  $d^8$  ML<sub>4</sub>L' structures, of which there are many,<sup>6,7,50,52</sup> show no consistent trend. Whether this is due to a trans effect of the lone axial ligand remains to be analyzed. Less symmetrical structures with polydentate ligands, of which **27** is but one example among many,<sup>20c,53</sup> often do possess structures showing the theoretically anticipated trend for a dominant  $\sigma$

Table I. ML Bond Lengths in Some ML<sub>5</sub> Structures

Molecule	Geom-etry <sup>a</sup>	Con-fig <sup>b</sup>	M-L, Å		Ref
			Axial or apical	Equatorial or basal	
Nb(NMe <sub>2</sub> ) <sub>5</sub>	C <sub>4v</sub>	d <sup>0</sup>	1.98	2.04	c
MnCl <sub>5</sub> <sup>2-</sup>	C <sub>4v</sub>	d <sup>4</sup> (hs)	2.58 (2.46)	2.30 (2.27)	d
Fe(N <sub>3</sub> ) <sub>5</sub> <sup>2-</sup>	D <sub>3h</sub>	d <sup>5</sup> (hs)	2.04	2.00	e
Co(C <sub>6</sub> H <sub>7</sub> NO) <sub>5</sub> <sup>2+</sup>	D <sub>3h</sub>	d <sup>7</sup> (hs)	2.10	1.98	f
Ni(CN) <sub>5</sub> <sup>3-</sup>	Int	d <sup>8</sup>	1.84	1.99, 1.91	g
	C <sub>4v</sub>	d <sup>8</sup>	2.17	1.86	
NiP <sub>5</sub> <sup>2+ h</sup>	D <sub>3h</sub>	d <sup>8</sup>	2.14	2.19	h
Fe(CO) <sub>5</sub>	D <sub>3h</sub>	d <sup>8</sup>	1.81	1.83	i
Co(CNCH <sub>3</sub> ) <sub>5</sub> <sup>+</sup>	D <sub>3h</sub>	d <sup>8</sup>	1.84	1.88	j
Pt(SnCl <sub>3</sub> ) <sub>5</sub> <sup>3-</sup>	D <sub>3h</sub>	d <sup>8</sup>	2.54	2.54	k
Pt(GeCl <sub>3</sub> ) <sub>5</sub> <sup>3-</sup>	Int	d <sup>8</sup>	2.40	2.43	l
Mn(CO) <sub>5</sub> <sup>-</sup>	D <sub>3h</sub>	d <sup>8</sup>	1.82	1.80	m
CuCl <sub>5</sub> <sup>3-</sup>	D <sub>3h</sub>	d <sup>9</sup>	2.30	2.39	n
CuBr <sub>5</sub> <sup>3-</sup>	D <sub>3h</sub>	d <sup>9</sup>	2.45	2.52	o
CdCl <sub>5</sub> <sup>3-</sup>	D <sub>3h</sub>	d <sup>10</sup>	2.53	2.56	p
InCl <sub>5</sub> <sup>2-</sup>	C <sub>4v</sub>	d <sup>10</sup>	2.42	2.46	q
AsF <sub>5</sub>	D <sub>3h</sub>	d <sup>10</sup>	1.71	1.66	r
Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>5</sub>	C <sub>4v</sub>	d <sup>10</sup>	2.12	2.22	s

<sup>a</sup> Int implies a C<sub>2v</sub> structure intermediate between D<sub>3h</sub> and C<sub>4v</sub>. See ref 4 for a detailed discussion of such structures. <sup>b</sup> hs = high spin. <sup>c</sup> C. Heath and M. B. Hursthouse, *Chem. Commun.*, 143 (1971). Similar distances were obtained for a pentakis(piperidinato)niobium complex. <sup>d</sup> I. Bernal, N. Elliot, and R. Lalancette, *Chem. Commun.*, 803 (1971). The distances in parentheses are for another salt, with a phenanthroline cation: M. Matsui, S. Koda, S. Ooi, H. Kuroya, and I. Bernal, *Chem. Lett.*, 51 (1972). <sup>e</sup> J. S. Wood and J. Drummond, *Chem. Commun.*, 1373 (1969); W. Beck, W. P. Fehlhammer, P. Pollmann, E. Schuierer, and K. Feldt, *Chem. Ber.*, 100, 2335 (1967). The distances listed in the table are from ref 6. The given equatorial Fe-N distance is somewhat longer than in the original crystallographic report. <sup>f</sup> B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 9, 767 (1970). <sup>g</sup> Reference 21b. See also A. Terzis, K. N. Raymond, and T. G. Spiro, *Inorg. Chem.*, 9, 2415 (1970) and the recent paper by F. A. Jurnak and K. N. Raymond, *ibid.*, 13, 2387 (1974). The structure of Cr(en)<sub>2</sub>-Ni(CN)<sub>5</sub> contains two crystallographically distinct anions. <sup>h</sup> The ligand is 2,8,9-trioxo-1-phosphaadamantane: E. R. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, 4, 407 (1970). <sup>i</sup> B. Beagley and D. G. Schmidling, *J. Mol. Struct.*, 22, 466 (1974); B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robiette, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 25, 737 (1969). See also A. Almendinger, A. Haaland, and K. Wahl, *Acta Chem. Scand.*, 23, 2245 (1969); M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, 69, 3405 (1965); 71, 775 (1967); J. Donohue and A. Caron, *ibid.*, 70, 603 (1966); 71, 777 (1967); *Acta Crystallogr.*, 17, 663 (1964). <sup>j</sup> F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 4, 318 (1965). <sup>k</sup> R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt and U. G. Stolberg, *J. Amer. Chem. Soc.*, 87, 658 (1965). <sup>l</sup> E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 12, 2932 (1973). The structure is closer to the trigonal-bipyramidal limit, but the angles in the equatorial plane are 111, 107, and 141°. The distances given in the table are averages for the trigonal-bipyramidal limit. The actual structure has a long bond (2.48 Å) opposite the largest equatorial angle, which is consistent with our predictions for the square-pyramidal limit. <sup>m</sup> B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 11, 1109 (1972). <sup>n</sup> Reference 21a; I. Bernal, N. Elliott, R. A. Lalancette, and T. Brennan, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 518. <sup>o</sup> S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 10, 2604 (1971). <sup>p</sup> E. F. Epstein and I. Bernal, *J. Chem. Soc. A*, 3628 (1971). <sup>q</sup> D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 8, 14 (1969). <sup>r</sup> F. B. Clippard, Jr., and L. S. Bartell, *ibid.*, 9, 805 (1970). <sup>s</sup> A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, 90, 6675 (1968); P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964).

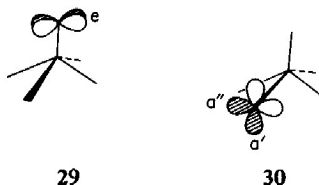
effect. A particularly instructive series of square-pyramidal Ni(II) complexes has been discussed by Orioli.<sup>20c</sup> The high-spin d<sup>8</sup> complexes have approximately equal basal and apical distances, with the basal distances perhaps slightly longer. The low-spin complexes have much elongated apical bonds, up to 0.6 Å longer than the corresponding basal separations.

Bond length comparisons for d<sup>1</sup>-d<sup>6</sup> complexes are rare. In

one of the two isomers of Ru(CO)(PPh<sub>3</sub>)<sub>2</sub>((CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>S<sub>2</sub>) we have one triphenylphosphine group which is apical and one basal, in square-pyramidal coordination.<sup>54</sup> In this d<sup>6</sup> complex we would anticipate weaker basal bonding, and in agreement Ru-P<sub>ba</sub> = 2.35 Å and Ru-P<sub>ap</sub> = 2.27 Å.

### π-Substituent Effects in the Square Pyramid

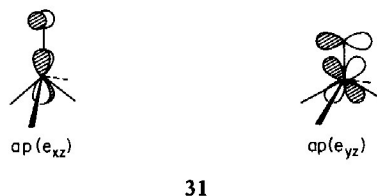
The important donor and acceptor interactions in the C<sub>4v</sub> geometry will now be analyzed. A pair of π-donor or -acceptor orbitals in the apical and basal positions of a square pyramid are shown in **29** and **30**, respectively. The molecular symmetry



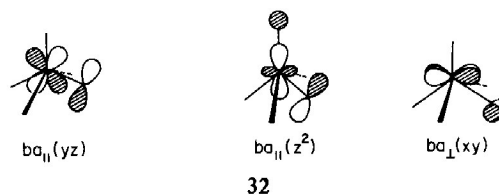
remains C<sub>4v</sub> upon apical substitution but is lowered to C<sub>s</sub> by a single basal substituent. That this symmetry is so low will prove a complication in our analysis. The d-orbital correlations C<sub>4v</sub> → C<sub>s</sub> are



The interacted pair of donor- or acceptor-framework molecular orbitals of e symmetry in the apical position are given in **31** and designated ap. For the case of basal π bonding there



are two framework orbitals of a' symmetry and one with a'' symmetry which are capable of considerable π interaction. These interactions for basal substitution are shown in **32**. The



basal interactions which are parallel to the pseudo-C<sub>4v</sub> axis are labeled as ba<sub>||</sub> while the one which is perpendicular is designated as ba<sub>⊥</sub>.

Is the interaction of the framework molecular orbitals of a square pyramid with a substituent carrying π orbitals greater in the apical or the basal position? In order to answer this question, the important framework orbital-π orbital interactions will be considered in detail. Overlap considerations alone may not suffice, because the square-pyramidal energy levels vary drastically with pyramidal angle, as was illustrated in Figure 3. In that figure note especially the slope of the e (xz, yz) levels, which are strongly involved in π bonding.

Just as the energy levels vary with the angle θ (see **2** for its definition), so do the important coupling overlaps between the donor or acceptor orbital and the framework orbital. That variation is exhibited in Figure 8. The ba<sub>⊥</sub>-xy and ba<sub>||</sub>-yz overlaps decrease from their maximum at θ = 180°, the "flat" square pyramid. The ap-xz,yz and ba<sub>||</sub>-z<sup>2</sup> overlaps increase

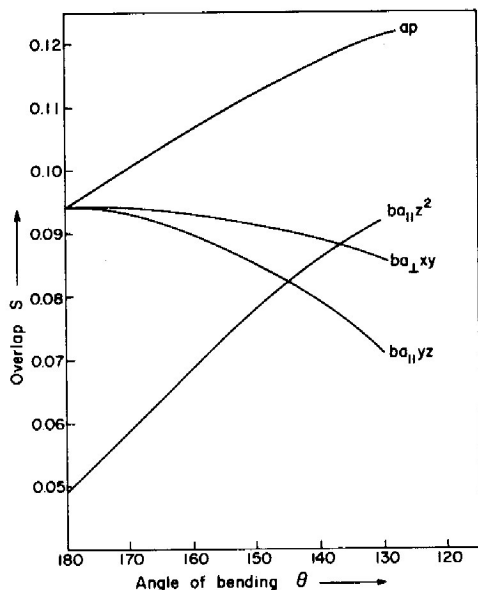


Figure 8. Computed variation of  $\pi$  overlap between donor or acceptor orbitals and the framework molecular orbitals of a square pyramid as a function of the bending angle  $\theta$ .

as  $\theta$  decreases. The  $ba_{\parallel}z^2$  effect is easily understood by a motion of the perturbing ligand toward the nodal plane of the  $z^2$  orbital.  $\pi$  bonding is maximized when the ligand is in that nodal plane. The increase in the  $ap-xz$  or  $-yz$  overlap is a result of the increasing hybridization, mixing in of  $p_x$  into  $d_{xz}$  and of  $p_y$  into  $d_{yz}$ , alluded to in the first section.

Calculations with model donors and acceptors show that the net  $ba_{\parallel}$  interaction, made up of  $z^2$  and  $yz$  components, is approximately constant as a function of  $\theta$ . One way of understanding this is to note that one component rises as the other falls, as  $\theta$  decreases from  $180^\circ$ . Another explanation comes to mind if instead of  $z^2$  and  $yz$  one considers the linear combinations  $c_1z^2 \pm c_2yz$ . In the  $yz$  plane such combinations possess nodal lines rotated by some angle from those of their components. This is shown below.

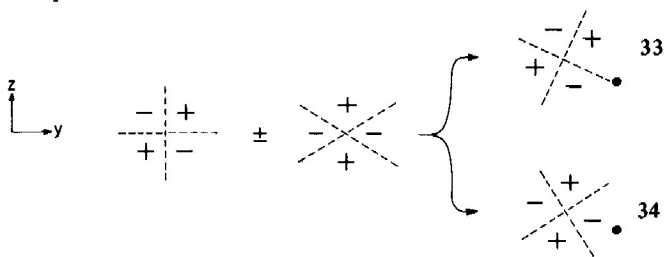


Figure 10. Interaction diagram for a cylindrically symmetric donor substituent in the apical and basal positions of a square pyramid.

Whether an acceptor or donor assumes that orientation will depend on the number of  $d$  electrons. The specific preferences can be obtained by constructing interaction diagrams analogous to Figure 7. For a low-spin  $d^8$  complex an acceptor substituent should prefer the  $ba_{\parallel}$  orientation, while a donor should assume  $ba_{\perp}$ .

2. A cylindrical  $\pi$  donor or acceptor finds greater interaction in the basal site at  $\theta = 180^\circ$  and in the apical site at lower  $\theta$ . In our model calculations the crossover comes at  $\theta \approx 175^\circ$ , nearly a flat square pyramid for a donor substituent, and at smaller  $\theta$ ,  $\sim 160^\circ$ , for an acceptor. Most square pyramids have  $\theta \approx 150^\circ$ , that is, an  $L_{ap}-M-L_{ba}$  angle of  $\sim 105^\circ$ .

The variety of interaction diagrams that could result from these conclusions is staggering, so that it is best to consider some individual cases.

The vanadyl ion is a ubiquitous structural type in vanadium chemistry.<sup>56</sup> A typical structure is that of  $VO(acac)_2$ ,<sup>57</sup> exhibiting square-pyramidal coordination, an apical oxygen, and a very short VO bond. Often a sixth ligand is weakly coordinated trans to the oxygen.<sup>58</sup> One trigonal-bipyramidal structure,  $VOCl_2(NMe_3)_2$ , is known.<sup>59</sup> These are formally V(IV). The oxide substituent, formally  $O^{2-}$ , has two lone pairs ready for  $\pi$  interaction. We have a  $d^1$  case with a cylindrical  $\pi$  donor. Figure 10 compares basal with apical oxygen substitution. The requirement in this case is to achieve maximum stabilization for the donor (oxygen) lone pairs while minimizing the destabilization of the lone "d" electron. Clearly this is better accomplished when the oxygen is apical. Nothing is changed if the system is viewed as V(II) with a neutral atomic oxygen ligand. The placement of the unpaired electron in an  $xy$  orbital is in agreement with other molecular orbital calculations.<sup>60-63,56</sup>

Clear-cut examples of  $ba_{\perp}$  vs.  $ba_{\parallel}$  preferences for

If the ligand bearing the  $p$  orbital is located at the dot in **33** or **34**, then the two rotated  $d$  orbitals are such that one, **34**, has negligible  $\pi$  overlap with the substituent, while the other, **33**, has maximal  $d-p$   $\pi$  overlap. To put it in another way  $yz$  and  $z^2$  combine to form one combination which "follows" the ligand position.

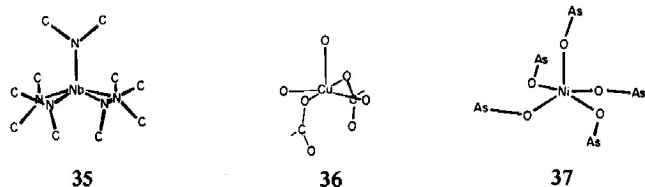
The net magnitude of the  $ba_{\parallel}$  interaction is, however, more than that of a simple  $d$  orbital on the metal center interacting with a ligand  $p$ . The  $z^2$  component of  $ba_{\parallel}$  is significantly hybridized away from the apical ligand. There are important consequences of this hybridization, which will be discussed elsewhere.<sup>55</sup> For the present case the consequence is that the  $ba_{\parallel}$  interaction, by virtue of the  $p$  admixture in  $z^2$ , acquires partial  $p-p$   $\pi$  character. At  $\theta = 180^\circ$  the  $ba_{\parallel}$  interaction is greater than all others.

Schematically, the net interactions behave as in Figure 9. Several corollaries follow.

1. A single-faced  $\pi$  acceptor or donor in a basal site will always have a greater interaction when it is in the  $ba_{\parallel}$  or-



single-faced  $\pi$  donors or acceptors are difficult to find. In the pentaamide complexes of Nb(V),<sup>64</sup> **35**, the basal amide ligands



are twisted around the Nb-N bond, so that they assume a geometry intermediate between parallel and perpendicular orientations of the donor nitrogen lone pair and the apical bond. If electronic effects were dominant, we would expect in this  $d^0$ , donor case the  $ba_{\parallel}$  orientation. We would guess that steric effects would favor the  $ba_{\perp}$  orientation and view the observed intermediate twist angle as an indication of the operation of an electronic effect consistent with our analysis.

In the crystal structure of bis(phenoxyacetato)triaquacopper(II),<sup>65</sup> **36**, the  $d^9$  copper atom is coordinated in basal sites by two monodentate phenoxyacetate ligands. Of interest to us is the orientation of the OCO planes of these ligands relative to the copper coordination polyhedron. The acetate oxygen ligand carries two donor functions. One is the  $sp^2$  lone pair; the other, an oxygen  $p$  type lone pair which is part of a delocalized four-electron  $\pi$  system. It is likely that the donor effect of the latter dominates. For a  $d^9$  system a donor should prefer a  $ba_{\perp}$  geometry, which is consistent with this structure. Another case in which an oxygen atom serves as a basal ligand is the high-spin  $d^8$  system, of pentakis(trimethylarsine oxide)nickel(II)<sup>2+</sup>,<sup>66</sup> **37**. The oxygen  $p$  type lone pairs assume an approximate  $ba_{\parallel}$  orientation. We would expect a  $ba_{\perp}$  preference, but that may be sterically impossible in this case. If the observed geometry is set by the steric constraints, then it is easily seen from figure 10 why a high-spin complex is likely.

It is interesting to note at this point the many complexes of  $Fe(CO)_3$  with a conjugated diene,<sup>67</sup> exemplified by the parent compound  $C_4H_6Fe(CO)_3$ ,<sup>68</sup> **38**. The relative orientation of the butadiene and the  $Fe(CO)_3$  moiety is that depicted in **38** and is apparently common to all compounds whose structures have been determined. The structure is to be viewed as a square pyramid, with the diene occupying two basal sites. If the ethylene components of the diene were to be viewed individually, then their acceptor,  $\pi^*$ , orbitals are in the favored  $ba_{\parallel}$  orientation.



A general problem for many of the complexes under consideration is that it is difficult to determine what part of an observed conformational preference is due to the electronic effects analyzed by us and what part is set by the often large steric requirements of the coordinated ligands.

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## Appendix

In order to perform calculations on model pentacoordinate transition metal complexes it is necessary to choose a suitable transition metal along with a set of reasonable parameters. Toward this end it was decided to perform on  $PtCl_4^{2-}$  an extended Hückel calculation modified to incorporate a

**Table II.** Parameters Used in Calculations of Model Pt(II) Complexes

Orbital	Orbital exponent		$H_{ii}$ , eV
	1	2	
6s	2.554		-11.64
6p	2.554		-7.01
5d	6.013 (0.63340) <sup>a</sup>	2.696 (0.55125) <sup>a</sup>	-12.27

<sup>a</sup> Numbers in parentheses indicate coefficient of the contracted member of the 5d radial function.

self-consistent charge refinement of the diagonal one-electron Hamiltonian matrix elements,  $H_{ii}$ , for Pt. The basis set of valence atomic orbitals for Pt was 5d, 6s, and 6p wave functions expressed as Slater-type orbitals. The radial part of the platinum 5d orbital was taken as a normalized linear (contracted) combination of two Slater orbitals with principal quantum number 5, whereas the 6s and 6p orbitals were chosen as a single Slater-type orbital. The mixing ratios for the contracted 5d orbitals and the 5d exponents as well as the 6s and 6p exponents for platinum were obtained from wave functions computed by Basch and Gray.<sup>69</sup> The Slater orbitals used for Cl had exponents of 2.033 (3s and 3p); the  $H_{ii}$  were -30.00 eV (3s) and -15.00 eV (3p).<sup>70</sup> The Pt-Cl distance was 2.33 Å. The diagonal Hamiltonian matrix elements,  $H_{ii}$ , for platinum were approximated by valence-state ionization potentials, VSIP's, and the neutral values were obtained from Cotton and Harris.<sup>71</sup> A linear charge dependence for the  $H_{ii}$  on platinum was used and the slope was chosen as 2.5 eV. The  $H_{ii}$  for Cl were not corrected for charge. The charge iteration procedure was allowed to continue until the charges on both the platinum and chlorine did not change by more than  $1.0 \times 10^{-5}$  charge unit between the  $k$ th and  $k+1$  cycles.

A summary of the platinum parameters along with the final self-consistent  $H_{ii}$  for platinum is given in Table II. All other calculations mentioned in this paper were extended Hückel calculations without charge iteration unless otherwise specified. The parameters for platinum listed in Table II were used throughout.

The ML5 calculations referred to in the body of the paper were for a  $PtL_5^{3-}$  system, with the Pt-L distance 2.33 Å for both trigonal-bipyramidal and square-pyramidal geometries. The pseudoligands  $L^-$  carried a single 3s orbital, Slater exponent 2.033,  $H_{ii} = -18.00$  eV.

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