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Orbital Phase Control of Trigonal Pyramidal Structures of Tricoordinated Metal Complexes

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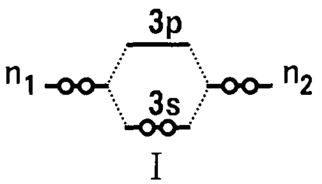
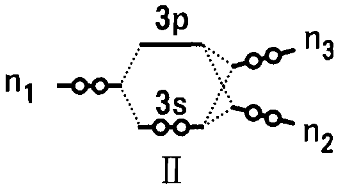
Trigonal pyramidal structures of some tricoordinated metal complexes ML_3 (M = Mg, Al, Si) are predicted by an orbital phase theory and confirmed by ab initio molecular orbital calculations to have acute L−M−L angles in spite of the steric congestion.

Recently, some metal (M) complexes with two ligands (L_1 and L_2) have been predicted by ab initio molecular orbital calculations to have acute L_1-M-L_2 angles.[1,2] Angles between the hybrid orbital axes cannot be less than 90° in the s−p hybridization. The anomaly has been proposed to be controlled by the orbital phase continuity−discontinuity properties.[1] The dicoordinated complexes with the $(3s)^2(3p)^0$ configuration of the metals involve a cyclic interaction of the 3s and 3p atomic orbitals and the ligand orbitals n_1 and n_2 (I), while the complexes assume noncyclic L−M−L geometry. The cyclic $\boxed{3s-n_1-3p-n_2}$ interaction in the noncyclic systems satisfies the phase continuity requirements[3] (**A**) at the geometry (**B**) with an acute angle, where one lobe of 3p interacts with both n_1 and n_2. Here, we designed tricoordinated complexes ML_3 with acute L−



I



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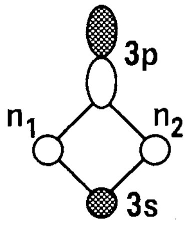
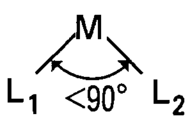
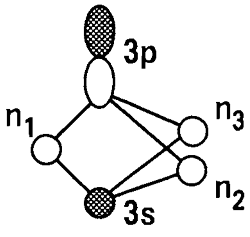


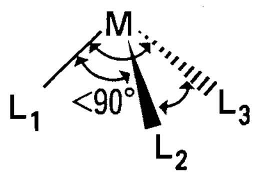
A



B



C



D

M–L angles.

In the tricoordinated complexes an additional orbital n_3 of the ligand L_3 interacts with 3s and 3p (II). The three cyclic interactions $\underline{\ulcorner \text{3s}-n_1-\text{3p}-n_2 \urcorner}$, $\underline{\ulcorner \text{3s}-n_2-\text{3p}-n_3 \urcorner}$, and $\underline{\ulcorner \text{3s}-n_3-\text{3p}-n_1 \urcorner}$ are involved. Each of the cyclic interactions meets the orbital phase requirements$^{3)}$ when the three n orbitals interact with the same lobe of a single 3p orbital (**C**). The electron–donating n orbitals are out of phase with the donating 3s, and in phase with the accepting 3p orbital. This suggests that the L–M–L angles should be acute (**D**).

The orbital phase continuity requirements are valid for the α– and β–spin spaces individually.$^{4)}$ The prediction is applicable to open–shell complexes, e.g. the $(3s)^1(3p)^0$ configurations.

Geometries of ML_3 were optimized$^{5)}$ by the R(O)HF method with the 6–31G basis set under the constraint of the C_3 or C_s symmetry. The results are summarized in Table 1.

Table 1. Optimized Geometries

	Metal State	C–M–C Angle/degree		M–C Distance/Å	
		OC–M–CO	OC–M–CN	M–CO	M–CN
$^{+}Mg(CO)_3$	$(3s)^1(3p)^0$	86.2		2.082	
$^{+2}Al(CO)_3$	$(3s)^1(3p)^0$	95.1		2.227	
$^{+}Al(CO)_3$	$(3s)^2(3p)^0$	82.2		3.224	
$Al(CO)_2(CN)$	$(3s)^2(3p)^0$	82.0	72.8	3.531	2.064
$^{+}Si(CO)_2(CN)$	$(3s)^2(3p)^0$	83.6	86.7	2.377	1.896

The prediction was confirmed by the acute C–M–C angles of $^{+}Al(CO)_3$, $Al(CO)_2(CN)$, and $^{+}Si(CO)_2(CN)$ with the metal $(3s)^2(3p)^0$ configuration.$^{6)}$ Figure 1 shows the dependences of the total energies and the Al–C distances of $^{+}Al(CO)_3$ on the C–Al–C angle. The decrease in the angle stabilizes the complex and shortens the Al–C distances.$^{7)}$ The cyclic orbital interaction (**C**) contains the n–3p interaction or the electron delocalization from L to M. The shortening of the Al–C distance may result from the electron delocalization enhanced by the phase continuity.

The total wave functions were decomposed into various electronic configurations, e.g., the locally–excited 3s→3p configuration E(3s→3p) and the electron–transferred n → 3p configuration T(n → 3p).$^{8)}$ The cyclic orbital interaction (**C**) involves the atomic polarization of the metal (mixing of E(3s→3p)) and the electron delocalization from L to M (mixing of T(n → 3p)). The coefficient ratio of E or T to the ground configuration G (C_E/C_G or C_T/C_G), or

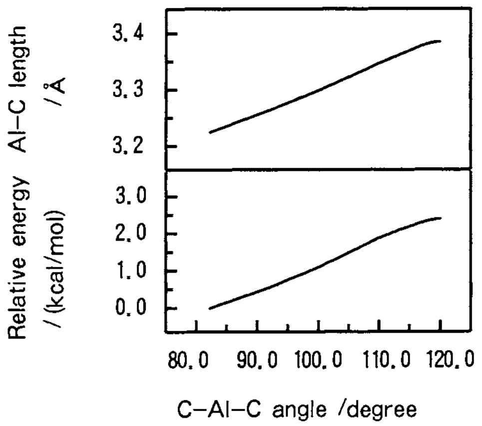


Fig. 1. Structural and energetical changes.

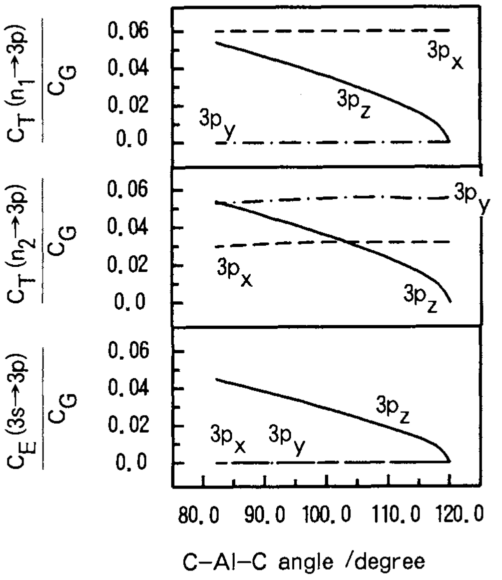


Fig. 2. Atomic polarization (C_E/C_G) and electron delocalization (C_T/C_G).

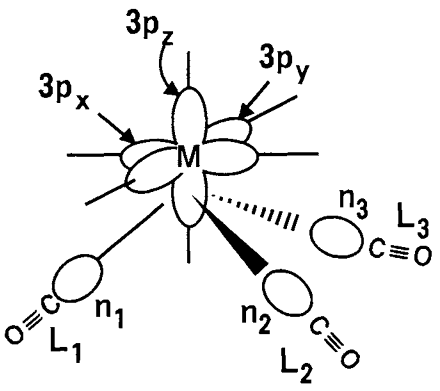


Fig. 3. Definition of orbitals.

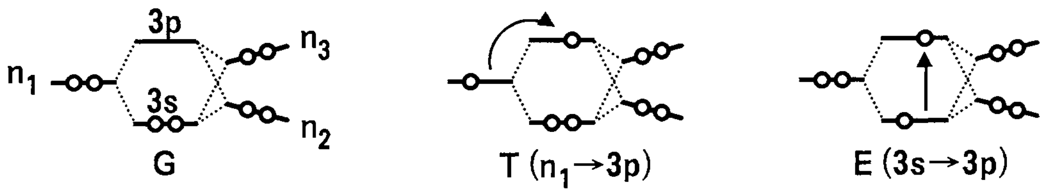


Fig. 4. Electronic configurations.

the measures[3b)] of the atomic polarization and the electron delocalization are plotted in Fig. 2.[9)] The $3p_z$ orbital is on the C_3 axis, and L_1 lies on the xz plane (Fig. 3). The polarization and the delocalization involving $3p_z$ are enhanced with the decrease in the angle. The result supports the orbital phase prediction that the cyclic interaction at the same lobe of a p orbital stabilizes the complexes.

The angle in $^{+}Mg(CO)_3$ is also acute (86.2°) in agreement with the prediction for the metal $(3s)^1(3p)^0$ configuration. However, $^{+2}Al(CO)_3$ with the same configuration has a little obtuse angle. The exception may be caused by insufficient stabilization due to the reduced number of electrons involved in the cyclic interaction.

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