an error of 3 kcal/mol at this level of theory is certainly possible, a reasonable argument can be put forth that the two isomers should be closer in energy in the gas phase than in the liquid phase. The dipole moment of **11** ($CH_3CH{=}NNHCH_3$) is calculated to be 1.95 D compared to a value of 0.05 D for **10** ($CH_3N{=}NCH_2CH_3$). Therefore, internal hydrogen bonding in the hydrazone form should be larger than in the azo form (the azo form also has no hydrogens suitable for hydrogen bonding), which would lead to a greater heat of vaporization for the hydrazone. Thus, while the hydrazone form is 3.3 kcal/mol more stable than the azo form in the liquid phase, in the gas phase the difference in the heats of formation would be reduced by the difference in the heats of vaporization.

Conclusion

The azo radical has more N–C double bond character than N–N double bond character as demonstrated by a calculation of structural parameters and the N–C and N–N rotational barriers. Addition of a hydrogen to the radical at either the carbon or nitrogen terminus produces either the azo form or the hydrazone form with nearly equal exothermicity. Substitution of a methyl for a hydrogen on carbon increases the stability of the hydrazone form while the substitution of a methyl for a hydrogen on the terminus nitrogen increases the stability of the azo form.

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Supplementary Material Available: Tables of absolute energies in hartrees (4 pages). Ordering information is given on any current masthead page.

Abnormally Narrow C–M–C Angle in $M(L_1)L_2$ Complexes (M = Si, Al, Mg, Na; L_1 and L_2 = CO, CN)

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Abstract: The geometries and the binding energies of AlCO and $Al(CO)_2$ were calculated by the ab initio molecular orbital methods. The geometry of AlCO is linear, and the calculated Al–C bond distance depends on the electron correlation effects. The bond angle C–Al–C in $Al(CO)_2$ is 70–74°, and the binding energy between the Al atom and CO is four or five times larger than that (2–4 kcal/mol) of AlCO. In AlCO, the electron repulsion between the n orbital of CO and the 3s orbital of the Al atom is essential. Important for $Al(CO)_2$ are the 3s → 3p polarization on Al induced by the delocalization from the n orbitals of two CO's to the 3p orbital (a_1 symmetry) of Al. The electronic reorganization involves the cyclic $\overline{\text{n–3s–3p–n}}$ orbital interaction that is controlled by the orbital phase continuity–discontinuity properties. The geometries of $M(L_1)L_2$ complexes for various electronic states of four main metal atoms were also calculated by the ab initio MO methods. M is silicon, aluminum, magnesium, and sodium atoms, and L_1 and L_2 are CO or CN molecules. From the calculated results, the C–M–C angle decreases with increasing occupation number for the metal state, which is an index for the electronic configuration of the metal and decreases with decreasing electronegativity of the metal atom.

1. Introduction

The interactions of small molecules with metal atoms, clusters, and surfaces have been extensively studied both experimentally and theoretically.[1-3] One of the recent focuses is the structure of $Al_x(CO)_y$ complexes. Matrix isolation spectroscopy has provided particularly valuable data. The products of condensation of Al and CO have been studied by IR[2] and ESR[3] methods. These studies showed that $Al(CO)_2$ is the major product. No evidence for the formation of AlCO was obtained. From the IR intensities of the symmetric and asymmetric CO stretching modes the C–Al–C angle was predicted to be about 110° on the assumption that the Al–C–O bonds are linear.

On the other hand, the AlCO and $Al(CO)_2$ complexes have been reported in a few theoretical papers.[4-6] These studies showed that the AlCO complex has small binding energy. In the $Al(CO)_2$ complex, the C–Al–C angle was predicted at about 70°.[5,6] Recently, Grev and Schaefer[7] reported the structure of $Si(CO)_2$ by the SCF MO and CI methods. The C–Si–C angle was estimated at about 78–80°. However, the abnormally narrow bond angles have not been interpreted in a convincing manner.

Table I. Geometry Parameters and Binding Energies of the AlCO Complex

optimization method	geometry, Å		binding energy, kcal/mol, 6-31G(d)			
	Al–C	C–O	HF	MP2	MP3	MP4-(SDTQ)
HF/3-21G	3.486	1.127	–0.79	–2.15	–1.82	–2.09
HF/6-31G(d)	3.740	1.113	–0.87	–1.85	–1.60	–1.79
MP2/3-21G	2.289	1.177	5.55	–3.97	–2.42	–3.89
MP2/6-31G(d)	2.128	1.165	6.33	–4.70	–3.32	–4.41

In this paper we first present the results of ab initio MO calculations on AlCO and $Al(CO)_2$ and propose that the geo-

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Table II. Geometry Parameters and Binding Energies of the $Al(CO)_2$ Complex

optimization method	geometry				binding energy, kcal/mol		
					3-21G		6-31G(d)
	Al-C[a]	C-O[a]	CAlC[b]	AlCO[b]	MP2	MP3	MP2
HF/3-21G	2.264	1.131	72.4	169.0	−19.9	−17.9	−15.6
MP2/3-21G	2.144	1.177	72.7	166.9	−21.5	−19.9	−19.5
MP2/6-31G(d)	2.089[c]	1.165[c]	69.6[c]	165.9[c]			−17.3[c]

[a] Angstroms. [b] Degrees. [c] Reference 6.

metrical abnormality results from the atomic polarization controlled by the orbital phase. In the following section, the main metal complexes generally formulated as $M(L_1)L_2$ (M = silicon, aluminum, magnesium, and sodium; L_1 and L_2 = CO and/or CN) were also calculated by the ab initio MO methods. The general rules for the L_1–M–L_2 bond angle are proposed.

2. Computational Methods

Ab initio molecular orbital calculations were carried out by using the GAUSSIAN82[8] and GAMESS[9] programs. The basis sets used were the split-valence 3-21G set[10] and the split-valence plus d polarization 6-31G(d) set.[11] All equilibrium geometries were determined with use of analytical energy gradients.[12] The stationary points were identified by the calculated vibrational frequencies. The force-constant matrix, and thereby the vibrational frequencies, was obtained with analytically calculated energy second derivatives.[13]

Additional calculations were performed, at the optimized structures, with electron correlation (excluding inner shells) incorporated through the second-, third-, and fourth-order Møller–Plesset perturbation theory (MP2, MP3, and MP4).[14]

3. Results and Discussion

A. AlCO. The ground state of the AlCO complex is the $^2\Pi$ state, and the geometry parameters and the binding energies are listed in Table I. The MP2 calculations gave Al–C bond distances 1.2–1.6 Å shorter than that calculated from the HF methods. The correlation effects are essential for the distance between the Al atom and CO.

The dissociation energy is about 2–4 kcal/mol at the MP4/6-31G(d) calculation level with various optimized geometries. The potential energy surface is very flat for the variation of the Al–C distance. These dissociation energies are in good agreement with the previous value,[6] 3.25 kcal/mol, at the MP4(SDTQ)/6-311G*[C,O]/6-31G(2d)[Al] level with the MP2 optimized geometry. Therefore, the basis set dependency is small.

In order to study the dependency of the potential energy on the distance between CO and the Al atom for various doublet electronic states of the Al atom, MC–SCF–CI calculations in conjunction with the 3-21G basis set for the Al–CO system were performed. Four active spaces corresponding to the valence orbitals of the Al atom were chosen for both the MC–SCF and CI calculations. All single, double, and triple excitations with respect to the ground state have been included. The calculated potential energy curves are shown in Figure 1. The CO bond length and the Al–C–O angle are fixed at 1.177 Å and 180° (the MP2/3-21G optimized values), respectively. The states with one electron in p_σ do not have energy minima, possibly due to the electron repulsion between the singly occupied p_σ orbital and the n orbital of CO. Furthermore, electrons in p_σ diminish the attraction due to electron delocalization from n to p_σ. Stable minima (about 60 kcal/mol) were found for the states, including a half-occupied or unoccupied s orbital. These results suggest that the electron repulsion between the doubly occupied 3s orbital of the Al atom and the n orbital of CO is very important.

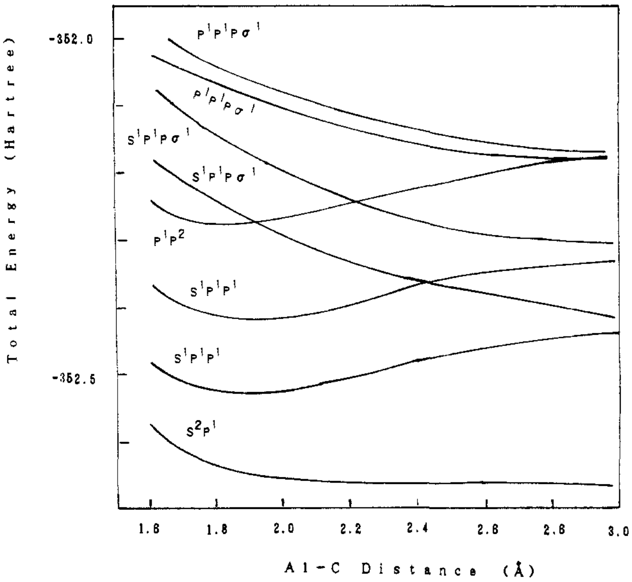

Figure 1. Potential energy curves of the ground and excited states for the change of the Al–C distance.

The binding energy in AlCO in its ground state is considered to be determined primarily by the attractive interaction between the n orbital of CO and the vacant p_σ orbital of the Al atom and the repulsive interaction of the n orbital of CO with the doubly occupied 3s of the Al atom, as shown in the following picture.

B. $Al(CO)_2$. The ground state of the $Al(CO)_2$ complex is the $^2B_1$ state, in agreement with previous results.[5,6] The geometry parameters of the complex and the binding energy are listed in Table II. The correlation effect on the Al–C distance is much smaller than that in the AlCO complex. The C–Al–C angle is about 70–74° and does not depend on the method of calculation. The C–C distance between the CO ligands is about 2.4–2.7 Å, much longer than the standard C–C single bond length (C–C = 1.53–1.54 Å in H_3CCH_3) obtained at similar levels of theory.[15] The calculated Al–C–O angle is about 166–169°, and it does not depend on the method of calculation. This reduces the repulsion of the n orbital of CO with the occupied 3s orbital of the Al atom, but it enhances the repulsion between the n orbitals. The two-CO

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Table III. Geometry Parameters of $M(L_1)L_2$ Complexes

metal	charge	metal state	L_1	L_2	ϕ, deg	α, deg	β, deg	MC_1, Å	MC_2, Å
Si	+1	s**2 p_π**1	CO	CO	80.3	174.6		2.2658	
Si	+1	s**1 p_π**2	CO	CO	101.1	178.6		1.8404	
Si	+1	s**2 p_π**0	CO	CN	85.6	178.1	177.7	2.3405	1.8656
Si	+1	s**1 p_π**1	CO	CN	105.8	179.0	176.8	1.9549	1.7909
Si	+1	s**1 p_π**0	CN	CN	110.1	177.7		1.7982	
Si	0	s**2 p_π**2	CO	CO	78.9	173.4		1.9240	
Si	0	s**2 p_π**1	CO	CN	83.7	176.0	177.1	2.1341	1.9070
Si	0	s**1 p_π**2	CO	CN	115.0	177.7	176.8	1.7789	1.8211
Si	0	s**2 p_π**0	CN	CN	93.9	177.1		1.8992	
Si	0	s**1 p_π**1	CN	CN	117.6	176.4		1.8172	
Si	-1	s**2 p_π**2	CO	CN	88.3	174.8	176.0	1.8429	1.9513
Si	-1	s**2 p_π**1	CN	CN	93.1	176.2		1.9423	
Al	+1	s**2 p_π**0	CO	CO	78.1	177.9		3.02	
Al	+1	s**1 p_π**1	CO	CO	92.5	177.2		2.0934	
Al	+1	s**0 p_π**2	CO	CO	180.0	180.0		1.8887	
Al	0	s**2 p_π**1	CO	CO	72.4	169.0		2.2637	
Al	0	s**1 p_π**2	CO	CO	87.3	179.8		1.9627	
Al	0	s**2 p_π**0	CO	CN	74.7	183.0	179.7	3.2913	2.0419
Al	0	s**1 p_π**1	CO	CN	102.8	177.6	178.4	2.0027	1.9468
Al	0	s**1 p_π**0	CN	CN	113.3	177.9		1.9507	
Al	0	s**0 p_π**1	CN	CN	180.0	180.0		1.8738	
Al	-1	s**2 p_π**1	CO	CN	87.0	174.2	176.1	2.0313	2.0816
Al	-1	s**2 p_π**0	CN	CN	91.7	175.7		2.0829	
Al	-1	s**1 p_π**1	CN	CN	112.6	177.0		1.9884	
Al	-1	s**0 p_π**2	CN	CN	180.0	180.0		1.9009	
Al	-2	s**2 p_π**1	CN	CN	91.2	175.2		2.1604	
Mg	+1	s**1 p_π**0	CO	CO	86.0	174.8		2.4864	
Mg	0	s**2 p_π**0	CO	CO			dissociation		
Mg	0	s**1 p_π**1	CO	CO	82.7	177.0		2.2538	
Mg	0	s**1 p_π**0	CO	CN	87.8	180.3	180.5	2.5582	2.0828
Mg	0	s**0 p_π**0	CN	CN	180.0	180.0			
Mg	-1	s**2 p_π**0	CO	CN			dissociation		
Mg	-1	s**1 p_π**0	CN	CN	111.7	177.2		2.1472	
Mg	-2	s**2 p_π**0	CN	CN	91.7	175.2		2.3375	
Mg	-2	s**1 p_π**1	CN	CN	110.4	177.2		2.2312	
Na	0	s**1 p_π**0	CO	CO	75.3	176.4		3.0608	
Na	-1	s**2 p_π**0	CO	CO			dissociation		
Na	-1	s**1 p_π**1	CO	CO	78.8	175.2		2.6493	
Na	-1	s**0 p_π**0	CN	CN	180.0	180.0		2.3068	
Na	-2	s**1 p_π**0	CN	CN	118.1	181.4		2.4340	

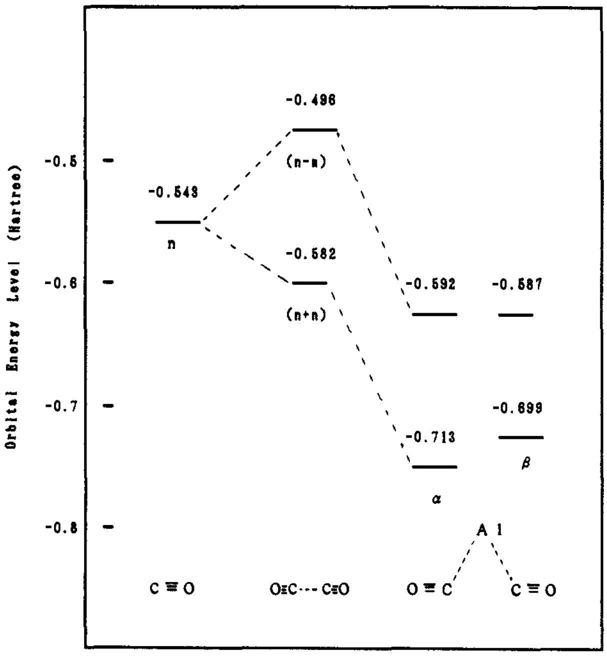


Figure 2. Orbital correlation diagram of n orbitals of CO, $(CO)_2$, and $Al(CO)_2$.

system in the complex is destabilized about 5.7 kcal/mol (HF/3-21G). The (n + n) and (n − n) orbital energy levels of the OC--CO system and the corresponding a_1 and b_2 orbitals of the complex are shown in Figure 2. The stabilization of the a_1 orbital in the complex is more than that of the b_2 orbital. The interaction with the p orbital of a_1 symmetry on the Al atom is larger than that with the p orbital of b_2 symmetry. The bond structure of the complex is primarily interpreted in terms of the interaction of the vacant 3p orbital of a_1 symmetry of the Al atom and the n orbitals of CO molecules (I).

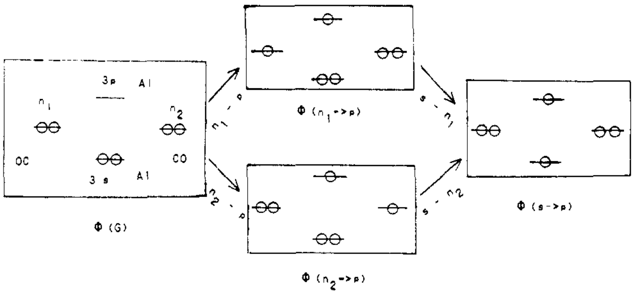
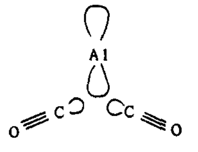
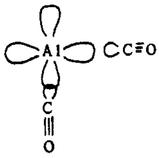


Figure 3. Diagram of one-electron-transfer configurations.

The stabilization energy of the complex is about 16–20 kcal/mol, which is four or five times that of the AlCO complex.

Three typical bonding structures (I–III) are conceivable for the $Al(CO)_2$ complex. In I, both CO molecules are coordinated to the same lobe of a p orbital. In structure II, two CO molecules coordinate to different p orbitals orthogonal to each other. The

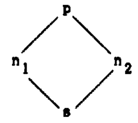

(I)


(II)

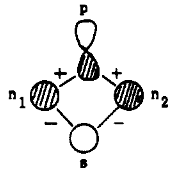

(III)

bonding between Al and CO is similar to that of the AlCO complex. In III, two CO molecules coordinate to one p orbital (similar to I), but to its opposite lobes. The preceding calculations have shown the $Al(CO)_2$ complex is represented by I. The reason can be provided by the orbital phase continuity–discontinuity principle that has been originally developed for cyclic interaction of three systems[16] and extended to noncyclic conjugated systems ("cyclic" orbital interaction in acyclic conjugation).[17] The $Al(CO)_2$ complex is a noncyclic system, OC--Al--CO.

We consider in-plane bonding closely related to the abnormal bond angles. The valence orbitals, 3s and 3p, of Al and two n orbitals, n_1 and n_2, of the CO molecules are important for the bond structure of the complex. The ground electronic configuration, $\Phi(G)$, has two electrons in 3s and two electron in each n orbital (Figure 3). The 3p orbital is vacant. There are two one-electron-transfer configurations, $\Phi(n_1 \rightarrow p)$ and $\Phi(n_2 \rightarrow p)$, and a one-electron locally excited configuration $\Phi(s \rightarrow p)$. The configuration interaction between $\Phi(G)$ and $\Phi(n_1 \rightarrow p)$ involves the n_1–p orbital interaction. Similary, the n_2–p interaction is involved in $\Phi(G)$–$\Phi(n_2 \rightarrow p)$. The $\Phi(n_1 \rightarrow p)$–$\Phi(s \rightarrow p)$ and $\Phi(n_2 \rightarrow p)$–$\Phi(s \rightarrow p)$ interactions involve the n_1–s and n_2–s interactions, respectively. As a result, the orbital interaction among the n_1, n_2, s, and p is cyclic (IV).



(IV)



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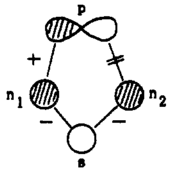
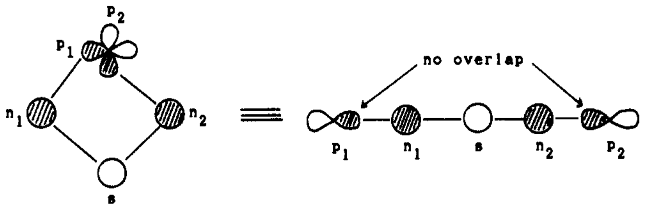


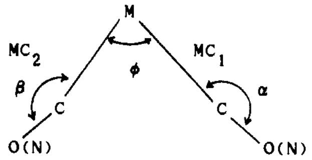
(VI)



(VII)

Therefore, the electronic reorganization implied in Figure 3 or the delocalization-induced atomic polarization is under the control of the orbital phase continuity–discontinuity properties. The phase continuity requirements[16] are (1) the donating orbitals out of phase, (2) the donating and accepting orbitals in phase, and (3) the accepting orbitals in phase. The orbitals in cyclic array IV meet the requirements in structure I (V) where one lobe of the 3p orbital interacts with both of the n orbitals. The polarization is promoted by the phase continuity. By contrast, the cyclic orbital interaction dissatisfies the phase continuity requirements for structure III (VI) where the opposite lobes interact with different CO molecules. The delocalization–polarization is disfavored. For structure II, no corresponding cyclic interaction is involved (VII), since the n orbitals of CO molecules interact with different p orbitals. The delocalization polarization is neither favored nor disfavored by the orbital phase properties. The resulting prediction that the structure is the most stable is consistent with the present computational results.

C. Generalization: $M(L_1)L_2$. In order to generalize the preceding theoretical arguments about $Al(CO)_2$, we investigated the $M(L_1)L_2$ complexes, where M = Na, Mg, Al, Si and L_1 and L_2 = CO and/or CN. The geometries were optimized under the constraint of C_s or C_{2v} symmetry. Doublet and triplet states were calculated for the open-shell system. The geometrical parameters for various electronic states are listed in Table III, where the "charge" indicates the total electric charge of the complex. The "metal state" showed an electron configuration of the metal defined as follows. The metal atom is supposed to be coordinated by neutral CO and/or anionic CN molecules. Remaining valence electrons on the metal atom were separated into σ (3s) and π ($3p_\pi$) electrons, denoted as n_1 in s••n_1 and n_2 in p_π••n_2, respectively. The ϕ, α, and β are the angles of C–M–C, M–C–O(N), and another M–C–O(N) in the complex. The MC_1 and MC_2 are the bond distances of M–C(L_1) and M–C(L_2), respectively.



In all complexes with s••0 in the metal state the geometries are linear ($\phi = \alpha = 180°$). In these complexes the 3s orbital is vacant. The 3s–3p electron promotion is not possible. The results support the interpretation for abnormally narrow C–Al–C angle by the atomic polarization. The metal state for each total charge correlates with the C–M–C angle. In a series of Mg, Al, or Si complexes with the same number of total electronic charges, the C–M–C angle decreases with the 3s and $3p_\pi$ occupation numbers. The electrons in the 3s orbital are indispensable for the 3s–$3p_\sigma$ promotion. Increased 3s population facilitates the atomic polarization. The $3p_\pi$ electrons are expected to enhance the polarization, which reduces electron repulsion between the 3s and $3p_\pi$ orbitals. Accordingly, the correlation between the angle and the electron configuration of the metal atom is consistent with the delocalization–polarization mechanism proposed for the C–M–C bending.

For the complexes of the same metal state the C–M–C angle decreases as the electronegativity of the metal atom is lowered. The low electronegativity is accompanied by the reduction of the energy gap between the 3s and 3p orbitals. This is another factor promoting the atomic polarization.

In the complexes, $Mg(CO)_2$ (s••2 p_π••0) and $Na(CO)_2^-$ (s••2 p_π••0) were not located as energy minima (Table III). The C–M–C angle in $Mg(CO)_2$ is estimated to be very small (<70°) if it can be extrapolated. The very small angle may produce large repulsion between the ligand molecules. This is why these complexes are predicted to be unrealistic.

In order to examine the applicability of the relation between the angle and the metal state, $Si(N_2)N_2$ (s••2 p_π••2) and $Si(N_2)N_2^+$ (s••1 p_π••2) were calculated. The calculated NSiN angles for the $Si(N_2)N_2$ and $Si(N_2)N_2^+$ complexes are 79.7° and 98.9°, respectively. The deviations from the estimated values are negligibly small (0.8° and 2.2°, respectively).

4. Conclusions

For the AlCO complex, the electron repulsion between the n orbital of CO and the 3s orbital of the Al atom is essential for the binding energy of the complex. The repulsion and the attractive interaction between the n orbital of CO and the vacant 3p orbital of the Al atom contribute most to the complexation. From the balance of these interaction energies, the binding energy is only 2–4 kcal/mol.

In the $Al(CO)_2$ complex, the binding between Al and CO is about four to five times stronger than that of the AlCO complex. The C–Al–C angle is extraordinarily small (about 70°). This suggests the bond structure of type I. The anomaly was interpreted by the orbital phase continuity–discontinuity properties.

We found the good correlation between the L_1–M–L_2 angle in the complex $M(L_1)L_2$ and the electron configurations of the metal atoms defined as metal state (where M = Na, Mg, Al, and Si and L = CO, CN, and N_2). The L_1–M–L_2 angle decreases with the 3s and $3p_\pi$ occupation number of the metal state and as the electronegativity of the metal atom is lowered.

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