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Electronic Structure and Bonding in Tricoordinate Amido Complexes of Transition Metals

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A theoretical study of bonding and structure in tricoordinate amido complexes with different d^n electron configurations is presented. The relative stability of the high- and low-spin states of $[Co(NH_2)_3]$ is discussed, and the preferred orientation of the amido ligands relative to the coordination plane is analyzed for the high-spin state of the $[M(NR_2)_3]$ compounds, where M = V(IV), Cr(III), Mn(III), Fe(III), Co(III), or Ni(II) and R = H or SiH_3. Comparison of the computational results with experimental data provides information on the influence of electronic and steric effects. The existence of metal−ligand π bonding is discussed in the context of the electron configurations, calculated bond distances, and spin-density distributions.

Three-coordinate complexes of transition metals are believed to be rare,[1,2] except for the d^{10} ions of the late elements of the first transition series, whose ML_3 complexes obey the 16-electron rule. The number of trigonal complexes with σ donors only is indeed limited,[3] but ML_3 complexes with π-donor ligands form a growing family,[4,5] including those with amido,[6−18] imido,[19,20] or alkoxide and related XR[21−25] ligands. Three-coordinate metal centers are also present in a related family of binuclear M_2L_4 complexes (M = Cr, Mn, Fe, Co, Ni) prepared in recent years, which bear amido terminal ligands and amido or phosphido bridges.[4,26−29] Other than these compounds in which the bulky ligands may give sterical protection to the metal center, thus favoring the coordinative unsaturation, some remarkable cases of bare three-coordinate compounds are known. These include the mononuclear $[MN_3]^{6-}$ ions in Ca_6MN_5 (M = Mn, Fe) and A_3MN_3 families (A = alkaline earth; M = V, Cr, Mn, Fe),[30−32] some trihalides MX_3 (X = F, M = V, Cr, Fe; X = Cl, M = Ti, Fe; X = I, M = Ti) studied by electron diffraction in the gas phase,[33−35] and the mononuclear Hoppe anions $[MO_3]^{n-}$ (M = Fe, Co).[36−38] Tricoordinated metal atoms can also be found in the oxo-bridged binuclear $[M_2O_5]^{6-}$ (M = Fe[39−42] and Co[43,44]) and in the tetranuclear[45] $[Co_4O_9]^{10-}$

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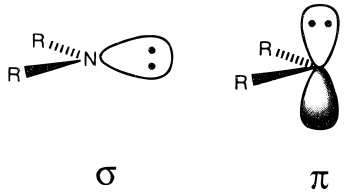
anions. Finally, edge-sharing tricoordinate transition metal atoms appear in the binuclear Hoppe anion[46] $[Co_2O_4]$,$^{4-}$ as well as in Cr_2Cl_4 and Co_2Br_4,[34] in which each metal atom is trigonally coordinated by bare oxide or halide anions.

The presence of π-donor ligands in all these complexes is noteworthy. Although the existence of metal−ligand π bonding has been claimed by several authors for coordinatively unsaturated complexes with π-donor ligands, its importance is not generally recognized. Metal−ligand multiple bonding is certainly a well-established characteristic of some hexacoordinated complexes,[47] but it has not been discussed in a general context for complexes of low coordination number. Furthermore, in most of the studied cases only one ligand is multiply bonded to the metal atom. A significant effort has been devoted recently to the design of "π-loaded" complexes, in which two or more ligands form multiple bonds to the same metal center.[48,49] In recent years, Eisenstein et al.[50−52] have shown that the presence of a π-donor ligand in the allegedly coordinatively and electronically unsaturated d^6 ML_5 complexes is important for the stability of such compounds.

In previous molecular-orbital studies of the nitrido- and oxide-coordinated MX_3 anions,[53,54] it has been shown that a significant degree of metal−ligand π bonding exists between such monatomic ligands with two π donor orbitals and the central metal ion. The amido ligands are single-faced π donors (**1**),[55] in the sense that there is only one π lone pair per donor atom. The spatial position of such a lone-pair orbital is determined by the orientation of the substituents, described from here on by ϕ, the rotation angle between the NR_2 and MN_3 planes (**2**). Hence, differences in the electronic structure can be expected for complexes with single-faced π donors depending on the orientation of the ligands. In fact, the known examples of amido complexes present a wide variety of rotation angles ($50 < \phi < 90°$, Table 1). In some cases only the room-temperature magnetic moment has been reported, while for two complexes the magnetic susceptibility has been reported down to 6 K. In all cases, the magnetic behavior indicates the prevalence of the high-spin states. In this paper we present a qualitative analysis of the electronic structure of the $[M(NH_2)_3]$ model complexes supported by semiempirical extended Hückel (EH) calculations. The resulting picture is further developed by studying the relative stability of the high- and low-spin states through density functional (DFT) calculations for the representative case of $[Co(NR_2)_3]$ ($R = H, SiH_3$). The orientation of the amido groups is also analyzed as a function of the electron configuration of the metal atom by geometry optimization of the model compounds $[M(NH_2)_3]$ and $[M\{N(SiH_3)_2\}_3]$ ($M = V^{IV}, Cr^{III}, Mn^{III}, Fe^{III}, Co^{III}$, and Ni^{II}) complemented by single-point calculations on $[M\{N(SiMe_3)_2\}_3]$ (M = Mn, Co). Finally, metal−ligand π bonding and the spin density distribution are discussed for all the studied complexes.



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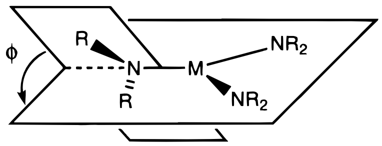

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Qualitative Molecular-Orbital Diagram for $[M(NH_2)_3]$ Complexes. Let us consider first the qualitative molecular-orbital diagrams for $[ML_3]$ complexes with ligands of different π-donor characteristics. We take NH_3 as a pure σ donor, NH_2^- as a single-faced π donor, and N^{3-} as a double-faced π donor. In general, the σ metal−ligand bonding can be described basically by bonding molecular orbitals with major contributions from the symmetry-adapted combinations of the ligands' lone pairs. Since we conventionally consider electronically saturated donor atoms, the M−N σ-bonding MOs are occupied in all cases. The corresponding antibonding MOs have the largest contributions from the in-plane s, p_x, and p_y atomic orbitals of the metal atom (i.e., the sp^2 hybridization expected from a valence-bond point-of-view). Since such MOs are empty for any transition-metal ion, three net M−N bonds result, regardless of the electron configuration of the metal ion and of the degree of substitution or orientation of the ligands. Hence, from now on we will not discuss the σ bonds, but will rather focus on the uppermost occupied and the lowest empty molecular orbitals, which have major contributions from the metal d orbitals and will be referred to, in what follows, as d-block orbitals. These are the orbitals that present variable occupation in the different complexes under study and are expected to be responsible for the π bonding and for the relative stability of electronic states with different spin multiplicities.

Considering metal−ligand σ interactions only, as in the model compound $[Co(NH_3)_3]^{3+}$, even if the metal d orbitals are formally nonbonding (remember the ideal sp^2 hybridization), the e′ orbitals (d_{xy} and $d_{x^2-y^2}$) interact with the ligands' σ-donor orbitals and incorporate some antibonding character. Such antibonding character is kept as small as possible through hybridization with the metal p_x and p_y orbitals (Figure 1, left). Thus, for σ-donor ligands, the expected energy ordering for the d-block orbitals (Figure 1, left) should present a 2 over 3 pattern, as actually found in extended Hückel calculations for $[Co(NH_3)_3]^{3+}$. Such an orbital pattern is similar to that found for octahedral ML_6 complexes,[69] with the difference being that the

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Table 1. Structural and Magnetic Data for Tricoordinate Amido Complexes of Transition Metals

compd[a]	config	M−N (Å)	ϕ (deg)[b]	μ_{eff} (μ_B)	ref
[M(NR$_2$)$_3$]					
[Sc{N(SiMe$_3$)$_2$}$_3$]	d^0	2.049			12
[Ti{N(SiMe$_3$)$_2$}$_3$]	d^1	1.938	50		56
[V{N(SiMe$_3$)$_2$}$_3$]$^+$	d^1	1.899	50	2.37 (6 K)	13
[Cr{N(SiMe$_3$)$_2$}$_3$]	d^3	1.889	51		57
[Cr{N(^{t}Bu)Ar}$_3$]	d^3	1.864 (11)		3.87	5
[Cr(N^{i}Pr$_2$)$_3$]	d^3	1.871	71 (3)	3.80	15
[Cr{N(tmpip)$_2$}$_3$]	d^3	1.916	58	4.23	58
[Cr{NAd(3,5-Me$_2$Ph)}$_3$]	d^3	1.867	68	3.97	58
[Mo{N(^{t}Bu)Ar}$_3$]	d^3	1.967	68 (5)	3.82 (5 K)	16,59
[Mn{N(SiMe$_3$)$_2$}$_3$]	d^4	1.890	50	5.38	10
[Mn{N(SiMe$_3$)$_2$}$_3$]$^-$	d^5	2.070	51		56
[Fe{N(SiMe$_3$)$_2$}$_3$]	d^5	1.918	49		9
[Fe{N(SiMe$_3$)$_2$}$_3$]$^-$	d^6	1.981	55		
		1.988	51		60
[Co{N(SiMe$_3$)$_2$}$_3$]	d^6	1.870	49	4.73	10
[Co{N(SiMe$_3$)$_2$}$_3$]$^-$	d^7	1.976	52		60
[Ni(NPh$_2$)$_3$]$^-$	d^8	1.887	57 (2)	2.6	17
[Al(N^{i}Pr$_2$)$_3$]	d^0	1.795	48		61
[Al{N(SiMe$_3$)$_2$}$_3$]	d^0	1.789	50		62
[Ga{N(SiMe$_3$)$_2$}$_3$]	d^{10}	1.863	49		61,63
[Ga{N(SiMe$_3$)$_2$}$_3$]·THF	d^{10}	1.872	49		64
[In{N(SiMe$_3$)$_2$}$_3$]	d^{10}	2.050	49		65
[Tl{N(SiMe$_3$)$_2$}$_3$]	d^{10}	2.086	49		66
[M(NR$_2$)$_2$L]					
[Mg{N(SiMe$_3$)$_2$}$_2$(2-Mepy)]	d^0	1.964	56		67
[Mg{N(SiMe$_3$)$_2$}$_2$(2,6-Me$_2$py)]	d^0	1.975	51		67
[V{N(SiMe$_3$)$_2$}$_2${SeSi(SiMe$_3$)$_3$}]	d^2	1.926	82 (18)		68
[V{N(SiMe$_3$)$_2$}$_2${TeSi(SiMe$_3$)$_3$}]	d^2	1.930	73 (6)		68
[V{N(SiMe$_3$)$_2$}$_2$(TeSiPh$_3$)]	d^2	1.914	75 (6)		68
[Mn{N(SiMe$_3$)(diprPh)}$_2$(thf)]	d^5	1.993 (7)	31 (8)		6
[Fe{N(SiMe$_3$)$_2$}$_2$(thf)]	d^6	1.915	67		7
[Co{N(SiMe$_3$)$_2$}$_2$(PPh$_3$)]	d^7	1.93, 1.92		4.84	18
[Co{NPh(BMes$_2$)}$_2$Cl]$^-$	d^7	1.930	90		11
[M(NR$_2$)L$_2$]					
Li[Mn{N(SiMe$_3$)$_2$}(OC^{t}Bu$_3$)$_2$]	d^5	2.001	88		22
[Co{N(SiMe$_3$)$_2$}(OC^{t}Bu$_3$)$_2$]$^-$	d^7	1.985	71		23
Li[Co{N(SiMe$_3$)$_2$}(OC^{t}Bu$_3$)$_2$]	d^7	1.907	82		23

[a] Ad = adamantyl; Ar = 3,5-Me$_2$C$_6$H$_3$; tmpip = 2,2,6,6-Me$_4$piperidine. [b] For nonequivalent angles, standard deviation given in parentheses.

gap in the present case is much smaller because of the formal nonbonding character of the e′ set as compared to the σ^* character of the e$_g$ set in the octahedral case. If we move now to the double-faced π donor nitrido ligands (Figure 1, right), in addition to the σ M−N interaction, the ligand lone pairs coplanar to the MN$_3$ core π-interact with the e′ metal orbitals (Figure 1, right), whereas the perpendicular lone pairs interact with the e″ set (d$_{xz}$ and d$_{yz}$). Hence, both the e″ and e′ molecular orbitals are destabilized relative to the σ-donor case. Notice that, due to the hybridization of d$_{xy}$ and d$_{x^2-y^2}$, these orbitals are more destabilized than d$_{xz}$ and d$_{yz}$, resulting in the level ordering shown (Figure 1, right), and consistent with those reported by Yee and Hughbanks[54] for [CrN$_3$]$^{2-}$ and by Schrock and coworkers[70] for [Os(NH)$_3$].

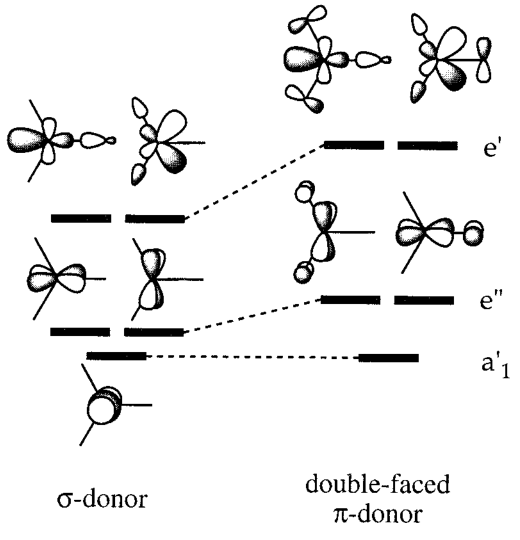

Figure 1. Ordering of the d-block molecular orbitals of a planar ML$_3$ molecule with σ-donor ligands (left) and with double-faced π-donor ligands (right).

Consider now the case of the single-faced π-donor amido ligands NR$_2^-$ and, for simplicity, assume that the three ligands

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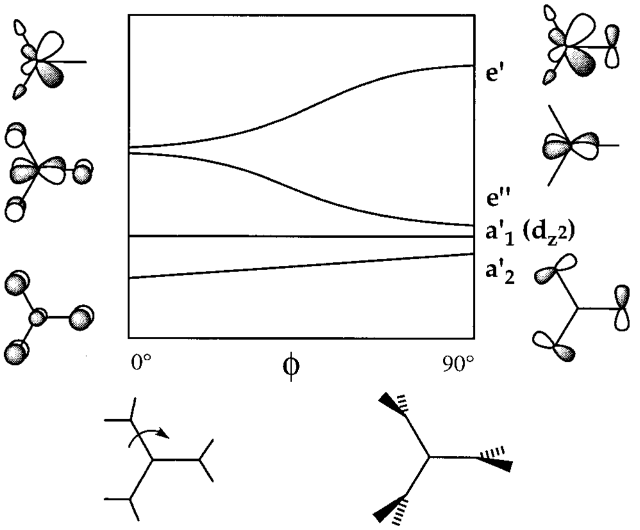

Figure 2. Variation of the energies of the d-block orbitals and the ligand-centered a$'_2$ orbital of a planar M(XR$_2$)$_3$ complex, where XR$_2$ is a single-faced π-donor, as a function of the rotation angle of the XR$_2$ groups (ϕ). The Walsh diagram represents the behavior of the Kohn–Sham orbitals in the DFT calculations for the high-spin complexes reported and is intended to reproduce the changes in energy and the most important energy differences rather than the numeric values.

present the same orientation relative to the MN$_3$ plane. The orientation of each ligand is defined by the average of the rotation angles ϕ for the three amido ligands (**2**). Thus, $\phi = 0°$ corresponds to a conformation of the amido groups coplanar with the coordination plane, whereas $\phi = 90°$ corresponds to a perpendicular orientation. In what follows we will always label the molecular orbitals according to their symmetry representation in the perpendicular orientation, for simplicity, even if the symmetry of the orbitals is different when the amido groups are rotated or coplanar. In the coplanar conformation, the π lone pairs are perpendicular to the coordination plane and the π-donor orbitals destabilize the e$''$ set relative to the σ-donor case. These d orbitals incorporate π antibonding character, resulting in the level ordering shown in Figure 2 (left). In the perpendicular conformation, the d$_{xy}$ and d$_{x^2-y^2}$ orbitals (e$'$ set) are the ones destabilized through π interaction with the ligands, opening a larger gap within the d-block orbitals (Figure 2, right). Besides the d-block orbitals, a ligand-centered MO is important for the subsequent discussion, and we have included it in the Walsh diagram. It is the a$_2'$ combination of the π-donor orbitals that is weakly M–N and N---N π-bonding in the coplanar case (Figure 2, left). In the perpendicular conformation, though, it has some N- - -N σ-antibonding character and is not allowed by symmetry to interact with the metal d orbitals in the perpendicular conformation (Figure 2, right). As a consequence, the a$_2'$ orbital increases its energy with ϕ.

There are two important questions about the electronic structure of the amido complexes that are in some way related: (1) Which is the preferred conformation of the amido ligands? (2) Which is the preferred spin state? Since the answers to such questions depend on the electron configuration, we discuss in the next section, in some detail, the case of a d^6 complex, exemplified by [Co(NR$_2$)$_3$]. Later on we will analyze other electron configurations.

Spin Multiplicity and Ligand Orientation in [Co(NR$_2$)$_3$] (R = H, SiH$_3$, SiMe$_3$). To analyze the quantitative aspects of the problem, notably, the relative stability of the high- and low-spin states and the preferred orientation of the amido groups, we have performed DFT calculations for the model compound [Co(NR$_2$)$_3$] (R = H, SiH$_3$) in its singlet and quintet states (see Appendix for computational details). Let us study first the singlet state, for which an (a$'_1$)^2(e$''$)^4 electron configuration should be expected, except for very small values of ϕ. By looking at the energy of the d orbitals in the Walsh diagram (Figure 2), one would predict the singlet state to be more stable in the perpendicular conformation ($\phi = 90°$). However, our DFT results (Figure 3, triangles) indicate that the optimum structure for the singlet corresponds to an intermediate rotation angle for both [Co(NH$_2$)$_3$] and [Co{N(SiH$_3$)$_2$}$_3$] (ϕ = 57 and 67°, respectively). Single-point calculations carried out for [Co(NR$_2$)$_3$] with the bulkiest ligand (R = SiMe$_3$) at different rotation angles (see Appendix for details) also indicate that the minimum is around 60°. Although steric effects may play an important role in determining the rotation angle, it is clear that the ligand-centered a$_2'$ orbital discussed above, which increases in energy with ϕ (Figure 2), opposes the preference of the d-block orbitals for the perpendicular orientation.

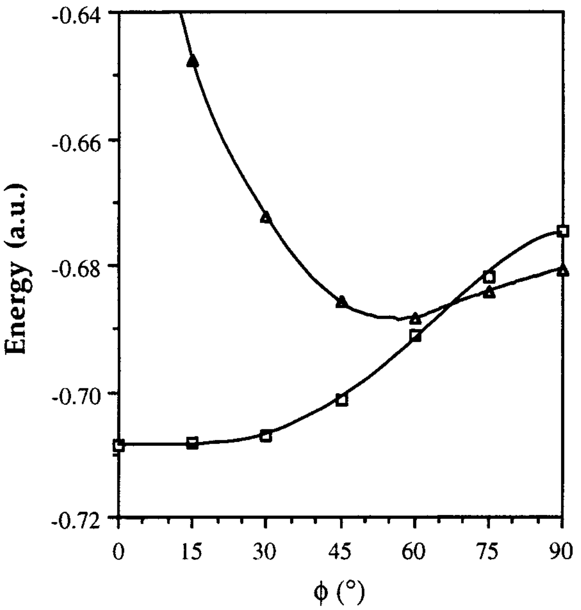

Figure 3. Relative energy of [Co(NH$_2$)$_3$] in its singlet (triangles) and quintet (squares) states as a function of the rotation angle of the amido groups.

The high-spin quintet state, resulting from an (a$'_1$)^2(e$''$)^2(e$'$)^2 configuration, is expected to have lower energy in the coplanar than in the perpendicular conformation, and its energy is expected to vary less with ϕ than in the singlet state, as actually was found in our calculations (Figure 3, squares). In its optimized geometry, the orientation of the amido ligands is close to the coplanar conformation, although significant deviation from planarity is found ($\phi = 14°$). Although the potential-energy surface is quite shallow at small rotation angles, we suspect that the slightly lower energy for a small rotation angle is due to repulsion between the hydrogen atoms of neighboring amido groups. We will address this problem later, but let us focus for the moment on the relative energies of the high- and low-spin states based on the results for the simplest model. It is worth stressing that the quintet state is found to be more stable than the optimized singlet by 12.4 kcal/mol (4333 cm^{-1}), as could be expected from the relatively small separation between the d-block orbitals produced by π interactions. Another interesting result is that the two spin states cross at some intermediate value

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Table 2. Calculated (DFT) and Experimental Structural Parameters for the High-Spin State of $[M(NR_2)_3]^{n+}$.[e] (Distances in Å, Angles in Degrees)

		M−N				N−Si		ϕ (deg)			
M	S	R = H	R = SiH_3	exp[a]	amines[f]	calcd	exp	R = H	R = SiH_3	exp	ref
V^{IV}	1/2	1.800	1.814	1.899	2.09	1.846	1.76	0	32	50 (3)	13
Cr^{III}	3/2	1.856	1.871	1.88[b]	2.07	1.789		62	72	71 (3)	15
Mn^{III}	2	1.880	1.895	1.890		1.788	1.755	*d*	55	50	10
		1.844[c]	1.880[c]								
Fe^{III}	5/2	1.875	1.899	1.918	2.04	1.795	1.731	0	32	49	9
Co^{III}	2	1.842	1.864	1.870	1.97	1.796	1.754	14	38	49	10
Ni^{II}	1	1.899	1.921	1.887	1.92	1.757		39	53	57	17

[a] See references in Table 1. [b] Average value. [c] Value for the unique N atom in the asymmetric structure **3**. [d] ϕ undetermined. [e] R = H, SiH_3; M = V ($n = 1$), Cr, Mn, Co ($n = 0$), and Ni($n = -1$). [f] The M−N distances in related complexes with amines[71] are also given for comparison.

of the rotation angle ϕ, thus suggesting the possibility of a temperature-dependent spin crossover if one were able to prepare a compound with the adequate rotation angle, maybe by choosing a ligand with the appropriate substituents.

The results for the quintet state with NH_2 ligands indicate that the electronically preferred coplanar conformation is disfavored by interligand interactions, thus suggesting that the optimum value of ϕ may be strongly influenced by the steric bulk of the substituents. An obvious experiment consists of introducing bulkier substituents in our calculations to check their effect on the rotation angle ϕ. The results for $[Co\{N(SiH_3)_2\}_3]$ (Table 2) confirm our expectations, since the optimized value of ϕ for the quintet state is increased to 38°. The difference in energy between the singlet and quintet states in this case is slightly larger than that found with the simpler model: 17.2 kcal/mol (6010 cm^{-1}). The calculated structural parameters are in excellent agreement with the experimental ones. The Co−N distance is little affected by the bulkiness of the substituents, whereas the Co−N−R angle decreases and the optimized rotation angle increases from R = H to R = SiH_3 (Table 2).

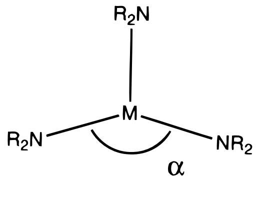
One can think that still bulkier substituents, such as $SiMe_3$, should favor a larger rotation angle. Single point calculations on the quintet state of $[Co\{N(SiMe_3)_2\}_3]$ at different rotation angles (see Appendix for details) while keeping the rest of its geometry as in the experimental structure clearly indicate that the molecule is most stable at intermediate rotation angles, consistent with the experimental value ($\phi = 49°$). In summary, we can conclude that the SiH_3 substituent provides a reasonable model for bulkier groups, even if the value of ϕ may be underestimated by about 10°. With such rotation angles, a quintet ground state should be expected, and only when ϕ is forced to be larger than 70° can the singlet become the ground state.

Results for Other $[M(NR_2)_3]^{n+}$ Complexes

According to the Walsh diagram, the d^6 configuration is the one for which the low-spin state should be most stabilized. But even for that configuration, the two electron terms, not accounted for in the Walsh diagram, result in the high-spin state being more stable than the low spin one. Consequently, the ground state is expected to result from a high-spin configuration for all the electron counts, as experimentally found for the V, Cr, and Fe complexes with bis(trimethylsilyl)amido ligands.[72] We therefore limit the study of electron configurations other than d^6 to their high-spin states. The results of the geometry optimization are shown in Table 2. Given the dependence of the d-orbital energies on the orientation of the amido ligands (Figure 2), it can easily be deduced that the occupation of the d orbitals may have an influence on the molecular conformation. Thus, for $[V(NH_2)_3]^+$ with a d^1 configuration, the orientation of the amido ligands is expected to affect the energy of the d electron little. In this case, the a_2' nonbonding combination of the ligand π orbitals should favor the coplanar conformation, as actually found in the optimized structure. Substitution of the bulkier SiH_3 groups for the hydrogen atoms takes the ligands out of the VN_3 plane ($\phi = 32°$), as previously found for the Co compounds. The larger angle found in the related experimental structures of the d^1 complexes $[Ti\{N(SiMe_3)_2\}_3]$ and $[V\{N(SiMe_3)_2\}_3]^+$ (Table 1) can be attributed to the increased bulkiness of the $SiMe_3$ groups.[13,56]

The partial occupation of the e″ orbitals in the d^3 complex $[Cr(NH_2)_3]$ should favor a nearly perpendicular conformation of the amido ligands. Such tendency is counterbalanced by the increasing energy of the a_2' orbital for larger values of ϕ, as reflected in the quite large optimized values ($\phi = 62$ and 72° for R = H and SiH_3, respectively). Such conformation is apparently good enough to avoid steric repulsions between the bulky substituents in the experimentally characterized Cr and Mo compounds ($\phi = 71$ and 68°, respectively).[15,16]

For the Mn(III) compound, the high-spin electron configuration is $(a_1')^1(e'')^2(e')^1$, for which an intermediate rotation angle should be expected, according to the Walsh diagram, which is in agreement with the experimental value of ϕ (50°). A Jahn−Teller distortion is predicted for such an electron configuration, a fact that shows up in the structure optimization of $[Mn(NH_2)_3]$. For this compound, a Y-shaped structure with approximately C_2 symmetry (**3**) is found ($\alpha = 141°$), in which two of the amido ligands are distorted from planarity. From symmetry point group arguments, one would predict distortion from the D_{3h} symmetry to be driven by A_2' or E' modes.[73] The latter corresponds into an angular distortion into a Y structure. With the bulkier SiH_3 substituents, the E′ Jahn−Teller mode destroying the trigonal axis is still present (calculated $\alpha = 140°$). It is interesting to



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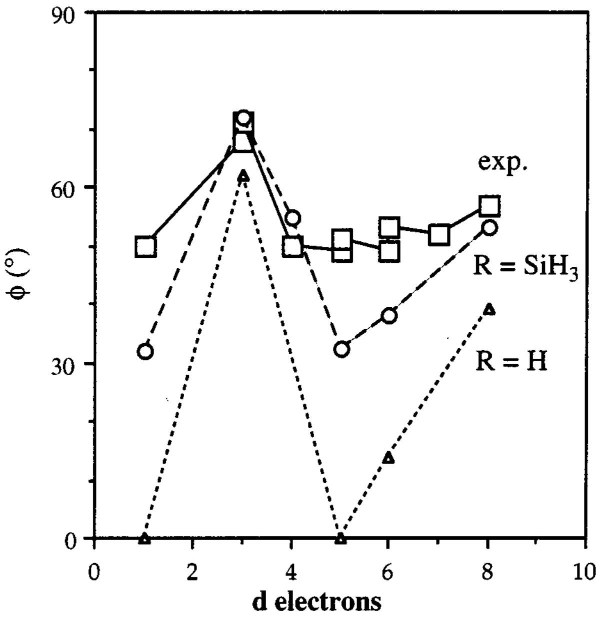

Figure 4. Rotation angles (ϕ) for $[M(NR_2)_3]$ complexes as a function of the number of valence d electrons obtained from DFT calculations for R = H (triangles) and SiH_3 (circles) compared to the experimental values (squares).

note that the structurally characterized compound with $SiMe_3$ substituents appears to be symmetric,[10] suggesting that steric effects are responsible for its symmetric structure. Single point calculations on $[Mn\{N(SiMe_3)_2\}_3]$ (see Appendix for details) clearly indicate that, contrary to what is found with the NH_2 and $N(SiH_3)_2$ ligands, in this case the asymmetric structure is strongly destabilized (some 110 kcal/mol for $\alpha = 140°$) relative to the symmetric one, thus confirming that the electronic Jahn–Teller distortion is quenched by the steric repulsion between the bulky ligands.

In a d^5 complex, $[Fe(NR_2)_3]$, the predicted conformation in the absence of important steric effects (R = H) is the coplanar one, as expected from the qualitative Walsh diagram (Figure 2). However, the presence of the SiH_3 groups forces the amido groups to adopt a rotated conformation ($\phi = 32°$), as in the case of d^1 complexes. The increased bulkiness of the $SiMe_3$ substituents in the experimentally characterized Fe compound accounts for a larger degree of rotation (49°).[9] A similar qualitative behavior was observed for the model d^6 cobalt complexes in the previous section and the corresponding experimental structure.[10] Finally, for a d^8 configuration, a large rotation angle is expected based on the Walsh diagram, as actually was found for the optimized structures of $[Ni(NR_2)_3]$ ($\phi = 39$ and 53° for R = H and SiH_3, respectively), in excellent agreement with the experimental value ($\phi = 57°$).

If all the theoretical and experimental values of the rotation angle for complexes with different electron configurations are compared (Figure 4), it becomes clear that the electronically driven changes in ϕ (calculated values for R = H) give two minima for the d^1 and d^5 configurations and two maxima for the d^3 and d^8 ions, in good agreement with the qualitative behavior expected from the Walsh diagram (Figure 2). Such electronic preference is modified by the presence of bulky substituents, yielding a threshold value of ~30° for R = SiH_3 (calculated values) and of ~50° for bulkier substituents such as $SiMe_3$ (experimental values), while the two maxima for d^3 and d^8 complexes remain. Notice that in $[M\{N(^tBu)Ar\}_3]$ (M = Ti, V; Ar = 3,5-$Me_2C_6H_3$) two of the amido groups deviate largely ($\phi = 73$ and 79°) from the expected rotation angle, a situation that is due to the coordination of the ipso and ortho carbon atoms of the phenyl rings in the two axial positions, thus relieving the coordinative unsaturation. Notice that the repulsion between the amido π lone pairs that forbids large rotation angles is highly decreased in bis(amido) and nonexistent in mono(amido) complexes, and it is in these two families that practically perpendicular amido groups can be found (Table 1). In summary, the electronically preferred conformations in tris(amido) complexes are restricted to the range $50° < \phi < 71°$ by the steric repulsion between ligands (for small angles) and by the repulsion between the ligands' lone pairs (for large angles).

The experimental M–N and N–Si bond distances are very well reproduced by the calculations with the SiH_3 substituents, except for the V^{IV} compound, for which the calculated V–N distance is too short and the N–Si distance too long. The optimized M–N–Si bond angles in the range between 119 and 123° are in excellent agreement with the experimental ones (119–120°). These bond angles are consistent with an sp^2 hybridization at the nitrogen atom. The effects on the M–N bond distance and M–N–R bond angles of substituting the hydrogen atoms in the amido ligands with silyl groups are negligible.

Metal–Ligand π Bonding. The existence of a significant interaction between the metal d-orbitals and the π lone pairs of the amido ligands can be seen by looking at the variation of the d-orbital energies with ligand rotation. Note that the π-bonding MOs (at lower energies, not shown in Figure 2) are always occupied. Hence, depending on the electron configuration, π bond orders of up to two can be accounted for by the molecular orbitals, though delocalized throughout three M–N bonds. For instance, in the singlet state of $[Co(NH_2)_3]$, with an $(a_1')^2(e'')^4$ configuration, the two π-antibonding e' orbitals are empty, and an overall bond order ($\sigma + \pi$) of 1.67 for every Co–N bond results. In contrast, for the quintet state in the coplanar conformation, the $(a_1')^2(e')^2(e'')^2$ configuration is consistent with a total π bond order of one for the set of three Co–N bonds, or a net bond order of 1.33 for each Co–N bond.

A formal π bond order of three would correspond to a formal description of three Co–N double bonds. However, this situation cannot be achieved due to the symmetry-imposed nonbonding nature of the a_2' combination of the amido lone-pair orbitals in the perpendicular conformation. One could hypothesize about the formation of π bonding via the metal p_z orbitals in the coplanar conformation (see a_2' in Figure 2, left). However, these orbitals have much higher energy than the d ones, and the interaction with the amido π orbitals is expected to be much weaker, as previously found for the Hoppe anions.[53] Hence, although strictly speaking there is some π bonding involving the metal p_z orbital, we do not consider this as a formal bond, in order to account for the difference with the much stronger π-bonding involving d orbitals. Besides, we have shown above that the coplanar conformation is highly unlikely for the usual bulky substituents of the amido group, for which the threshold rotation angle is 30°. In summary, depending on the electron configuration, formal M–N bond orders for this family of compounds may adopt values between 1 and 1.67 only.

There are important structural features that might be associated to the existence of M–N π bonding:

(1) The M–N bond distances in the amido complexes are significantly shorter (0.10 to 0.30 Å, Table 2) than in compounds of the same metal with ligands that are σ donors only such as amines[71] (Table 2), in agreement with the existence of π bonding

Table 3. Structural Data[a] for Binuclear Compounds with Tricoordinate Metal Atoms and Bridging Amido Ligands

compd	$M-N_b$	$M-N_t$	α_b	α_t	ϕ	ref
$[Cr_2(\mu\text{-}NCy_2)_2(NCy_2)_2]$	2.066	1.942	110.3	115.3	90.0	28
$[Cr_2(\mu\text{-}N^iPr_2)_2(N^iPr_2)_2]$	2.071	1.926	114.1	113.8	80.3	27
$[Mn_2\{N(SiMe_3)_2\}\{(Me_3Si)_2N\}_2Li(thf)]$	2.144	2.023	117.6	121.3	44.6	8
$[Mn_2(\mu\text{-}N^iPr_2)_2(N^iPr_2)_2]$	2.138	1.924	109.7	112.5	10.6	26
$[Mn_2\{\mu\text{-}N(SiMe_3)_2\}_2\{N(SiMe_3)_2\}_2]$	2.172	1.998	112.3	120.9	70.4	8,74
$[Mn_2(^tBuNSiMe_2OSiMe_2N^tBu)_2]$	2.164	1.993	121.9	128.3	56.2	75
$[Fe_2(^tBuNSiMe_2OSiMe_2N^tBu)_2]$	2.082	1.929	120.8	125.8	52.2	75
$[Co_2\{\mu\text{-}N(SiMe_3)_2\}_2\{N(SiMe_3)_2\}_2]$	2.062	1.915	112.7	119.0	71.8	8

[a] α_t and α_b are the R−N−R bond angles for the terminal and bridging amido groups, respectively, and ϕ is the rotation angle (**2**) of the terminal amido groups. All distances in Å, angles in degrees.

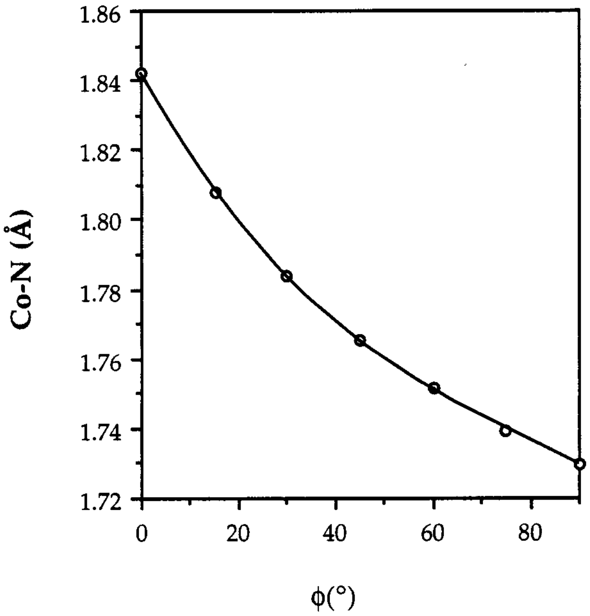

Figure 5. Optimized Co−N distance as a function of the rotation angle ϕ for the singlet state of $[Co(NH_2)_3]$.

in the former case. However, such comparison is not straightforward, since the tabulated metal−amine distances correspond to hexacoordinate complexes, and it is not clear whether the differences in bond distance should be ascribed to the difference in coordination number or to the existence of π bonding. It is more appropriate to look at those complexes with bridging and terminal amido ligands bound to the same metal atom. In those cases, the bridging group adopts an sp^3 hybridization that does not allow for metal−ligand π bonding, whereas the terminal ligand can adopt an sp^2 hybridization and give rise to metal−ligand π bonding. The features of the structural data in Table 3 clearly reflect the importance of the π bonding: (a) the M−N distances of the terminal amido groups are 0.12−0.21 Å shorter than those of the bridging groups, and (b) the R−N−R bond angles for the terminal groups (α_t) are significantly larger than those for the bridging ones (α_b) with only one exception.

(2) Depending on the electron configuration of the metal ion, significant variations in the M−N bond lengths are to be expected from changes in ligand orientation. For instance, the enhanced π^* bonding character of the e′ molecular orbitals in the coplanar conformation compared to that of the e′ molecular orbitals in the perpendicular one, results in a shortening of the calculated M−N bond distance in the latter case for the low-spin state of the d^6 compound $[Co(NH_2)_3]$ (Figure 5). An interesting feature of the π bonding in the perpendicular conformation is that the π electron density is located in the plane of the MN_3 core rather than perpendicular to it as happens in the classical examples of AB_3 molecules with π bonding, such as the nitrate or carbonate ions.

(3) Significant differences in the M−N bond lengths are also predicted for different spin states. In $[Co(NH_2)_3]$, the M−N distance for the quintet is predicted to be longer than that for the singlet state, according to the corresponding electron configurations. Such behavior is confirmed by the optimized distances of 1.842 and 1.755 Å in the quintet and singlet states of $[Co(NH_2)_3]$, respectively.

How much these complexes are stabilized by π bonding is not easy to evaluate. A rough estimate of an upper limit can be obtained by comparing the energy of the optimum rotated conformation (Figure 3) of $[Co(NH_2)_3]$ in its quintet state with that of the singlet at $\phi = 0°$ (when no significant π interaction exists). The former case is representative of the amount of π bonding encountered in the experimental structure, whereas the latter corresponds to an electron configuration having the π^* (e″, Figure 2) orbitals occupied and no net π bonding. From such comparison, an estimate of at most 21 kcal/mol per M−N bond results.

The calculated structural parameters for $[M\{N(SiH_3)_2\}_3]$ (Table 2) are in excellent agreement with the experimental ones. By comparing the results obtained for $[M(NR_2)_3]$ with the lighter (R = H) and bulkier (R = SiH_3) substituents, one can obtain some idea of the steric effects on the structural parameters other than the ligand rotation discussed in the previous section. The M−N distance is seen to be little affected by the bulkiness of the substituents, resulting in a lengthening by, at most, 0.024 Å. Substitution of the H atoms by the bulkier SiH_3 groups also results in an increased M−N−R bond angle, in excellent agreement with the experimental values for the $SiMe_3$ substituents.

Since the empirical electron-counting (18-electron and 16-electron) rules that apply to organometallic and carbonyl complexes can be explained within the framework of molecular orbital theory by invoking only σ metal−ligand interactions, it is worth spending a little effort in analyzing the possible applicability of electron-counting rules in compounds with π-donor ligands, such as those studied here. Consider the case of $[Co(NR_2)_3]$: the six d electrons of Co(III), together with the six σ electrons donated by three amido ligands, give a total of 12 valence electrons for the Co atom. Taking into account that there is a net donation of four π electrons in the singlet state, the resulting electron count is 16. Therefore, this compound in its singlet state might be said to comply with the 16-electron rule that applies to planar complexes. However, for the more stable quintet state in the parallel conformation, the molecular orbitals of π^*(M−N) character (e″) are partially occupied. Hence, the net π donation is of only two electrons, and the total electron count is 14, i.e., an electronically unsaturated situation. Electronic unsaturation is still clearer for other metal ions with configurations d^1−d^5, for which even donation of four π electrons by the amido ligands is not enough to reach 16 valence electrons. Hence, the 16-electron rule has little predictive value

Table 4. Calculated (DFT) Atomic Spin Densities for $[M(NR_2)_3]$ (R = H, SiH_3) in the Optimized Geometry of Their High-Spin States for Metals with d^n Configuration and *t* Unpaired Electrons

			R = H			R = SiH_3			
M	*n*	t	M	N	H	M	N	Si	H
V	1	1	1.202	−0.070	0.001	1.131	−0.041	0.001	−0.036
Cr	3	3	3.282	−0.124	0.015	3.203	−0.097	0.014	0.000
Mn	4	4	3.989	−0.050	0.014	3.972	−0.022	0.008	0.003
				0.053[a]	0.002[a]		−0.007[a]	0.003	0.003
Fe	5	5	4.013	0.325	0.002	4.008	0.292	−0.009	0.00
Co	6	4	2.793	0.397	0.002	2.783	0.365	−0.010	0.01
Ni	8	2	1.571	0.148	−0.002	1.545	0.140	−0.008	0.004

[a] Value for the unique N atom in the asymmetric structure **3**.

when applied to single-face π-donor ligands, even if π donation is considered for electron counting.

Spin-Density Distribution. Understanding the distribution of the spin density in a paramagnetic transition-metal complex is useful in interpreting the NMR data and to compare with those values obtained from polarized neutron diffraction. For those reasons, we present here the calculated values of the atomic-spin densities and briefly discuss them in the light of qualitative criteria.[76] Some features of the calculated spin-density distributions (Table 4) are found to be common for those compounds with R = H or SiH_3:

(1) The largest spin density is located at the metal atom, in agreement with the formal description of these complexes as d^n. Deviations from the number of unpaired electrons can be attributed to spin delocalization or polarization (see below).

(2) For those metal ions with empty π^* orbitals (e″ for $\phi \approx 0°$, e′ for $\phi \approx 90°$), the spin density is slightly larger than the number of unpaired electrons (V^{IV}, Cr^{III}). This results from the formal nonbonding character of the occupied d orbitals which precludes significant delocalization of the positive spin to the ligands, combined with the spin polarization of the occupied bonding MOs with participation of the metal d orbitals. In contrast, for those metal ions with unpaired electrons in the π^* MOs (Mn^{III}, Fe^{III}, Co^{III}, and Ni^{II}), the spin density is significantly smaller than the number of unpaired electrons, as a result of the delocalization of such MOs.

(3) The spin density at the N atoms is small and negative for those complexes for which no significant spin delocalization exists (V^{IV} and Cr^{III}), as a result of the spin-polarization mechanism. In contrast, a positive spin density is found at the N atoms for those compounds with one unpaired electron in each of the two π^* (e′) MOs (i.e., Fe^{III}, Co^{III}, and Ni^{II}). In the case of Mn^{III}, with three unpaired electrons in nonbonding MOs and one unpaired electron in the π^* MO, the delocalization and polarization effects approximately cancel out, resulting in a small spin density at the N atoms. Furthermore, in the C_2 structure of the Mn complex (**3**), the N atom at a shorter distance from Mn shows a positive spin density consistent with spin delocalization, whereas spin polarization predominates for the N atoms at greater distances, and a negative spin density results.

(4) The spin densities of the H atoms of the NH_2 and $N(SiH_3)_2$ ligands are not easy to rationalize, since they result from the combined effects of spin delocalization and polarization. On the other hand, the spin density at the Si atoms always has the opposite sign to that at the N atoms, indicating that the polarization mechanism is predominant in this case.

Concluding Remarks

The high-spin configuration in the amido complexes is expected to be more stable than the low spin one in all cases, the latter being not thermally accessible at room temperature. The separation between high- and low-spin states is controlled by the orientation of the amido ligands.

The orientation of the NR_2 ligands depends on combined electronic and steric effects. The electronic effects most favor the rotated conformation for the d^3, d^4, and d^8 ions, and the coplanar conformation for the d^1 and d^5 ions. Steric factors prevent the coplanar conformation and set a computationally estimated threshold value of the rotation angle of about 30° for the $N(SiH_3)_2$ ligand. On the other hand, repulsion between the π lone pairs of the amido groups prevents a perpendicular orientation ($\phi \approx 90°$). A threshold rotation angle is found in the experimental data for the bulkier $N(SiMe_3)_2$ ligand, of about 50°, and the maximum value of ϕ in tris(amido) complexes is 71°.

The calculated M−N distances for the optimized structures are in good agreement with the experimental values. Those distances are clearly shorter than those in amino complexes, in keeping with the partial double-bond character attributed to the existence of metal−ligand π bonding. For the Mn complex, a Jahn−Teller distortion is predicted for the NH_2 and $N(SiH_3)_2$ ligands, but the bulkiest ligand, $N(SiMe_3)_2$ is found to give a symmetric complex, allowing us to conclude that the Jahn−Teller distortion is quenched by steric effects.

Since these compounds are electronically and coordinatively unsaturated, they might be expected to be able to interact with Lewis bases, since the p_z orbital is well suited to accept electron density from further donors, thus forming tetracoordinate complexes. The existence of bulky substituents that favor a quasiperpendicular conformation probably creates a steric protection at both sides of the molecular planes that should lower their lability, allowing the nucleophilic attack of only small molecules, as in the coordination of dinitrogen[59] or CO[77] to $[Mo\{N(^tBu)Ar\}_3]$ (Ar = 3,5-dimethylphenyl), giving place to interesting subsequent reactions, or in the atom abstraction reactions observed by Cummins and coworkers.[78,79] For more information on the reactivity of these species, the reader is referred to the recent comprehensive review of Cummins.[5,95] Another consequence of the coordinative insaturation is the secondary bonding between the Fe atom and two fluoro substituents of the amido ligand above the otherwise trigonal planar FeN_3 skeleton in $[Fe\{N(C[CD_3]_2Ph)(2\text{-}F,5\text{-}MePh)\}_2py]$[80]

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or the η^3 coordination mode of the $N(^tBu)Ar$ ligand in the V and Ti compounds,[14,81,82] in which the ipso and ortho carbon atoms of the phenyl ring each occupy an axial position at a short distance (2.5 Å) to the metal atom.

The spin-density distribution indicates delocalization to the donor atoms for the metal ions with d^4-d^8 configurations, but not for those with d^1-d^3 configurations, in agreement with the M−N nonbonding nature of the a_1' and e'' molecular orbitals and the π^* character of the e' orbitals.

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Appendix: Computational Details

Molecular orbital calculations of the extended Hückel type[83,84] were carried out with the CACAO program,[85] using the modified Wolfsberg−Helmholz formula[86] on the anionic complexes $[Co(NH_x)_3]^{n-}$ ($x = 0, 2, 3$; $n = 6, 0, -3$, respectively), with the atomic parameters taken from the literature.[84,87] The bond distances used in the idealized symmetric models were Co−N = 1.872 and N−H = 1.010 Å.

All DFT calculations have been performed with the Gaussian94 program.[88] Local density calculations were carried out using the Slater exchange[89] and Vosko, Wilk, and Nusair correlation[90] functionals. Generalized Gradient Corrections have been introduced using the Lee, Yang, and Parr correlation part[91] and the adiabatic connection method with three parameters proposed by Becke (abbreviated B3LYP)[92] to incorporate an orbital-dependent exchange contribution. An all-electron basis set[93,94] was used according to the following contraction scheme: (311) for H, (62 111/411) for N and C, (5311/511) for Si, and (842 111/6311/411) for the transition metals. For the model compounds with NH_2 and $N(SiH_3)_2$ ligands, geometry optimizations were carried out imposing only the restriction that the NR_2 and SiH_3 groups were symmetric in their bond distances and angles. Single-point calculations were carried out for $[Co\{N(SiMe_3)_2\}_3]$ at rotation angles $\phi = 15$, 45, 60, and 90° for the quintet state and at 15, 45, and 90° for the singlet state. For $[Mn\{N(SiMe_3)_2\}_3]$, single-point calculations were performed in the symmetric and Y-distorted structures (**3**) by imposing $\alpha = 120$, 130, and 140°, keeping the rotation angle as optimized for the R = SiH_3 case ($\phi = 55°$). The rest of the geometry was kept frozen as in the experimental structures[10] for both complexes.

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