

A Theoretical Investigation of the Nonrigid Six-Coordinate Compounds [Mo(R)F₅], [W(R)F₅], and Related Compounds

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Abstract: Density functional calculations for [M(CH₃)F₅], [M(CF₃)F₅], [M(CH₃S)F₅], and [M(CF₃S)F₅] (M=Mo, W) show that they are expected to be nonrigid molecules, with energy barriers for the octahedral–trigonal-prismatic interchange as low as 7.2 kJ mol⁻¹. The ground state for the CH₃⁻ and CF₃⁻ compounds is trigonal prismatic, for the CH₃S⁻ and CF₃S⁻ compounds, (distorted) octahedral. All calculated compounds [M(C₆F₅)_nF_{6-n}] (M=Mo, W) have a trigonal-prismatic ground state, whereas the situation for [M(C₆H₅)_nF_{6-n}] (M=Mo, W) is more complex.

Keywords: density functional calculations • fluorides • fluxionality • molybdenum • tungsten

Introduction

The principle structure for the vast majority of six-coordinate compounds is octahedral. However, there are three classes of six-coordinate compounds that deviate from this symmetry: a) Jahn–Teller distorted complexes, b) distortion by nonbonding electron pairs (pseudo-seven-coordinate compounds), and c) d⁰, d¹, and d² metal complexes with only σ-bonding ligands, such as [Mo(CH₃)₆]. The latter have a completely different structure, namely C_{3v}-distorted trigonal prismatic.^[1] The latter phenomenon was first postulated in 1986 by Eisenstein^[2] and subsequent theoretical work confirmed this.^[3,4] Landis offered a very simple explanation, namely that, in the case of σ-only bonded ligands, sd⁵ hybridization should generate bond angles of 55° and 180–55=125°, which excludes the octahedron.^[5] Values close to these extreme bond angles were observed recently in matrix-isolated WH₆ (62.4 and 114.7°).^[6] This entire phenomenon is now theoretically well understood.^[7,8]

If the C_{3v}-distorted trigonal prism is the principal structure for [Mo(CH₃)₆], [W(CH₃)₆], etc. (Figure 1), then an explanation is required for the octahedral structure of isoelectronic

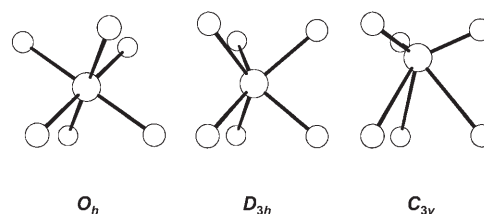


Figure 1. Structures of six-coordinate molecules: octahedron (*O_h*), trigonal prism (*D_{3h}*), and *C_{3v}*-distorted trigonal prism.

[MoF₆] and [WF₆]: a) The metal–F bonds are much shorter than metal–C–ligand bonds, resulting in a stronger interligand-repulsion effect. b) Partial ligand-to-central atom back-donation raises the electron density at the central metal atom to beyond 12.^[8]

Nevertheless, it seems that [MoF₆] and [WF₆] have a low-lying transition state with regular trigonal-prismatic structure, as has been calculated on two occasions by using various methods.^[8,9] This state is only ≈25 kJ mol⁻¹ ([MoF₆]) or ≈42 kJ mol⁻¹ ([WF₆]) higher in energy than the octahedral ground state. This implies that, at elevated temperatures, both hexafluorides should undergo intramolecular interchange of the fluorine atoms by an octahedral–trigonal-prismatic–octahedral twist mechanism, sometimes called a Bailar twist mechanism. This has not yet been established experimentally for [MoF₆] and [WF₆], because the convenient dynamic NMR method fails, due to the equivalence of all fluorine atoms during the dynamic process.

We were able, however, experimentally (and theoretically) to establish this dynamic process for derivatives of

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[MoF₆] and [WF₆], in particular for compounds of the type [Mo(RO)F₅] and [W(RO)F₅] (R = CF₃CH₂⁻, C₆F₅⁻, and (CF₃)₃C⁻).^[9] The introduction of these oxygen ligands raises the energy separation between the octahedral ground state and the trigonal-prismatic state by up to ≈52 kJ mol⁻¹ for [Mo(RO)F₅] and ≈63 kJ mol⁻¹ for [W(RO)F₅], so that intermolecular ligand-exchange is only observable at fairly high temperatures.^[9] Although there are several geometrical possibilities for interconverting an octahedron into a trigonal prism and vice versa, it has been shown that the Bailar twist represents the minimal-distortion pathway, and the experimental structures of hexakis (thiolato), tris(bidentate), and encapsulated hexacoordinate complexes conform closely to this pathway.^[10,11]

Deviations from ideal octahedral or trigonal-prismatic structures are in many cases difficult to describe. A crude picture is obtained if only bond angles are regarded. If three angles are close to 180°, and twelve in the vicinity of 90°, the structure is clearly close to octahedral. An ideal trigonal prism, in which all interligand distances are equal, would have six angles of 135.6° and nine of 81.8°. Another simplified model considers the Bailar twist angle of 60° for the octahedron and 0° for the trigonal prism, or deviations thereof. However, this possibility is restricted to molecules that have some remaining symmetry. In completely irregular structures, different twist angles can be defined.

A comprehensive description has been offered in references [10, 11]. An irregular six-coordinate structure is defined by six bond lengths and nine bond angles. With these data, the program SHAPE^[11] generates a quantitative description of the structure in a two-dimensional symmetry map (see Figure 5 below).

In the present work, we have looked for species that have very similar energies for the octahedral and trigonal-prismatic structures. If the energy for both structures was coincidentally the same, and if there was no significant barrier between the states, the structure of the molecule could not be described by a static model.

Experimentally, not much is known about mixed-substituted compounds: [W(CH₃)₅Cl], [Mo(CH₃)₅OCH₃], and [Mo(CH₃)₄(OCH₃)₂] are all trigonal prismatic, whereas [W(CH₃)₃Cl(OCH₃)₂] is octahedral.^[12] Another compound of interest here, [W(CH₃)Cl₅], has been prepared several times, but has not yet been characterized structurally.^[13,14] Here, we investigate the molybdenum and tungsten fluorides [Mo(R)_nF_{6-n}] and [W(R)_nF_{6-n}]. As auxiliary ligands to replace one or several fluorine atoms in [MoF₆] and [WF₆], we chose CH₃⁻, CF₃⁻, C₆H₅⁻, C₆F₅⁻, CH₃-S⁻, and CF₃-S⁻.

In a similar study, Kaupp performed calculations for compounds of the type [W(CH₃)_nCl_{6-n}]. He observed that for higher substitutions of chlorine, such as in [W(CH₃)₂Cl₄], [W(CH₃)Cl₅], and [WCl₆], the octahedral structure prevails, whereas for the higher-methylated products, the trigonal-prismatic arrangement is favored.^[15]

The energy separation between octahedral and trigonal-prismatic states is expected to be smaller for fluorine compounds than for the chlorides, as mentioned by Kaupp.^[15]

Furthermore, the computations are less time-consuming, they can be performed at higher accuracy for the lighter-atom combinations, and fluorides are expected to be more stable than the heavier halides. Nevertheless, all attempts to synthesize any of the computed compounds have failed. A short description of our fruitless attempts is presented below.

Results

The method chosen for modeling the compounds is DFT in the widely used variation of Becke,^[16] and Lee, Yang, and Parr.^[17] This method delivered very satisfying structural results for [Mo(CH₃)₆], [W(CH₃)₆], and [Re(CH₃)₆],^[18,19] as well as fairly good predictions of the trigonal twist barrier in [Mo(RO)F₅] and [W(RO)F₅].^[9]

Structures and energies of [Mo(CH₃)F₅], [W(CH₃)F₅], [Mo(CF₃)F₅], and [W(CF₃)F₅]: The introduction of one methyl or trifluoromethyl group into [MoF₆] and [WF₆] changes the ground-state structure from octahedral to trigonal prismatic (Figure 2 and Table 1). The averaged twist angle is 0° in all compounds and the symmetry is always C_{3v}. The octahedron is now a transition state, as evidenced by one imaginary frequency (Tables 1 and 2). This observation alone is surprising. The difference in energy is small, although the molybdenum compounds have a slightly larger energy difference, which is expected, as [MoF₆] is already closer in energy than [WF₆] to trigonal prismatic (Table 2). There remains the subtle question of whether the compounds are trigonal prismatic (as [Re(CH₃)₆]), or C_{3v}-distorted trigonal prismatic (as [Mo(CH₃)₆] and [W(CH₃)₆]) structures. If C_{3v}-distorted trigonal prismatic, then the methyl or trifluoromethyl group should be positioned within the hemisphere with elongated

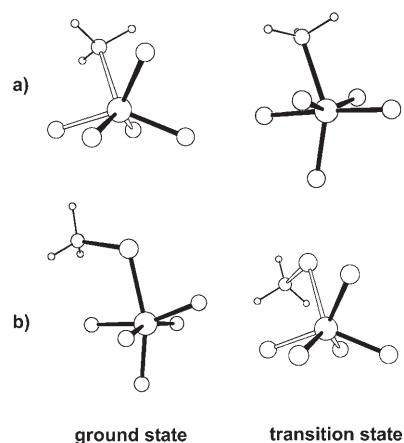


Figure 2. Calculated structures of a) [Mo(CH₃)F₅], trigonal-prismatic ground state (left) and distorted-octahedral transition state (right); b) [Mo(CH₃S)F₅], distorted-octahedral ground state (left) and trigonal-prismatic transition state (right). The structures of [W(CH₃)F₅], [Mo(CF₃)F₅], [W(CF₃)F₅], [W(CH₃S)F₅], [Mo(CH₃S)F₅], and [W(CF₃S)F₅] are very similar (Tables 1 and 3).

Table 1. Results of DFT calculations for the trigonal-prismatic ground state and octahedral transition state $[M(\text{CH}_3)_5\text{F}_5]$ and $[M(\text{CF}_3)_5\text{F}_5]$ ($M = \text{Mo}, \text{W}$). Bond lengths in [pm], bond angles in [°].

	[MoXF ₅]		[W XF ₅]	
	X = CH ₃ -	X = CF ₃ -	X = CH ₃ -	X = CF ₃ -
trigonal-prismatic ground state				
M-F	187.8–188.7	186.3–187.8	189.0–189.7	187.6–188.4
M-C	215.0	224.4	214.0	224.6
C-M-F	75.4/81.5/128.6	74.2/78.2/130.6	76.0/83.5/128.1	74.5/80.1/130.2
F-M-F	79.7–93.9/133.1,140.7	80.6–92.0/129.9,129.9	79.1–93.9/134.3,140.0	80.1–91.7/131.1,141.1
octahedral transition state				
M-F	186.4–193.0	185.2–192.3	187.3–191.1	186.2–190.8
M-C	214.1	222.4	213.5	222.5
C-M-F	74.8–108.2/150.6	72.6–116.9/149.1	77.3–96.2/155.7	75.7–110.3/153.6
F-M-F	75.8–101.2/157.8,177.0	76.5–105.2/149.7,170.5	78.3–108.1/169.1,173.6	78.0–102.1/155.8,174.0

Table 2. Energies + zero-point energy (Z.P.E) [a.m.u] and lowest vibrational frequency (in parentheses, [cm⁻¹]) for [MXF₅] derivatives ($M = \text{Mo}, \text{W}$; X = CH₃-, CF₃-, CH₃S-, CF₃S-).

	[MoXF ₅]		[W XF ₅]	
	X = CH ₃ -	X = CF ₃ -	X = CH ₃ -	X = CF ₃ -
trigonal prismatic, Gs ^[a]	-607.581770 (70.76)	-905.396589 (55.18)	-606.535676 (40.46)	-904.348097 (40.32)
octahedral, Ts ^[b]	-607.573662 (115.68 <i>t</i>)	-905.390411 (90.65 <i>t</i>)	-606.532377 (106.74 <i>t</i>)	-904.344166 (81.95 <i>t</i>)
ΔE [kJ mol ⁻¹]	21.31	16.24	8.67	10.34
octahedral, Gs ^[a]	X = CH ₃ S-	X = CF ₃ S-	X = CH ₃ S-	X = CF ₃ S-
trigonal prismatic, Ts ^[b]	-1005.826729 (59.82)	-1303.635647 (35.64)	-1004.783166 (52.69)	-1302.595198 (33.60)
ΔE [kJ mol ⁻¹]	-1005.824001 (20.18 <i>t</i>)	-1303.631493 (40.51 <i>t</i>)	-1004.776542 (43.42 <i>t</i>)	-1302.58643 (51.61 <i>t</i>)
	7.16	10.93	17.42	23.03

[a] Gs = Ground state. [b] Ts = Transition state.

bonds and smaller angles between the three ligands. The SHAPE analysis indicates a small C_{3v} distortion (see Figure 5 below).

Remarkably, the angle between the two fluorine atoms opposite to the CH₃ or CF₃ groups is always larger than 90°, whereas all other angles between ligands of the same hemisphere are smaller than 90°. A satisfying explanation for this cannot be given. Not unexpectedly, the Mo-C and W-C bond lengths are longer for CF₃ compounds than for CH₃ compounds, as is usually observed in compounds of electron-poor central atoms.

The structures of the octahedral transition states are actually quite distorted, as has also been observed for cases of octahedral ground states if the trigonal-prismatic ground state has a similar energy. The distortion of the octahedral transition state in $[\text{Mo}(\text{CH}_3)_5\text{F}_5]$ and similar molecules is greater if the energy of the octahedral state is close to that of the trigonal-prismatic ground state. It can be anticipated that compounds with higher contents of methyl groups, such as $[\text{Mo}(\text{CH}_3)_2\text{F}_4]$ or $[\text{Mo}(\text{CH}_3)_3\text{F}_3]$, will have larger energy differences between the trigonal-prismatic structures and the octahedral transition states.

Structures and energies of $[\text{Mo}(\text{CH}_3\text{S})_5\text{F}_5]$, $[\text{W}(\text{CH}_3\text{S})_5\text{F}_5]$, $[\text{Mo}(\text{CF}_3\text{S})_5\text{F}_5]$, and $[\text{W}(\text{CF}_3\text{S})_5\text{F}_5]$: In contrast to the species discussed above, all four of these molecules are octahedral, as was also found for $[\text{Mo}(\text{RO})_5\text{F}_5]$ and $[\text{W}(\text{RO})_5\text{F}_5]$ ^[9]

(Figure 2 and Table 3). However, the difference in energy between the octahedral structure and the trigonal-prismatic transition state is smaller in the former two cases (Table 2). This can be attributed to the lower electronegativity of sulphur relative to oxygen. Furthermore, molybdenum compounds are even less rigidly octahedral than tungsten compounds, which follows the known trend.

All octahedral structures are quite distorted. The three bond angles, which are 180° in a regular octahedron, are calculated to be 159.8–165.8° for the molybdenum compounds, and 164.9–176.0° for the tungsten compounds. Again, the closer in energy the trigonal-prismatic structure, the more distorted the octahedral structures. The type of distortion in these octahedral ground states resembles closely the distortion of the octahedral transition states in compounds like $[\text{Mo}(\text{CH}_3)_5\text{F}_5]$, and the trigonal-prismatic transition state of the $[\text{Mo}(\text{RS})_5\text{F}_5]$ and $[\text{W}(\text{RS})_5\text{F}_5]$ compounds is similar in every detail to the ground state of $[\text{Mo}(\text{CH}_3)_5\text{F}_5]$.

Structures of phenyl- and perfluorophenyl-substituted molybdenum and tungsten fluorides: Due to the larger size of phenylated compounds, only ground-state structures were calculated. As described below, the two groups C₆H₅- and C₆F₅- differ markedly in their influence on the structure. Because the resulting overall picture is simpler for the C₆F₅- substituent, we discuss these compounds first. With the exception of $[\text{W}(\text{C}_6\text{H}_5)_5\text{F}_5]$ and $[\text{W}(\text{C}_6\text{F}_5)_5\text{F}_5]$, only molyb-

Table 3. Results of DFT calculations for the octahedral ground state and trigonal-prismatic transition state $[M(\text{CH}_3\text{S})\text{F}_5]$ and $[M(\text{CF}_3\text{S})\text{F}_5]$ ($M = \text{Mo}, \text{W}$). Bond lengths in [pm], bond angles in $^\circ$.

	[MoXF ₅]		[WXF ₅]	
	X = CH ₃ S ⁻	X = CF ₃ S ⁻	X = CH ₃ S ⁻	X = CF ₃ S ⁻
octahedral ground state				
M–F	187.9–189.8	187.6–188.5	188.0–190.5	187.3–189.7
M–S	234.4	238.1	235.3	239.6
S–C	181.8	185.7	182.9	185.5
S–M–F	80.1–97.9/162.0	78.8–97.6/165.8	83.4–97.7/167.9	82.0–95.7/176.0
F–M–F	81.8–116.3/160.1,161.9	84.2–115.4/159.8,160.4	84.0–106.7/164.9,168.7	84.5–101.9/167.4,167.9
C–S–M	111.4	111.1	111.6	109.2
trigonal-prismatic transition state				
M–F	188.2–189.9	187.5–189.8	189.2–190.6	188.5–190.4
M–S	234.0	237.6	235.3	239.2
S–C	182.1	186.1	183.0	185.9
S–M–F	74.0/85.7/128.3	72.0/87.2/128.6	74.4/86.7/128.5	72.3/87.2/128.9
F–M–F	79.9–91.7/135.4,138.6	80.1–89.8/135.1,137.9	79.5–91.2/136.0,137.7	79.6–89.3/135.4–137.2
C–S–M	104.9	109.2	104.7	108.8

denum species were calculated. $[\text{Mo}(\text{C}_6\text{F}_5)\text{F}_5]$ and $[\text{W}(\text{C}_6\text{F}_5)\text{F}_5]$ are both trigonal prismatic, and the bond angles are quite similar to the corresponding CH_3^- and CF_3^- compounds (Figure 3 and Table 4).

The (averaged) twist angle is 2° for $[\text{Mo}(\text{C}_6\text{F}_5)\text{F}_5]$ and 5.3° for $[\text{W}(\text{C}_6\text{F}_5)\text{F}_5]$, indicating the tendency of tungsten compounds to shift, even if slightly, to the octahedral situation.

For trigonal-prismatic $[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$, three isomers are expected. These are energetic minima on the hypersurface, with a variation in energy differences of only 36.3 kJ mol^{-1} (Table 5). For sterical reasons, the isomer with approximate C_2 symmetry and two C_6F_5 groups

in different hemispheres has, as expected, the lowest energy. This is an indication that sterical congestion now plays an

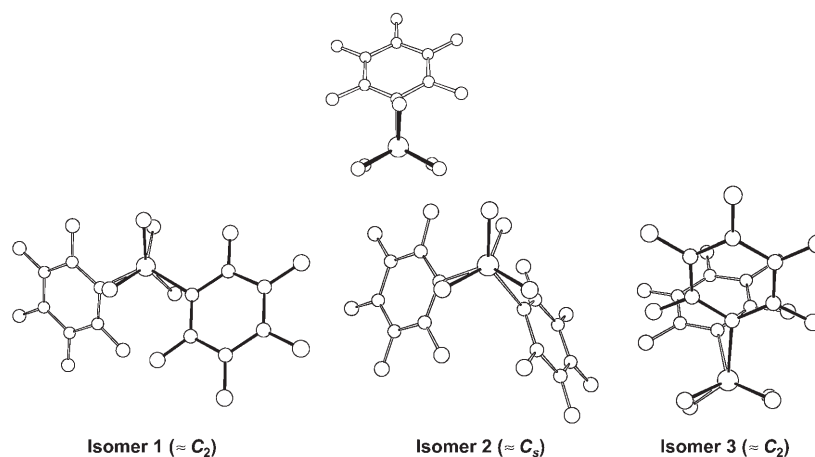


Figure 3. Calculated structures of trigonal-prismatic $[\text{Mo}(\text{C}_6\text{F}_5)\text{F}_5]$ (top) and the three isomers of $[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ (bottom), isomer 1 being the most stable. The structure of $[\text{W}(\text{C}_6\text{F}_5)\text{F}_5]$ is very similar (Table 4). Numerical values for two isomers of $[\text{Mo}(\text{C}_6\text{F}_5)_3\text{F}_3]$ and for $[\text{Mo}(\text{C}_6\text{F}_5)_4\text{F}_2]$, all trigonal prismatic, are also given in Table 4.

Table 4. Results of DFT calculations for the trigonal-prismatic ground states of $[\text{W}(\text{C}_6\text{F}_5)\text{F}_5]$ and $[\text{Mo}(\text{C}_6\text{F}_5)_n\text{F}_{6-n}]$ ($n \geq 1$). Bond lengths in [pm], bond angles in $^\circ$.

	$[\text{Mo}(\text{C}_6\text{F}_5)\text{F}_5]$	$[\text{W}(\text{C}_6\text{F}_5)\text{F}_5]$	$[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ (isomer 1, $\approx C_2$)	$[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ (isomer 2, $\approx C_3$)
M–F	187.1–189.3	188.2–190.0	188.3–190.4	188.2–189.4
M–C	212.8	214.2	212.2, 212.3	215.1, 218.1
C–M–C	–	–	134.3	81.5
C–M–F	77.1/84.1,84.5/129.3, 131.6	77.3/84.9,85.0/126.8, 133.8	77.9–90.6/125.8	78.6–84.2/118.6–145.9
F–M–F	79.0–90.3/133.7–138.1	78.7–90.5/131.6–140.3	79.9–81.4/127.1–146.2	79.4–89.5/123.2,149.8
	$[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ (isomer 3, $\approx C_2$)	$[\text{Mo}(\text{C}_6\text{F}_5)_3\text{F}_3]$ (isomer 1)	$[\text{Mo}(\text{C}_6\text{F}_5)_3\text{F}_3]$ (isomer 2)	$[\text{Mo}(\text{C}_6\text{F}_5)_4\text{F}_2]$
M–F	187.3,189.0	188.0–192.6	186.5–190.8	187.7, 190.1
M–C	215.9	211.5–220.1	215.0–219.0	209.2–227.9
C–M–C	76.2	95.1/126.4/129.4	77.8/79.7/131.2	77.2–92.8/124.2–135.1
C–M–F	80.8–85.4/123.8, 139.3	76.4–91.3/128.2,140.7	80.6–87.2/131.5–136.9	76.4–97.5/116.8, 131.1
F–M–F	80.3/86.5/135.3, 144.8	77.4/136.9, 142.1	79.0/82.9/137.5	149.0

Table 5. Energies + zero-point energy (Z.P.E.) and lowest vibrational frequency, ν , for the ground state of phenyl-substituted Mo and W fluorides.

Molecule	Energy + Z.P.E. [a.m.u]	ΔE [kJ mol ⁻¹] ^[a]	ν [cm ⁻¹]
[Mo(C ₆ H ₅)F ₅], tp ^[b]	-799.304256		31.44
[W(C ₆ H ₅)F ₅], oct. ^[b]	-798.261443		12.79
[Mo(C ₆ F ₅)F ₃], tp	-1295.617031		15.58
[W(C ₆ F ₅)F ₃], tp	-1294.575079		4.97
[Mo(C ₆ F ₅) ₂ F ₄], tp isomer 1, $\approx C_2$	-1923.652531	0	17.08
[Mo(C ₆ F ₅) ₂ F ₄], tp isomer 2, $\approx C_s$	-1923.638701	36.33	19.61
[Mo(C ₆ F ₅) ₂ F ₄], tp isomer 3, $\approx C_2$	-1923.647415	13.44	26.64
[Mo(C ₆ F ₅) ₃ F ₃], tp isomer 1	-2551.671066	0	14.55
[Mo(C ₆ F ₅) ₃ F ₃], tp isomer 2	-2551.667638	9.00	18.93
[Mo(C ₆ F ₅) ₄ F ₂], tp	-3179.684616		8.14
[Mo(C ₆ H ₅) ₂ F ₄], oct. isomer 1, C _s	-931.018799	0	29.84
[Mo(C ₆ H ₅) ₂ F ₄], tp isomer 2, C _s	-931.009140	25.37	23.16
[Mo(C ₆ H ₅) ₂ F ₄], tp isomer 3, C ₂	-931.009259	25.08	8.46

[a] Relative to isomer 1. [b] tp = trigonal-prismatic, oct. = octahedral.

increasing role. The (averaged) twist angles of 12.1–19.8° can also be interpreted similarly.

The compounds [Mo(C₆F₅)₃F₃] could also exist in three different isomers. Two of these were found as energetic minima and both are trigonal prismatic. One of the three possible cases of [Mo(C₆F₅)₄F₂] was also calculated, and again, this is trigonal prismatic. To the best of our knowledge, no such C₆F₅-substituted compounds are known.

The situation for C₆H₅-substituted compounds is more complex (Figure 4 and Table 6). [Mo(C₆H₅)F₅] is trigonal prismatic, although with a fairly large (averaged) twist angle of 18.9°. The ground state of [W(C₆H₅)F₅], however, is octahedral. This is certainly distorted, but in the same manner as the transition state of [Mo(CH₃)F₅]. In particular, the C-W-F angle is narrowed from the ideal 180° to 153.7°.

The situation for the compounds of the composition [Mo(C₆H₅)₂F₄] is even more complex. If the starting geometry in the optimization procedure is set as an assumed ideal *trans* octahedral structure, the molecule finally refines to a fairly distorted, but still octahedral, *trans* structure. If a *cis* octahedral structure is assumed as the starting arrangement, then the end result is an almost perfect trigonal-prismatic structure, in which the two C₆H₅ groups occupy positions in the same hemisphere. The third isomer is also trigonal prismatic. The *trans* octahedral isomer is ≈ 25 kJ mol⁻¹ more stable than the trigonal-prismatic isomers.

Again, it should be noted that such phenyl derivatives have not yet been isolated. The closest relatives to these compounds may be [Ta(C₆H₅)₆]⁻ and [Ta(C₆H₄-4-CH₃)₆]⁻, which are both fairly regular trigonal-prismatic species, according to their crystal structures.^[20]

Attempts to prepare [M(C₆H₅)_nF_{6-n}], [M(C₆F₅)_nF_{6-n}], and [M(CF₃S)_nF_{6-n}] (M = Mo, W): [Zn(C₆H₅)₂] reacts with [MoF₆] or [WF₆], although

probably under reduction, to form brown, unidentifiable solids. Freshly sublimed [Li(C₆H₅)] does not react in hexane with [WF₆], even at room temperature. [MoF₆] gives only some coloration to red or orange at -40°C. [WF₆] and [MoF₆] do not react with [B(C₆F₅)F₂],^[21] [Si(C₆H₅)F₃],^[22] [Si(C₆F₅)F₃],^[22,23] or [Sn(C₆F₅)-(CH₃)₃]^[24] at temperatures up to +40°C. [MoF₆] and [Hg-(SCF₃)₂]^[25] form small amounts of CF₃-S-S-CF₃ at room temperature.

In addition, [WCl₆] and [Li(C₆H₅)] in (C₂H₅)₂O do not react at room temperature within 24 h, whereas [Si(C₆H₅)Cl₃] results in reduction of [WCl₆].

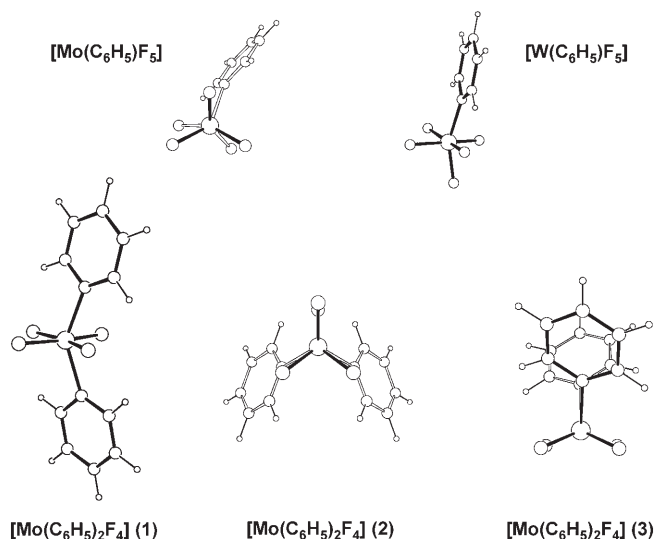


Figure 4. Top, calculated structures of trigonal-prismatic [Mo(C₆H₅)F₅] and distorted-octahedral [W(C₆H₅)F₅]. Bottom, the three isomers [Mo(C₆H₅)₂F₄]: (1) = octahedral (*trans*, C_s), (2) = trigonal prismatic (C_s), and (3) = trigonal prismatic (C₂).

Table 6. Results of DFT calculations for [W(C₆H₅)F₅] and [Mo(C₆H₅)_nF_{6-n}] (n = 1, 2). Bond lengths in [pm], bond angles in [°].

	[Mo(C ₆ H ₅)F ₅] ^[a]	[W(C ₆ H ₅)F ₅] ^[b]	
M-F	188.5–189.4	188.6–191.3	
M-C	211.7	210.9	
C-M-F	78.4–88.3/113.3–142.0	80.3–101.0/153.7	
F-M-F	79.2–96.1/121.5–154.6	80.4–108.9/164.7, 166.1	
	[Mo(C ₆ H ₅) ₂ F ₄] (C _s) ^[b]	[Mo(C ₆ H ₅) ₂ F ₄] (C _s) ^[a]	[Mo(C ₆ H ₅) ₂ F ₄] (C ₂) ^[a]
M-F	189.1–195.4	189.6–190.6	189.0–190.7
M-C	209.2	214.9	214.9
C-M-C	142.2	82.1	74.4
C-M-F	82.9–112.3	78.0–80.7/129.9, 133.7	80.7, 83.3/128.6, 130.7
F-M-F	82.8, 84.4/163.3, 164.9	78.7–91.2/138.7	80.0, 88.7/140.6, 146.2

[a] Trigonal-prismatic ground state. [b] Octahedral ground state.

Conclusion

The structural parameters of all compounds calculated here have been drawn as a symmetry map, according to references [10, 11] (Figure 5). Clearly, structures close to octahedral

rier approaches zero, as in $[\text{W}(\text{CH}_3)\text{F}_5]$ (8.7 kJ mol^{-1}) or $[\text{Mo}(\text{CH}_3)\text{F}_5]$ (7.2 kJ mol^{-1}), it will be difficult to describe the molecule by using one static structural model.

Computational Methods

DFT calculations were performed by using the GAUSSIAN 03 program revision B04,^[26] by the method of Becke^[16] in the variation of Lee, Yang, and Parr,^[17] as implemented in the program. Basis sets: 6-311 G (d,p) for C, H, O, and F. The relativistically corrected pseudopotentials and basis sets for Mo and W were obtained from the Institut für Theoretische Chemie, Universität Stuttgart: Mo: 28 core electrons, 14 valence electrons; W: 60 core electrons, 14 valence electrons, 8s, 7p, 6d valency basis. All structures were fully optimized within the given symmetry. Some structures are very close to a higher symmetry, but if calculated with higher symmetry, showed small imaginary-frequency vibrations, for example, for C_6H_5 torsion. They were calculated with C_1 symmetry. The nature of the stationary points was characterized by the harmonic vibrational-frequency analysis in all cases. The lowest calculated frequency of ground states and the calculated imaginary frequency of transition states are included in the tables.

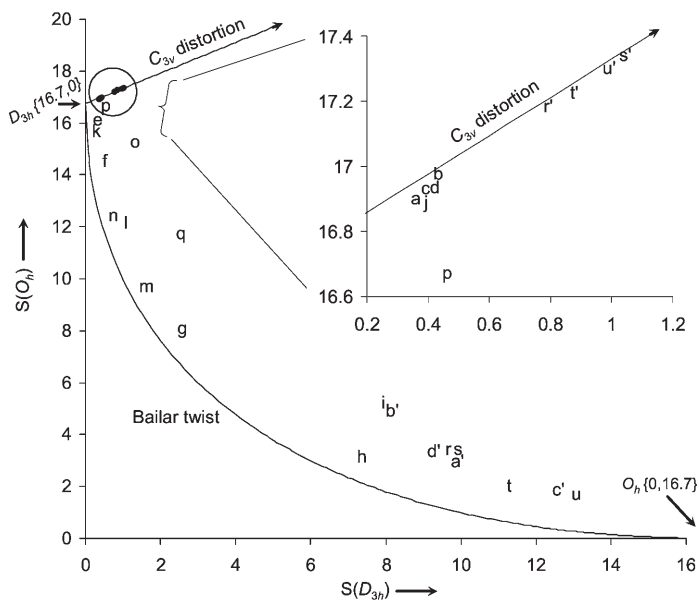


Figure 5. Shape analysis of the calculated six-coordinate structures. Transition states (Ts) are marked with prime signs. For definitions of $S(O_h)$ and $S(D_{3h})$, see references [9, 10]. The line connecting the ideal octahedral structure (O_h) and the ideal trigonal-prismatic structure (D_{3h}) represents the minimum distortion pathway of the Bailar twist mechanism. a = $[\text{Mo}(\text{CH}_3)\text{F}_5]$, b = $[\text{Mo}(\text{CF}_3)\text{F}_5]$, c = $[\text{W}(\text{CH}_3)\text{F}_5]$, d = $[\text{W}(\text{CF}_3)\text{F}_5]$. a' = $[\text{Mo}(\text{CH}_3)\text{F}_5]$ Ts, b' = $[\text{Mo}(\text{CF}_3)\text{F}_5]$ Ts, c' = $[\text{W}(\text{CH}_3)\text{F}_5]$ Ts, d' = $[\text{W}(\text{CF}_3)\text{F}_5]$ Ts. e = $[\text{Mo}(\text{C}_6\text{F}_5)\text{F}_5]$, f = $[\text{W}(\text{C}_6\text{F}_5)\text{F}_5]$, g = $[\text{Mo}(\text{C}_6\text{H}_5)\text{F}_5]$, h = $[\text{W}(\text{C}_6\text{H}_5)\text{F}_5]$, i = $[\text{Mo}(\text{C}_6\text{H}_5)_2\text{F}_4]$ C_s isomer 1, octahedral, j = $[\text{Mo}(\text{C}_6\text{H}_5)_2\text{F}_4]$ C_s trigonal-prismatic isomer 2, k = $[\text{Mo}(\text{C}_6\text{H}_5)_2\text{F}_4]$ C_2 trigonal-prismatic isomer 3, l = $[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ C_2 isomer 1, m = $[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ C_s isomer 2, n = $[\text{Mo}(\text{C}_6\text{F}_5)_2\text{F}_4]$ C_2 isomer 3, o = $[\text{Mo}(\text{C}_6\text{F}_5)_3\text{F}_3]$ isomer 1, p = $[\text{Mo}(\text{C}_6\text{F}_5)_3\text{F}_3]$ isomer 2, q = $[\text{Mo}(\text{C}_6\text{F}_5)_4\text{F}_2]$ isomer 1. r = $[\text{Mo}(\text{CH}_3)\text{F}_5]$ Ts, s = $[\text{Mo}(\text{CF}_3)\text{F}_5]$ Ts, t = $[\text{W}(\text{CH}_3)\text{F}_5]$ Ts, u = $[\text{W}(\text{CF}_3)\text{F}_5]$ Ts. r' = $[\text{Mo}(\text{CH}_3)\text{F}_5]$ Ts, s' = $[\text{Mo}(\text{CF}_3)\text{F}_5]$ Ts, t' = $[\text{W}(\text{CH}_3)\text{F}_5]$ Ts, u' = $[\text{W}(\text{CF}_3)\text{F}_5]$ Ts.

are always more or less distorted in the direction of trigonal prismatic, because they lie in the vicinity of the minimum distortion pathway. On the other hand, the majority of trigonal-prismatic structures are distorted often in the direction of octahedral. Structures close to ideal trigonal prismatic are always slightly C_{3v} distorted.

All single-substituted $[\text{MRF}_5]$ ($\text{R} = \text{CH}_3^-$, CF_3^- , C_6H_5^- , C_6F_5^- , CH_3-S^- , CF_3-S^-) compounds presented have energy barriers between trigonal-prismatic and octahedral states of up to 23.0 kJ mol^{-1} , most of them much less than this. This means that, at room temperature, they all should exhibit nonrigid behavior, some of them even at low temperature. This can complicate their identification if a successful synthesis is ever achieved. The otherwise very sensitive ^{19}F NMR probe could fail here due to rapid, temperature-dependent exchange. In the extreme case, if the energy bar-

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