Exploring Early Transition Metal Coordination: A Synthetic and Computational Study of Tripodal Ligand Complexes

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Table of Roots for Calculations:

Metal	dn	Multiplicity	Roots	CASSCF(X, Y)
Ti^{3+}	1	1	5	(1, 5)
V^{3+}	2	1 3	15 10	(2, 5)
Cr^{3+}/Mo^{3+}	3	2 4	40 10	(3, 5)
Fe^{3+}	5	2 4 6	75 24 1	(5, 5)

Table S1. Table of roots used for CASSCF/NEVPT2 calculations.

NMR Spectra of Metal Complexes

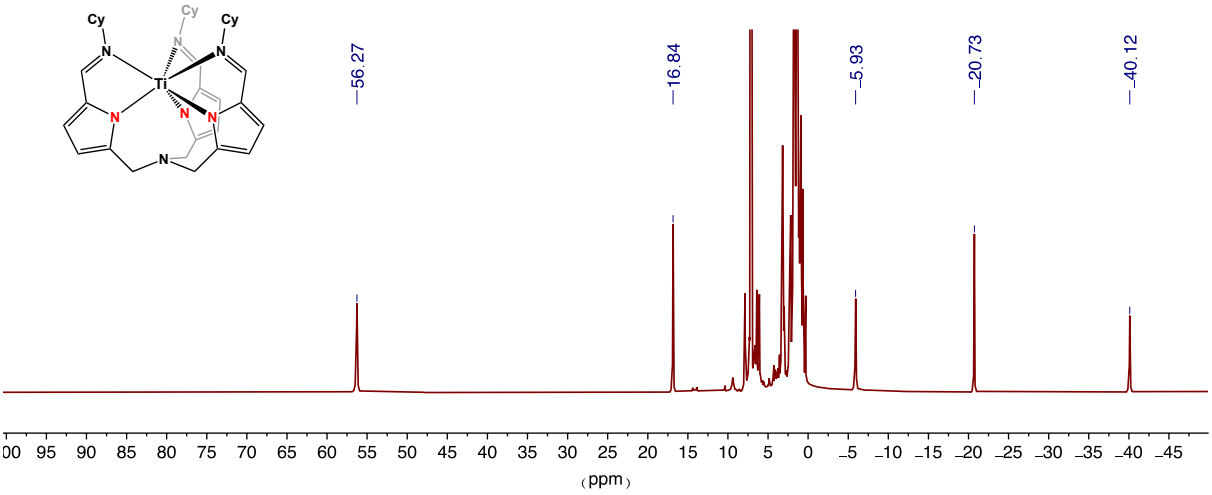


Figure S1. ^1H NMR Spectrum of $L^{Cy}Ti$ (Benzene-d_6).

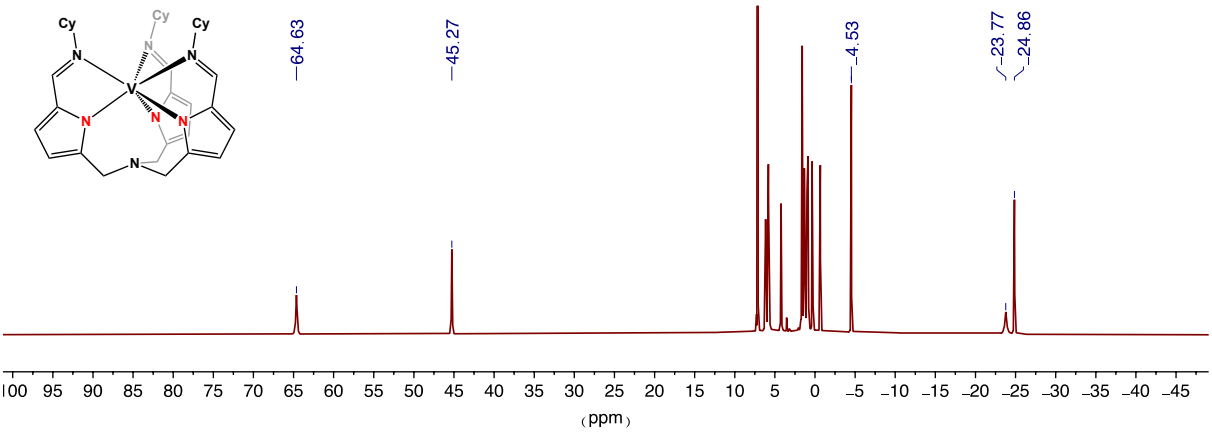


Figure S2. ^1H NMR Spectrum of $L^{Cy}V$ (Benzene-d_6).

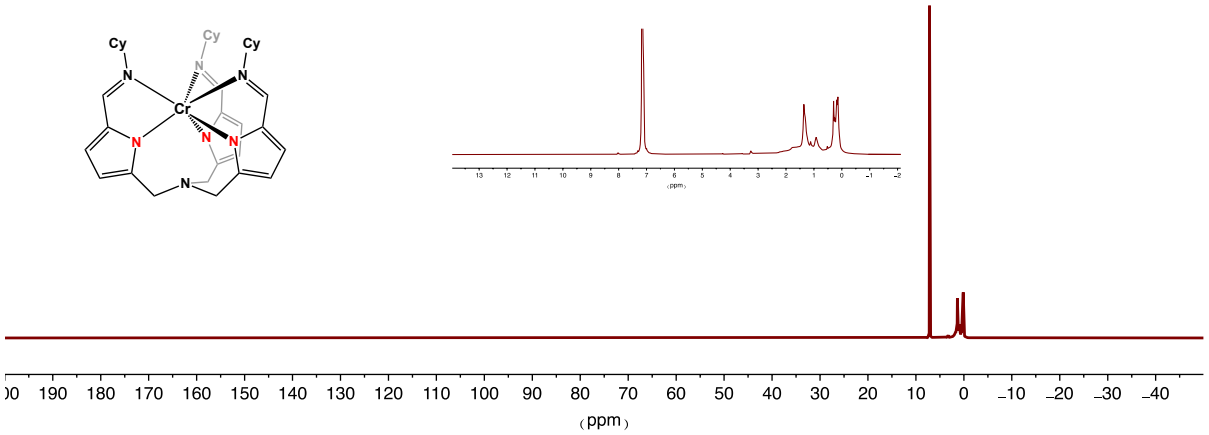


Figure S3. ^{1}H NMR Spectrum of $L^{Cy}Cr$ (Benzene-d_6).

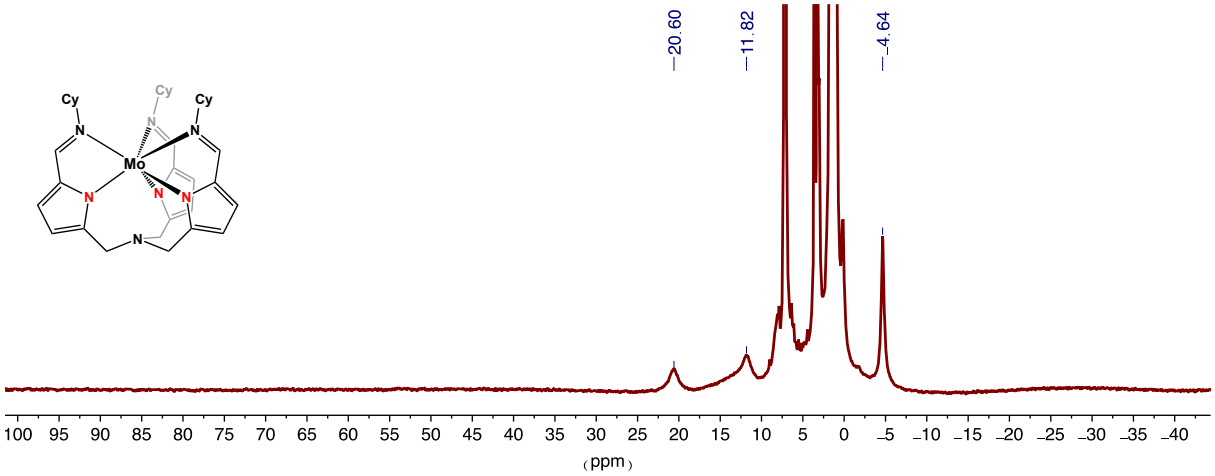


Figure S4. ^{1}H NMR Spectrum of $L^{Cy}Mo$ (Benzene-d_6).

Electronic Absorbance Spectra of Metal Complexes

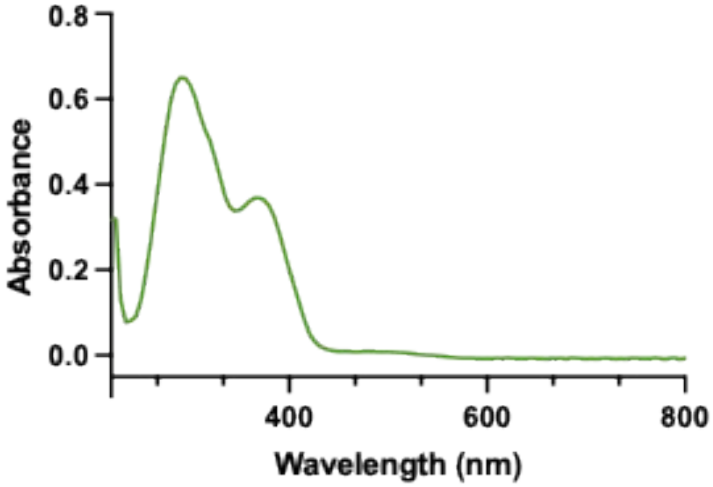


Figure S5. Electronic absorbance spectrum of $L^{Cy}Ti$ (0.03 mM in THF, 25°C)

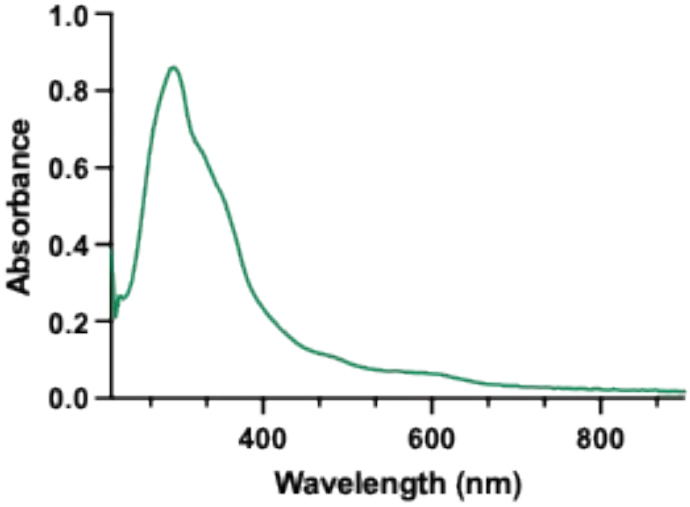


Figure S6. Electronic absorbance spectrum of $L^{Cy}V$ (0.03 mM in THF, 25°C)

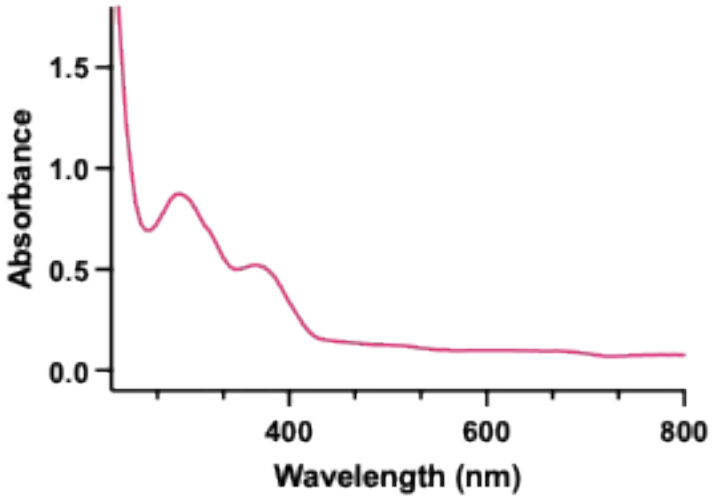


Figure S7. Electronic absorbance spectrum of $L^{Cy}Cr$ (0.03 mM in THF, 25°C)

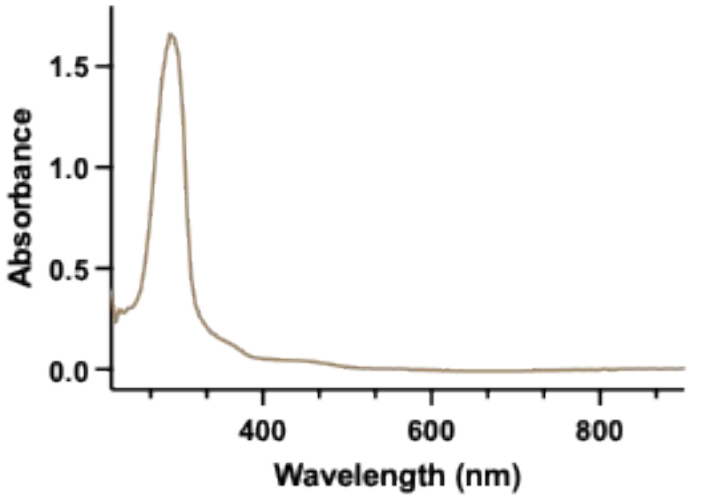
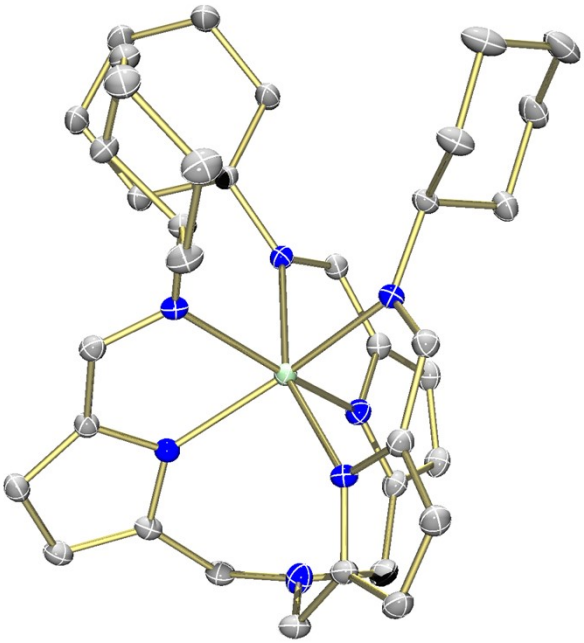
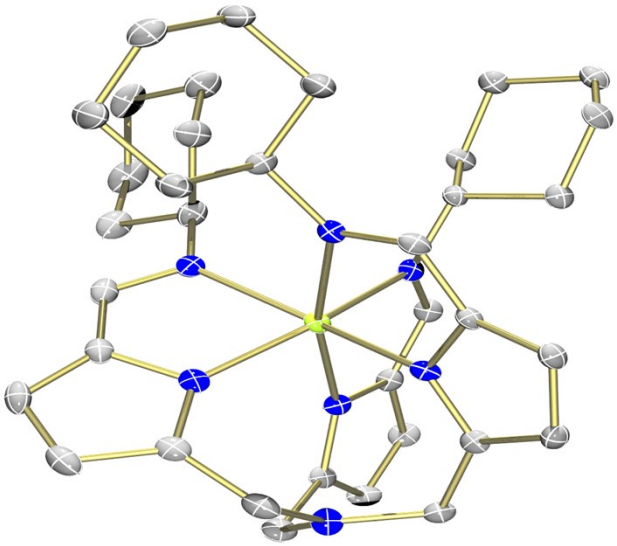


Figure S8. Electronic absorbance spectrum of $L^{Cy}Mo$ (0.03 mM in THF, 25°C)

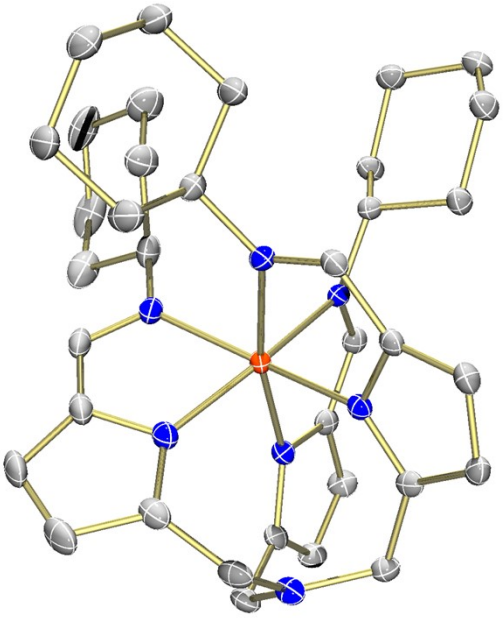
Solid State Structures of [N(pi^{Cy})$_3$]M

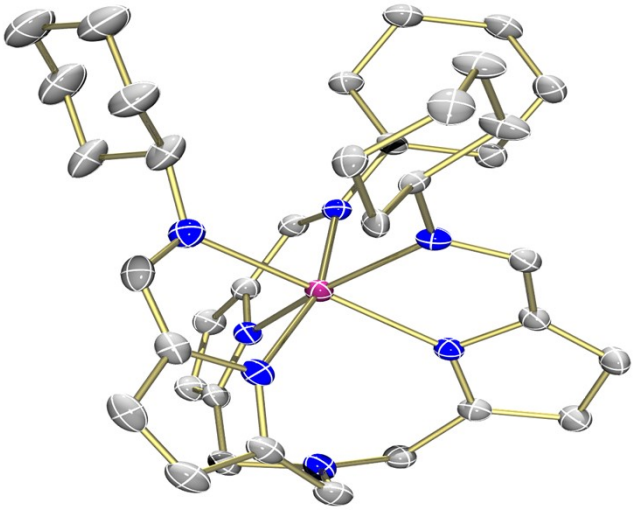


$L^{Cy}Ti$



$L^{Cy}V$





$L^{Cy}Cr$

Crystallographic Parameters

	$[N(pi^{Cy})_3]Ti$	$[N(pi^{Cy})_3]V$	$[N(pi^{Cy})_3]Cr$	$[N(pi^{Cy})_3]Mo$
Empirical Formula	$C_{36}H_{48}TiN_7$	$C_{36}H_{48}VN_7$	$C_{36}H_{48}CrN_7$	$C_{36}H_{48}MoN_7$
Formula Weight	626.70	629.75	630.83	674.75
Temperature	100.0 K	100.15 K	100.0 K	100.0 K
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit Cell Dimensions	a = 9.0932(2) Å b = 19.1304(4) Å c = 21.7114(4) Å α = 90° β = 90° γ = 90°	a = 10.5749(9) Å b = 20.9201(15) Å c = 14.2707(11) Å α = 90° β = 95.455(4)° γ = 90°	a = 10.4451(4) Å b = 20.8052(7) Å c = 14.3671(6) Å α = 90° β = 95.520(2)° γ = 90°	a = 10.7803(5) Å b = 20.8514(9) Å c = 14.1302(6) Å α = 90° β = 95.3340(17)° γ = 90°
Volume	3776.84(13) Å	3142.8(4) Å	3140.1(2) Å	3162.5(2) Å
Z	4	4	4	4
Reflections Collected	80245	34079	86073	71092
Independent Reflections	11512	5772	5767	6459
Goodness-of-fit on F^2	1.053	1.020	1.167	1.100
Final R Indices [I>=2σ (I)]	R_1 = 2.94% wR_2 = 7.35%	R_1 = 5.77% wR_2 = 14.15%	R_1 = 5.04% wR_2 = 12.47%	R_1 = 2.98% wR_2 = 7.17%

*Table S2. Crystallographic Parameters for **1-M**.*

Selected Bond Distances for 1-M

	$[N(pi^{Cy})_3]Ti$	$[N(pi^{Cy})_3]V$	$[N(pi^{Cy})_3]Cr$	$[N(pi^{Cy})_3]Mo$
M-$N_{pyrrole1}$ (Å)	2.1114(14)	2.026(3)	2.027(2)	2.1232(17)
M-$N_{pyrrole2}$ (Å)	2.1088(13)	2.031(3)	2.014(2)	2.1213(17)
M-$N_{pyrrole3}$ (Å)	2.1069(13)	2.096(3)	2.005(2)	2.1360(17)
M-N_{imine1} (Å)	2.2539(13)	2.169(3)	2.108(2)	2.2158(17)
M-N_{imine2} (Å)	2.2324(14)	2.211(3)	2.118(2)	2.1906(17)
M-N_{imine3} (Å)	2.2466(13)	2.127(3)	2.128(2)	2.2121(18)
M···N_{apical} (Å)	3.1991(16)	3.510(3)	3.549(2)	3.3349(19)

*Table S3. Selected Bond Distances for **1-M**.*

Octahedral Distortion Parameters as Calculated by OctaDist 3.1.0[10]

	Ti	V	Cr	Fe	Mo
ζ ( )	0.52432	0.210036	0.308959	0.705223	0.30806
Σ (°)	127.6685	85.95815	73.25126	124.828	64.68293
Θ (°)	328.7087	260.5775	227.2179	322.351	204.8405

Table S4. Octahedral Distortion Parameters as Calculated by OctaDist 3.1.0.

Calculated Molecular Orbital Diagrams

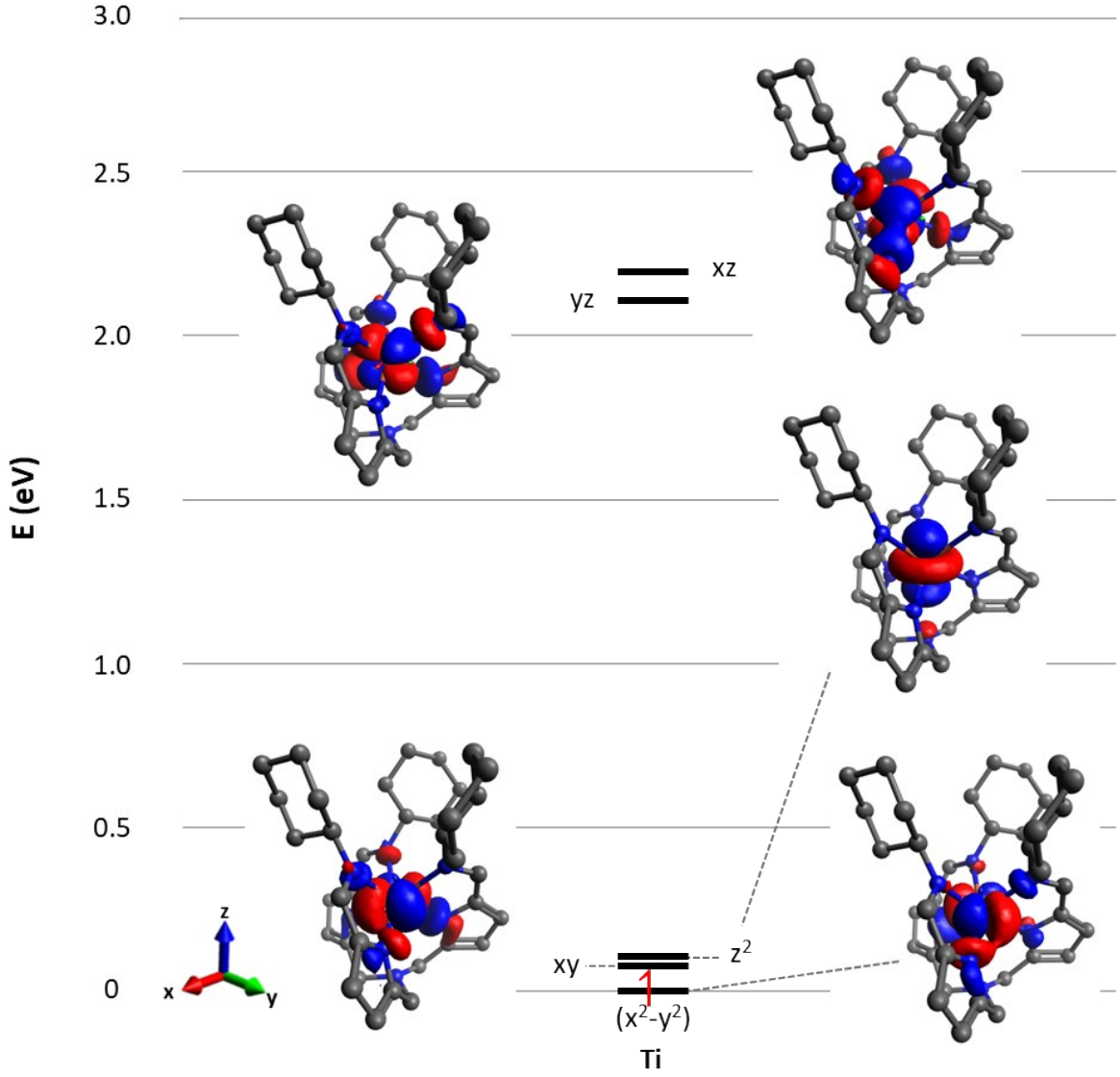


Figure S9. CASSCF generated molecular orbitals and their respective energies for $L^{Cy}Ti$. Hydrogen atoms removed for clarity.

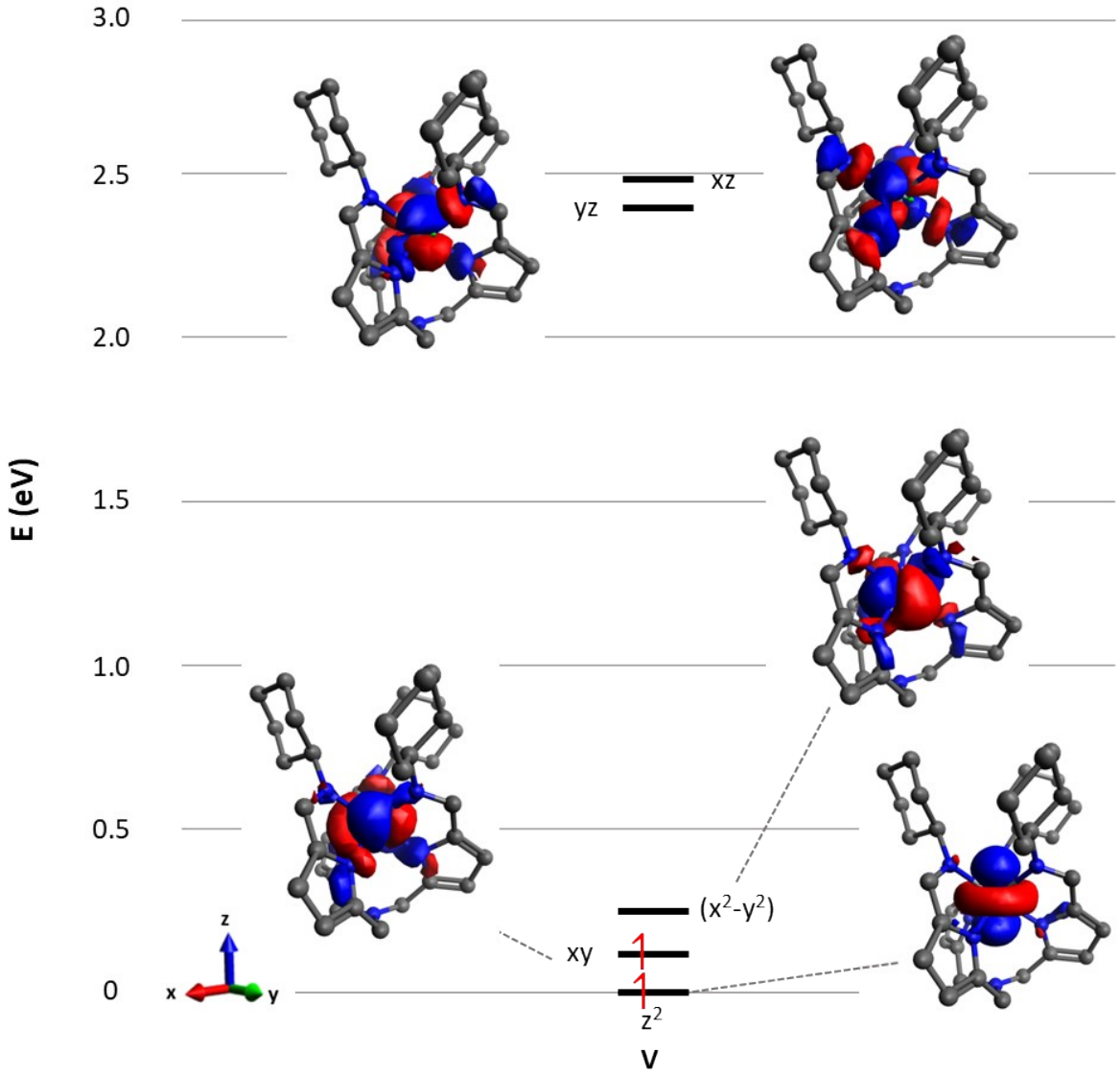


Figure S10. CASSCF generated molecular orbitals and their respective energies for L^{Cy}V. Hydrogen atoms removed for clarity.

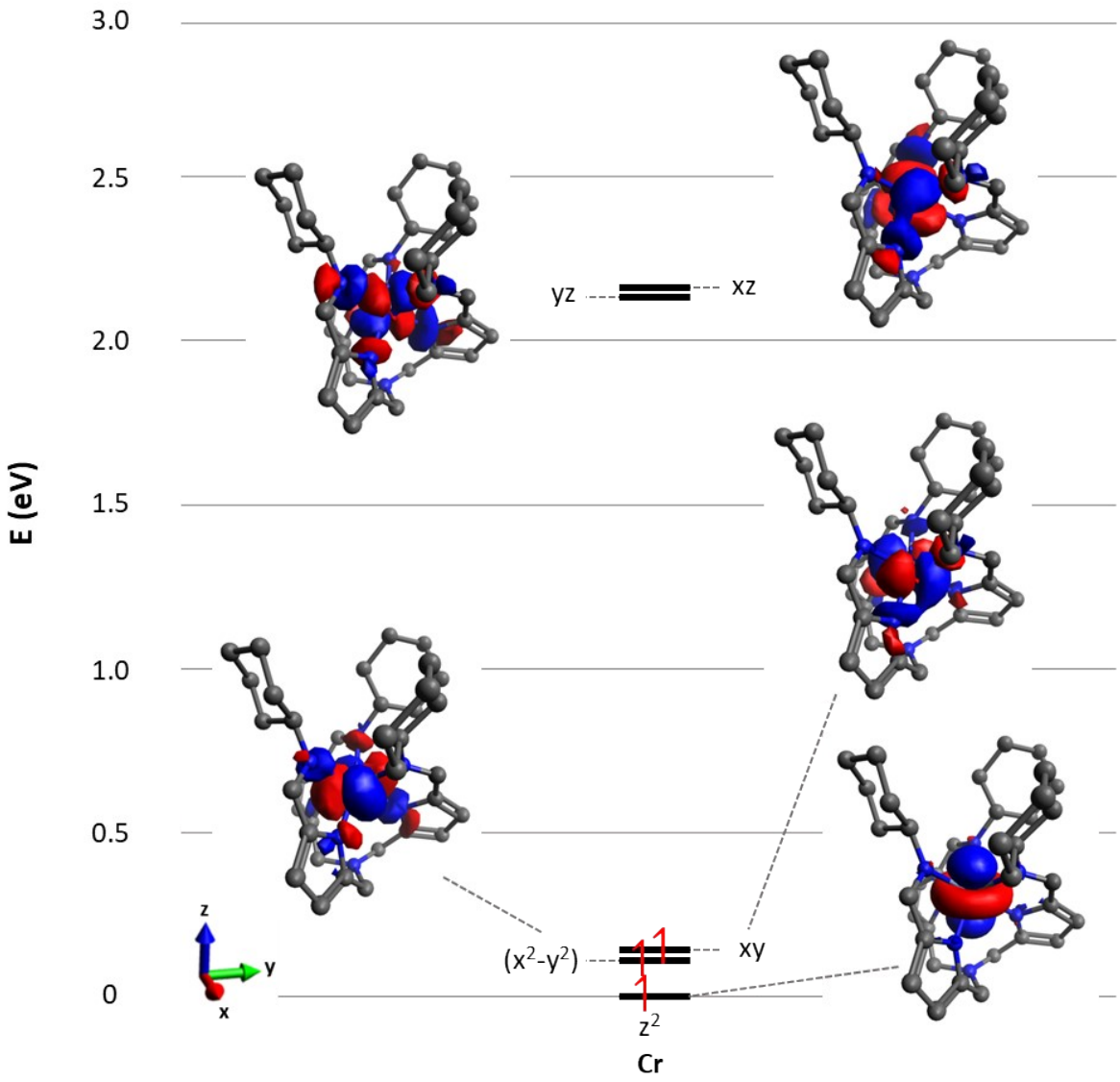


Figure S11. CASSCF generated molecular orbitals and their respective energies for $L^{Cy}Cr$. Hydrogen atoms removed for clarity.

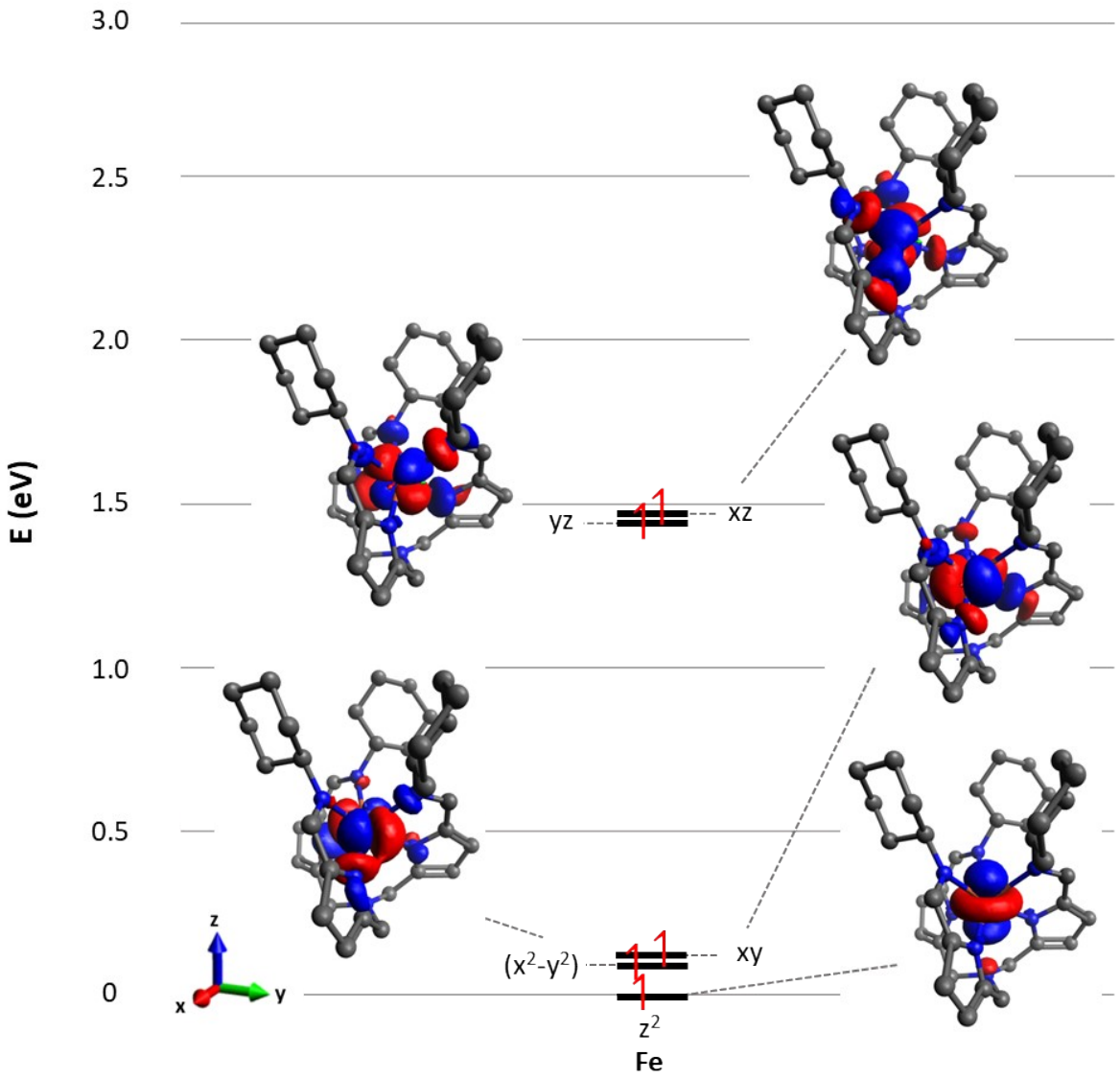


Figure S12. CASSCF generated molecular orbitals and their respective energies for $L^{Cy}Fe$. Hydrogen atoms removed for clarity.

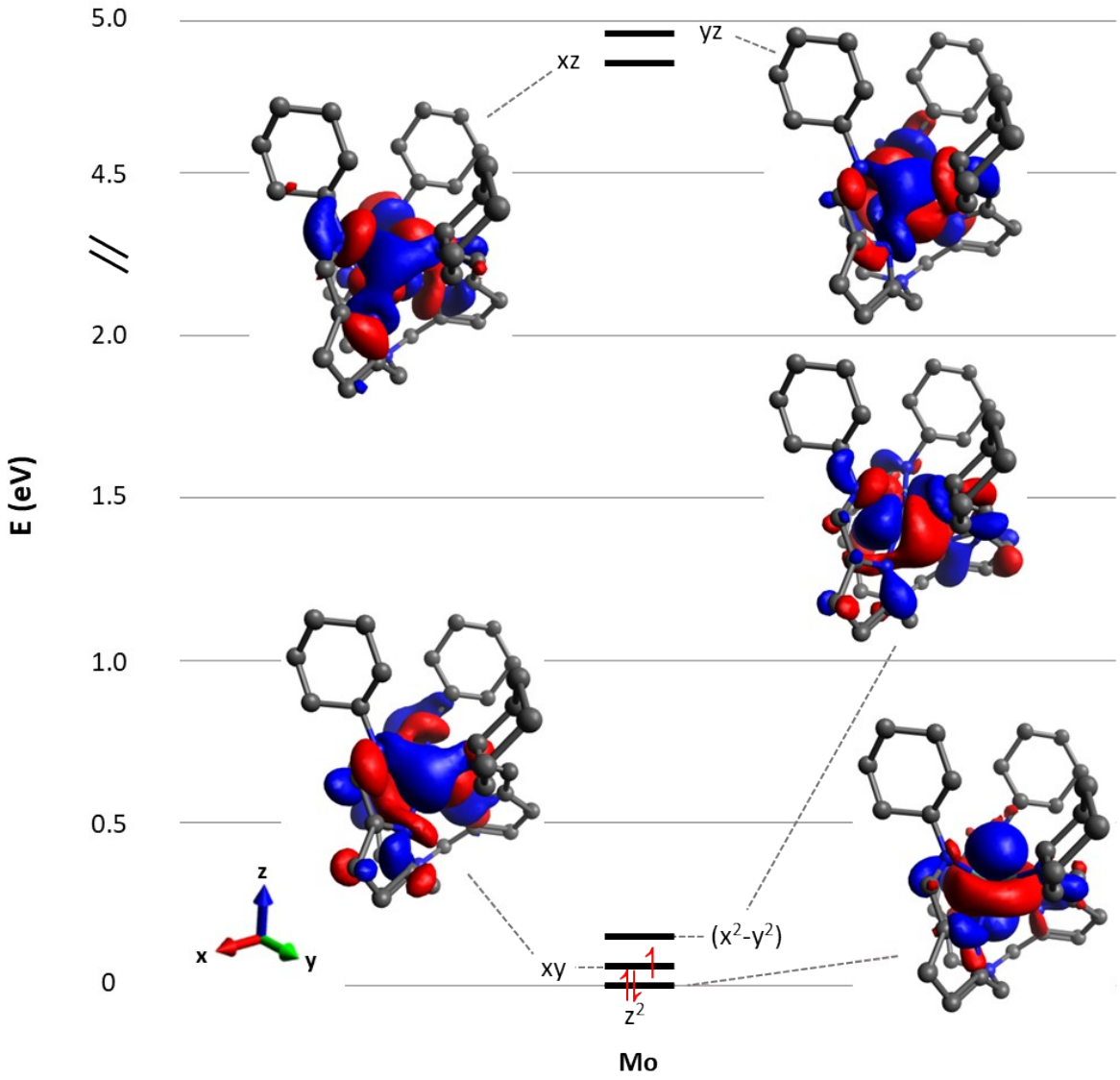


Figure S13. CASSCF generated molecular orbitals and their respective energies for L^{Cy}Mo. Hydrogen atoms removed for clarity.

References

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