

## Electronic Supporting Information

### **Sn–H Bond Additions to Asymmetric Trigonal Phosphinidene-Bridged Dimolybdenum Complexes**

M. Angeles Alvarez, Inmaculada Amor, M. Esther García, Daniel García-Vivó,\*  
Miguel A. Ruiz,\* and Jaime Suárez

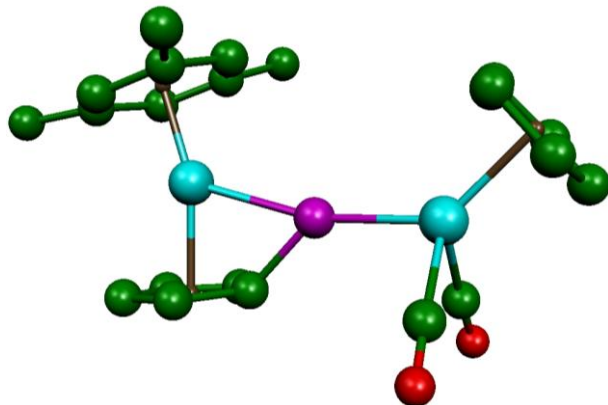
*Departamento de Química Orgánica e Inorgánica / IUQOEM, Universidad de  
Oviedo, E-33071 Oviedo, Spain.*

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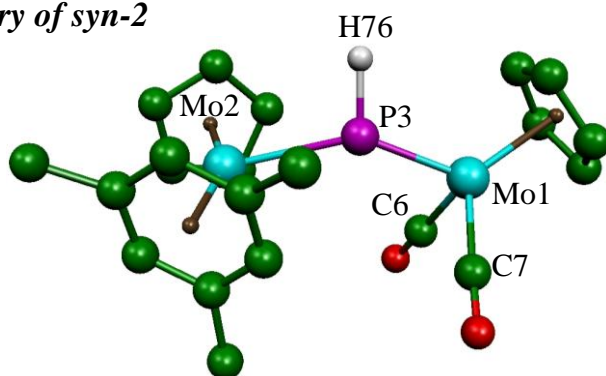
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DFT-optimized geometries for complexes 1 to 3 and some derivatives, with <sup>t</sup>Bu groups (except the C<sup>1</sup> atoms) and most H atoms omitted for clarity.

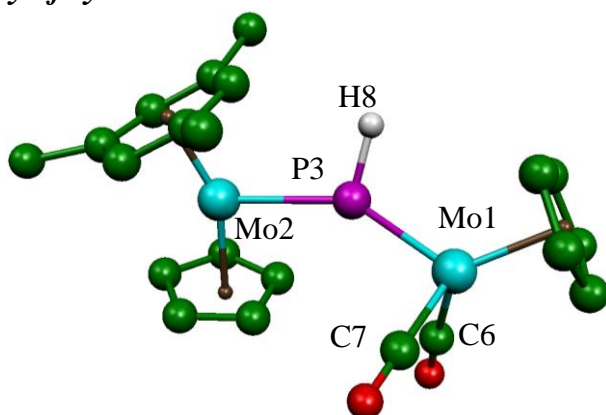
*Optimized geometry of 1*



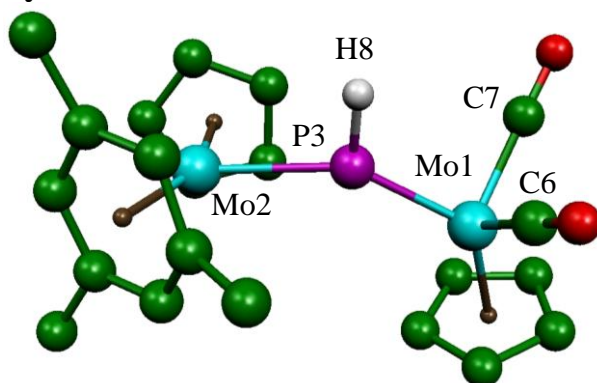
*Optimized geometry of syn-2*



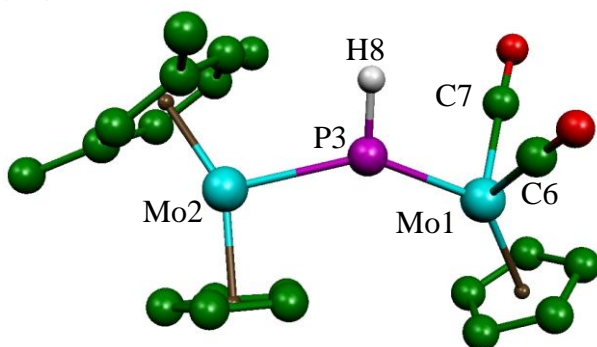
*Optimized geometry of syn-2R*



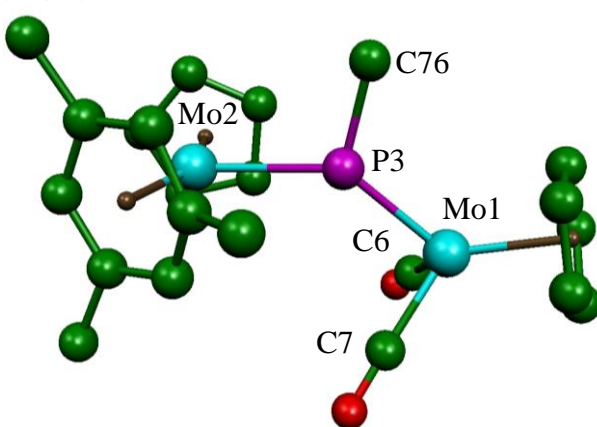
**Optimized geometry of *anti-2***



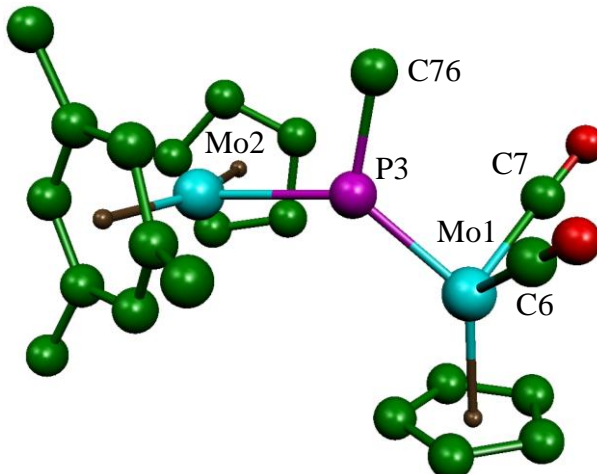
**Optimized geometry of *anti-2R***



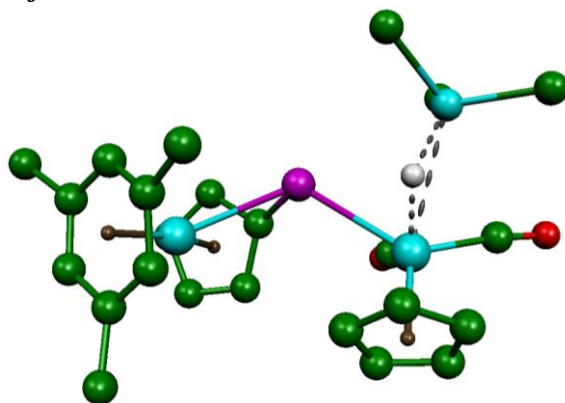
**Optimized geometry of *syn-3***



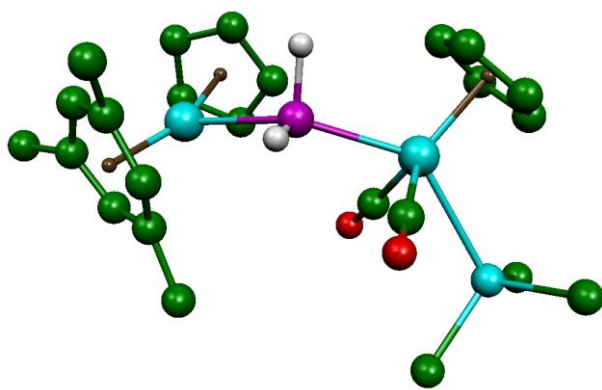
**Optimized geometry of *anti-3***



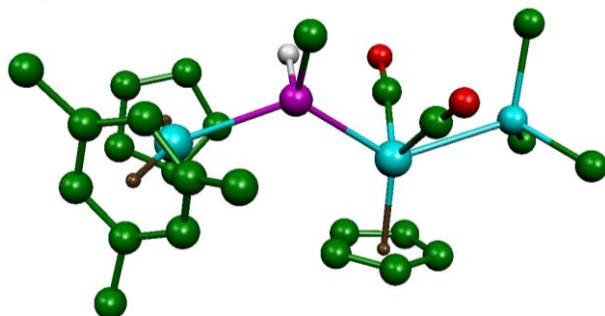
*Optimized geometry of M1-mod*



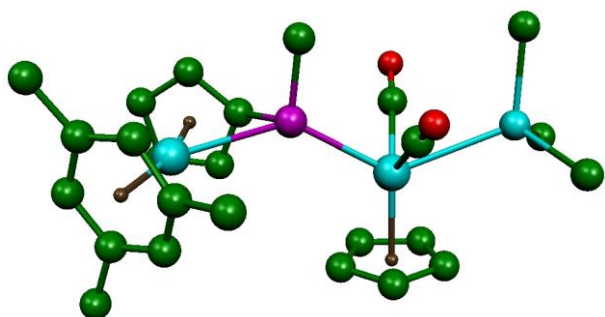
*Optimized geometry of 5-mod*



*Optimized geometry of P-mod*



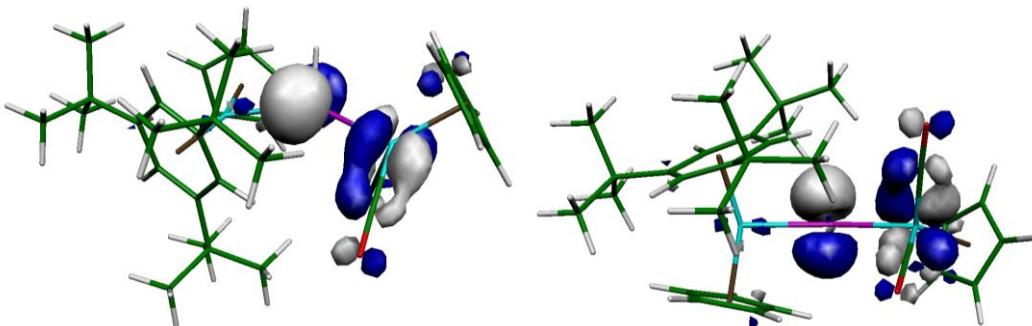
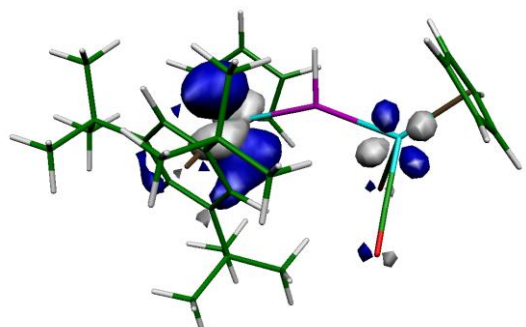
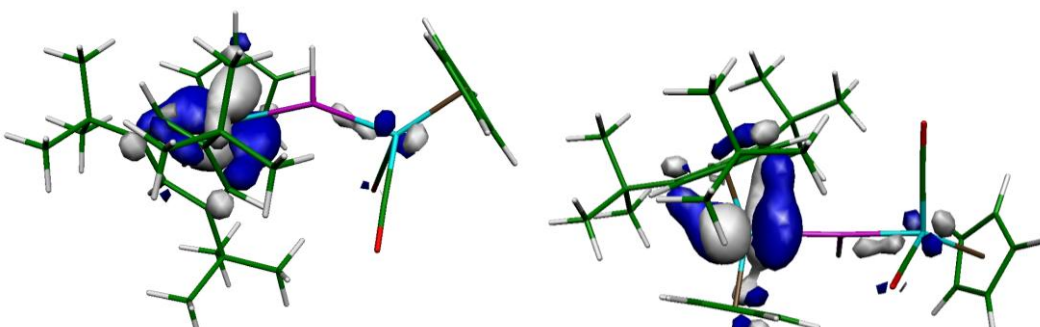
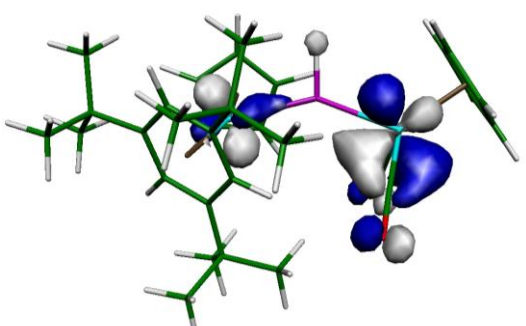
*Optimized geometry of 7-mod*



**Table S1:** Selected geometrical parameters for compounds **2** and **3** (distances in Å, angles in deg.)

<b>Parameter</b>	<b><i>syn-2</i></b>	<b><i>syn-2R</i></b>	<b><i>anti-2</i></b>	<b><i>anti-2R</i></b>	<b><i>syn-3</i></b>	<b><i>anti-3</i></b>
Mo1 – P3	2.292	2.301	2.287	2.314	2.300	2.285
Mo2 – P3	2.581	2.590	2.592	2.600	2.603	2.609
P3 – H/C	1.436	1.426	1.429	1.419	1.886	1.875
Mo1 – C6	1.966	1.970	1.964	1.966	1.970	1.965
Mo1 – C7	1.970	1.965	1.976	1.961	1.957	1.970
Mo1 – P3 – Mo2	144.1	146.4	139.9	144.4	138.4	134.1
Mo1 – P3 – H/C	111.1	108.6	117.2	111.7	116.2	119.6
Mo2 – P3 – H/C	102.5	104.8	102.6	103.9	105.3	105.5
C6 – Mo1 – C7	82.8	82.9	82.1	82.5	80.8	82.6
C6 – Mo1 – P3	90.5	98.4	90.8	89.0	95.7	91.5
C7 – Mo1 – P3	98.8	93.9	90.9	87.9	93.7	89.9

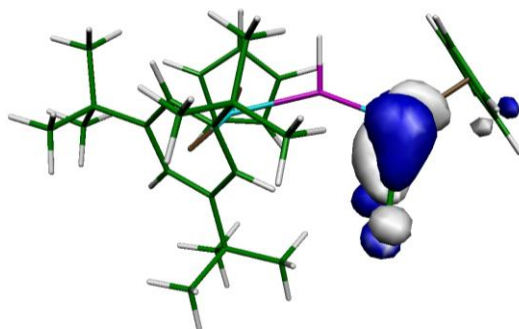
**Table S2:** Molecular orbitals of *syn-2*.

OM	Energy (eV)	Assignment	Projection
LUMO 141	-1.73	$\pi^*_{\text{MoP}}$	 <p>Contributions (%): Mo1 29, Mo2 4, P3 35, H76 0, CO's 13, Ar 6, Other 13</p>
HOMO 140	-4.52	$\text{LP}_{\text{Mo2}} + \text{LP}_{\text{Mo1}}$	 <p>Contributions (%): Mo1 12, Mo2 62, P3 2, H76 1, CO's 4, Ar 14, Other 5</p>
MO 139	-4.66	$\text{LP}_{\text{Mo2}}$	 <p>Contributions (%): Mo1 7, Mo2 55, P3 2, H76 1, CO's 2, Ar 22, Other 11</p>
MO 138	-4.87	$\text{LP}_{\text{Mo2}} + \pi_{\text{M-CO}}$	 <p>Contributions (%): Mo1 49, Mo2 19, P3 3, H76 2, CO's 17, Ar 6, Other 5</p>

MO 137

-5.02

$\pi_{\text{Mo-CO}}$

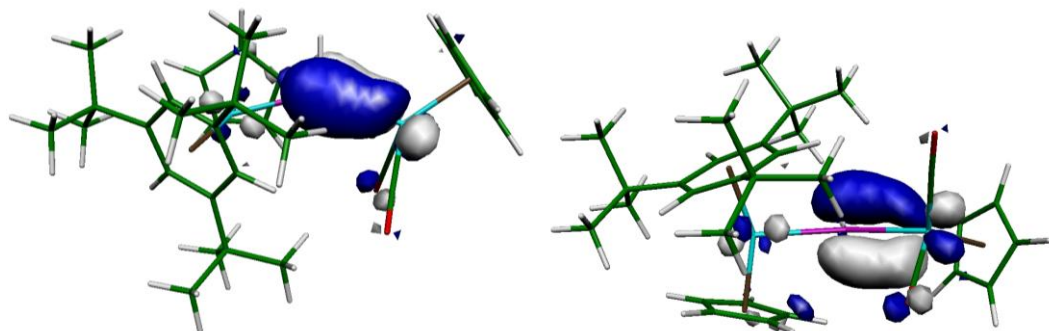


Contributions (%): Mo1 61, Mo2 0, P3 2, H76 1, CO's 28, Ar 1, Other 7

MO 136

-5.52

$\pi_{\text{MoP}}$

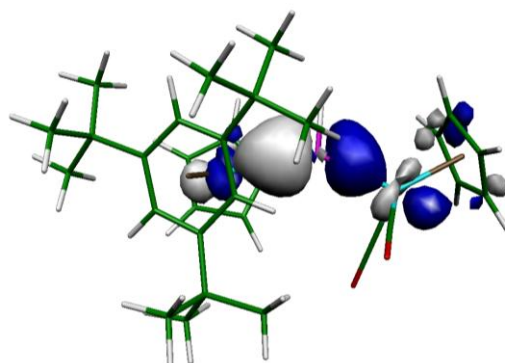


Contributions (%): Mo1 30, Mo2 7, P3 39, H76 0, CO's 6, Ar 4, Other 13

MO 132

-7.24

$\sigma_{\text{MoP}}$

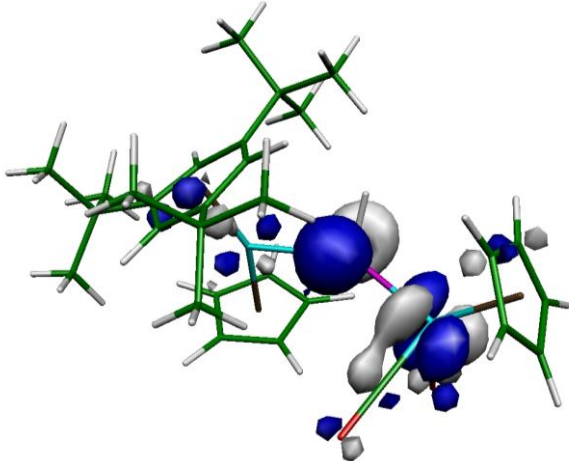
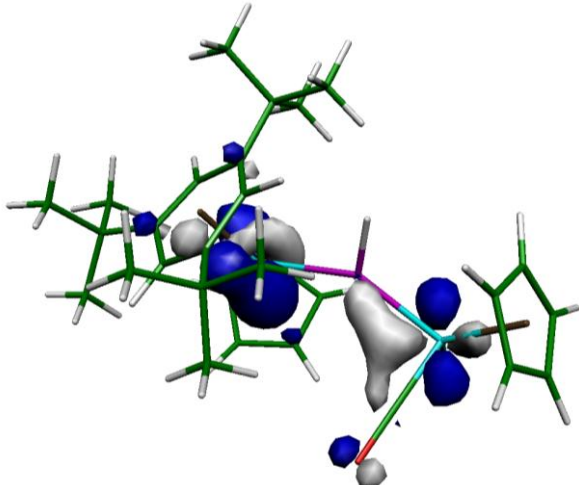
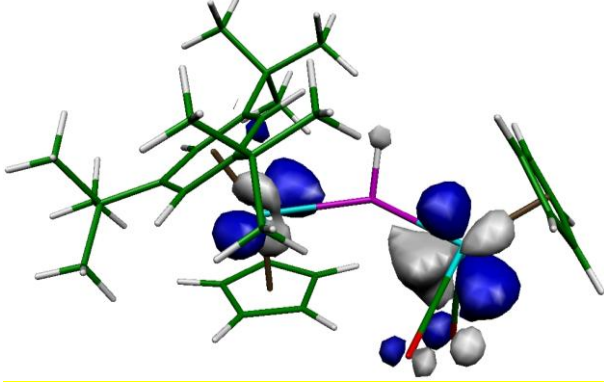


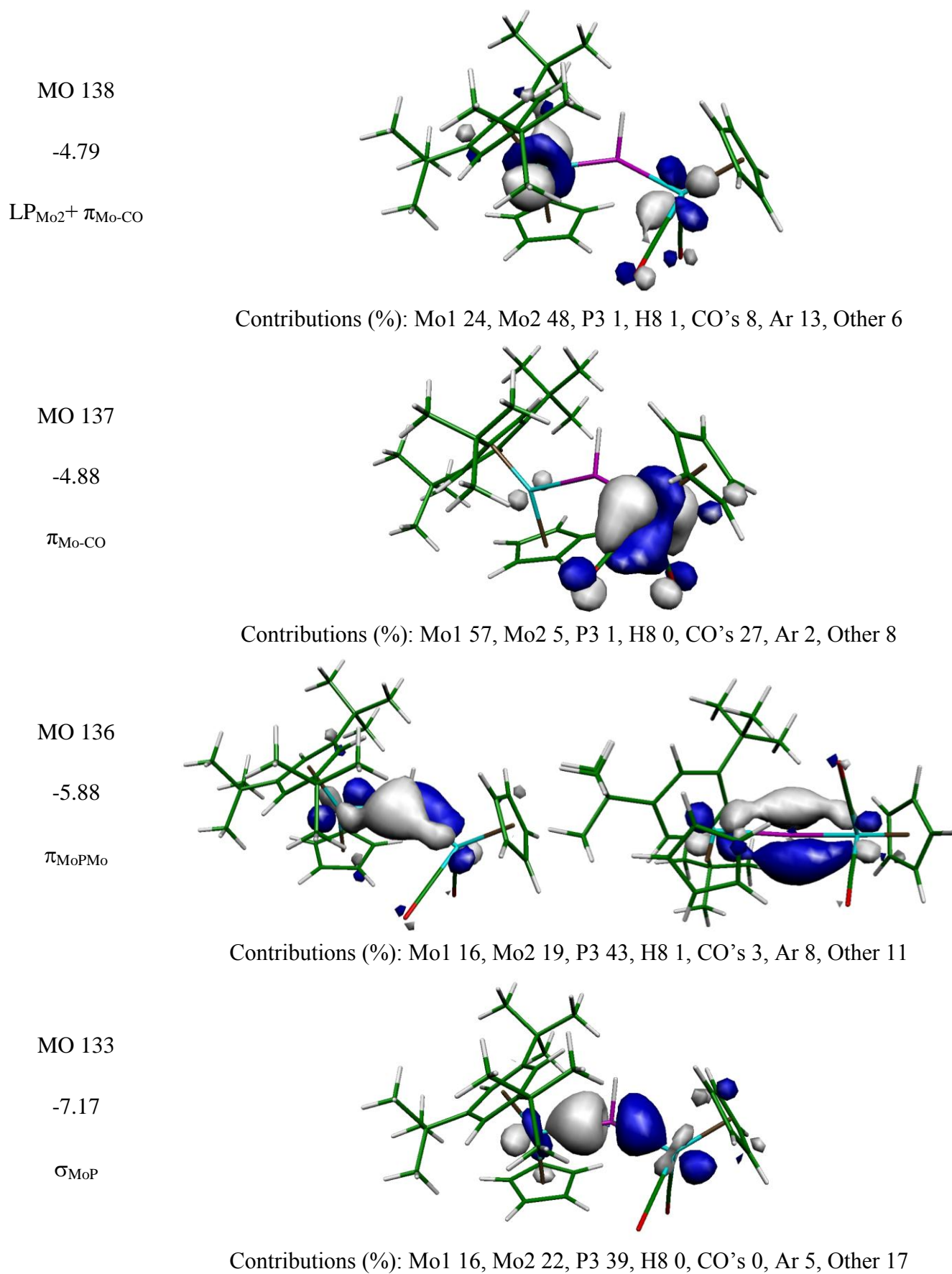
Contributions (%): Mo1 17, Mo2 21, P3 38, H76 0, CO's 1, Ar 5, Other 18

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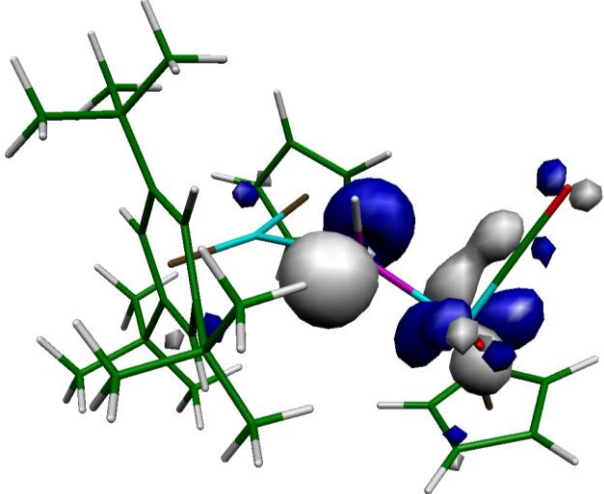
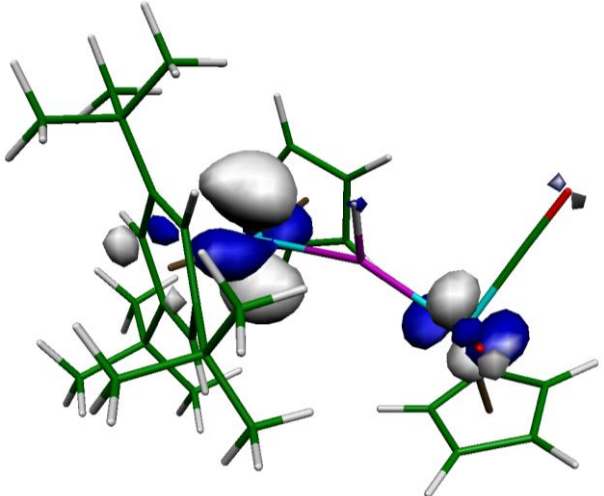
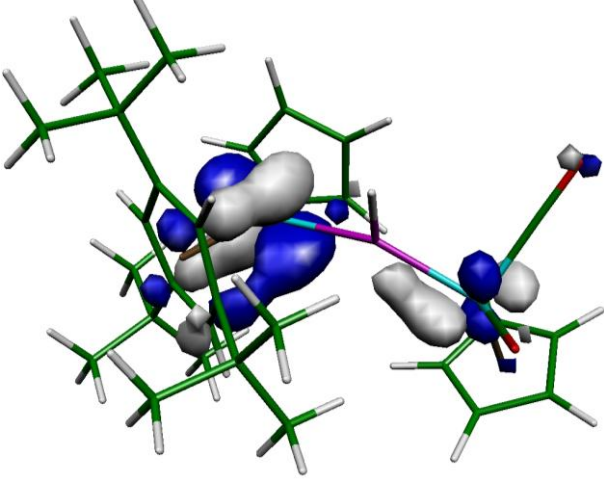


**Table S3:** Molecular orbitals of *syn-2R*.

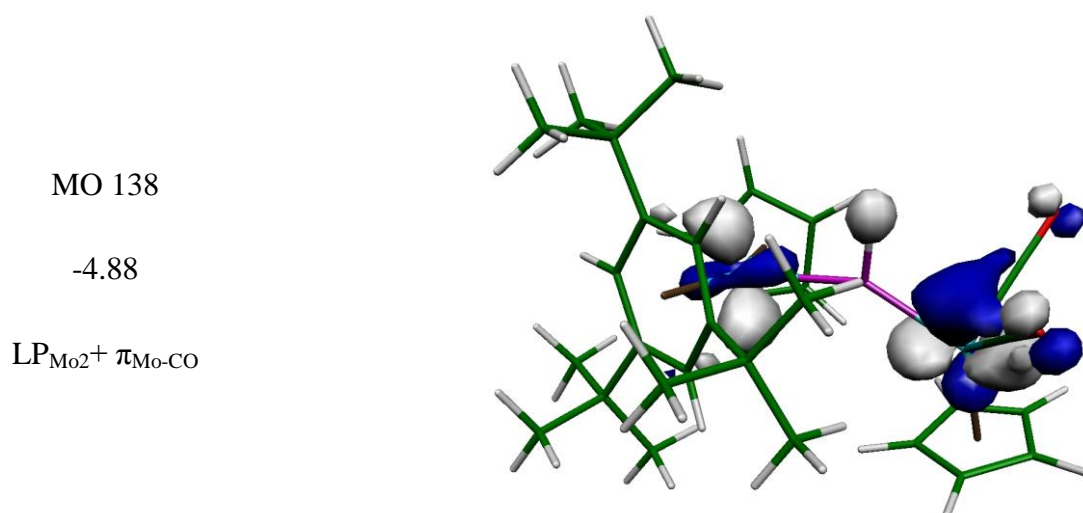
OM	Projection
Energy (eV)	
Assignment	
LUMO 141	
-1.59	
$\pi^*_{\text{MoP}}$	
Contributions (%): Mo1 26, Mo2 6, P3 31, H8 0, CO's 13, Ar 12, Other 12	
HOMO 140	
-4.56	
$\text{LP}_{\text{Mo2}} + \pi_{\text{MoP}}$	
Contributions (%): Mo1 22, Mo2 40, P3 5, H8 0, CO's 5, Ar 18, Other 9	
MO 139	
-4.63	
$\text{LP}_{\text{Mo2}} + \pi_{\text{Mo-CO}}$	
Contributions (%): Mo1 42, Mo2 24, P3 4, H8 2, CO's 14, Ar 8, Other 6	



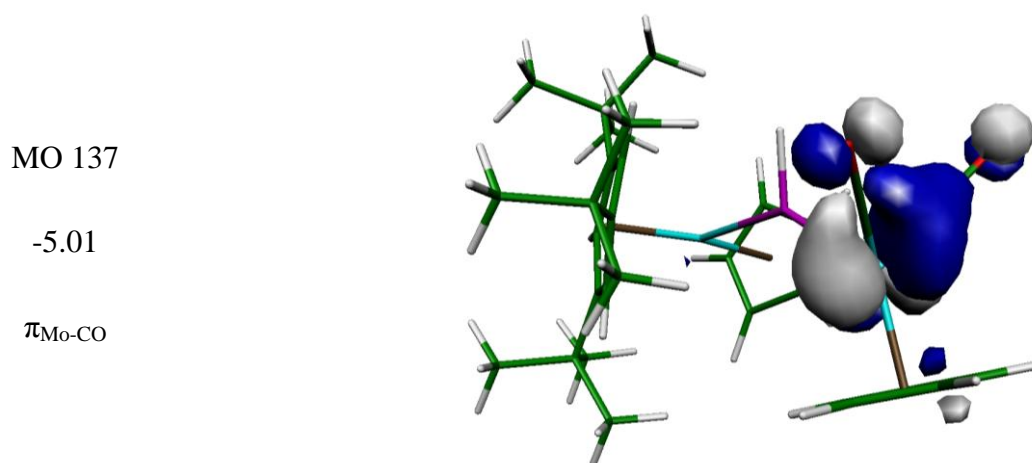
**Table S4:** Molecular orbitals of *anti-2*.

OM	Energy (eV)	Assignment	Projection
LUMO 141	-1.69	$\pi^*_{\text{MoP}}$	
Contributions (%): Mo1 31, Mo2 3, P3 34, H8 0, CO's 12, Ar 7, Other 13			
HOMO 140	-4.60	$\text{LP}_{\text{Mo2}}$	
Contributions (%): Mo1 17, Mo2 58, P3 1, H8 1, CO's 5, Ar 12, Other 6			
MO 139	-4.81	Mo-Ar	

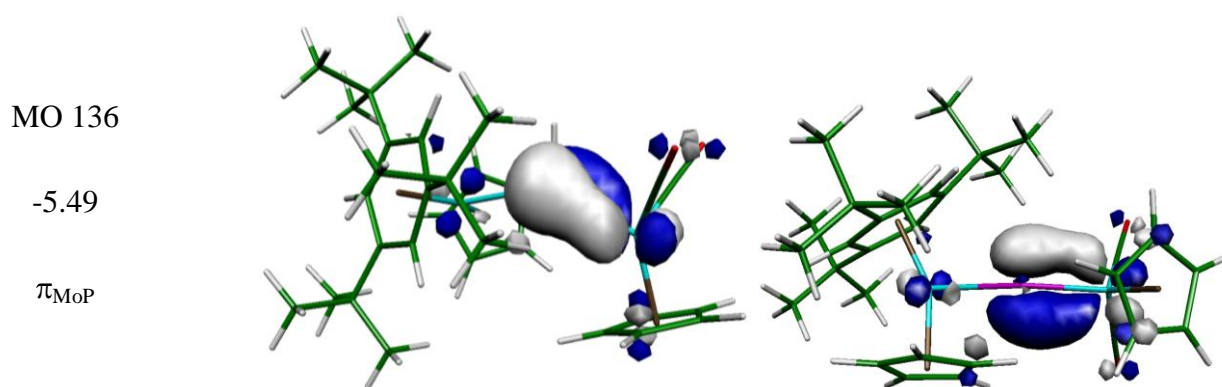
Contributions (%): Mo1 14, Mo2 47, P3 3, H8 0, CO's 4, Ar 21, Other 10



Contributions (%): Mo1 42, Mo2 27, P3 2, H8 4, CO's 12, Ar 9, Other 5



Contributions (%): Mo1 60, Mo2 2, P3 2, H8 0, CO's 27, Ar 1, Other 7

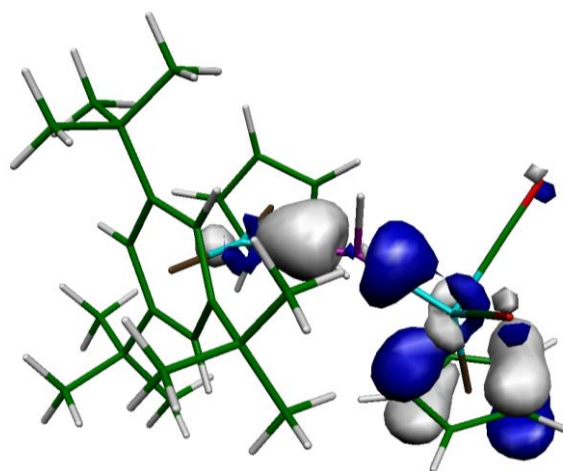


Contributions (%): Mo1 28, Mo2 7, P3 41, H8 0, CO's 5, Ar 5, Other 14

MO 135

-6.45

$\sigma_{\text{MoP}}$

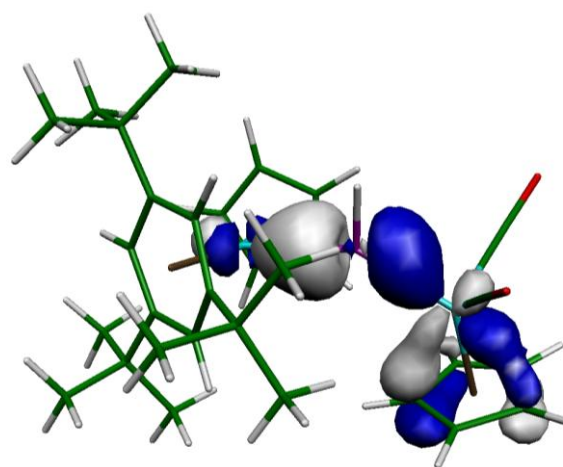


Contributions (%): Mo1 10, Mo2 10, P3 23, H8 0, CO's 5, Ar 2, Other 49

MO 132

-7.36

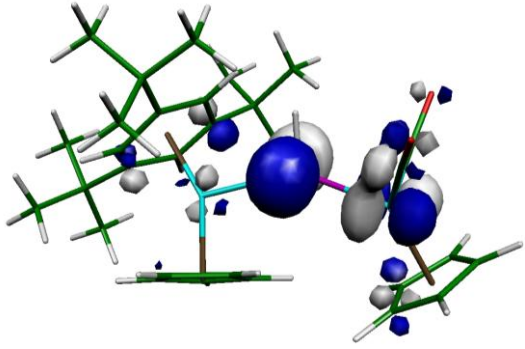
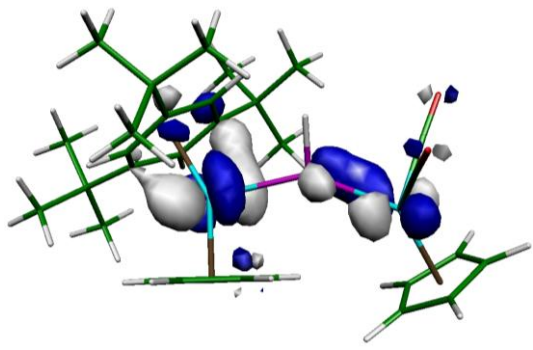
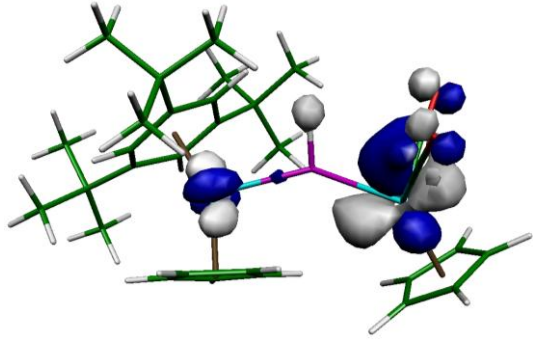
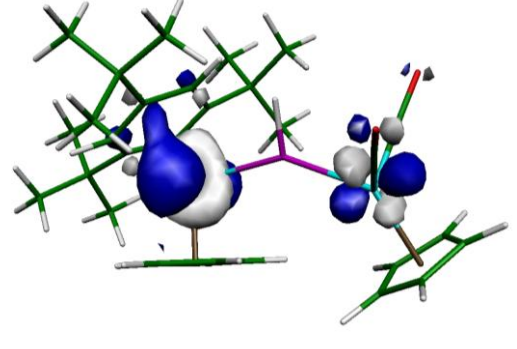
$\sigma_{\text{MoP}}$



Contributions (%): Mo1 18, Mo2 18, P3 27, H8 0, CO's 1, Ar 4, Other 31

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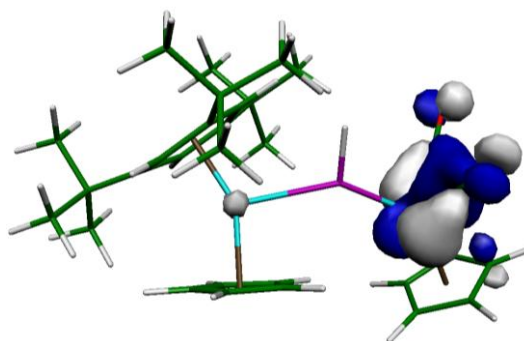
**Table S5:** Molecular orbitals of *anti-2R*.

OM	Energy (eV)	Assignment	Projection
LUMO 141	-1.52	$\pi^*_{\text{MoP}}$	
Contributions (%): Mo1 28, Mo2 5, P3 32, H8 0, CO's 10, Ar 14, Other 12			
HOMO 140	-4.56	$\text{LP}_{\text{Mo2}} + \pi_{\text{MoP}}$	
Contributions (%): Mo1 20, Mo2 39, P3 7, H8 0, CO's 4, Ar 18, Other 10			
MO 139	-4.64	$\pi_{\text{Mo-CO}} + \text{LP}_{\text{Mo2}}$	
Contributions (%): Mo1 55, Mo2 17, P3 2, H8 3, CO's 14, Ar 4, Other 5			
MO 138	-4.80	$\text{LP}_{\text{Mo2}} + \pi_{\text{Mo-CO}}$	
Contributions (%): Mo1 17, Mo2 55, P3 1, H8 1, CO's 5, Ar 15, Other 6			

MO 137

-4.90

$\pi_{\text{Mo-CO}}$

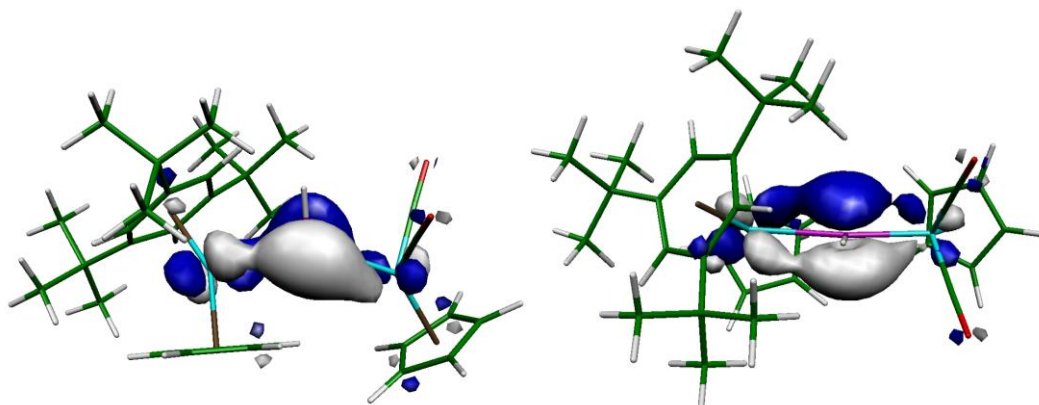


Contributions (%): Mo1 58, Mo2 5, P3 1, H8 0, CO's 27, Ar 2, Other 7

MO 136

-5.85

$\pi_{\text{MoPMo}}$

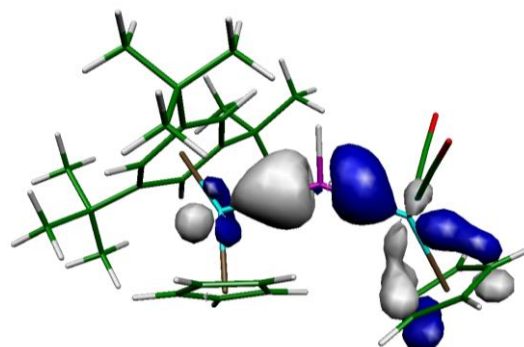


Contributions (%): Mo1 13, Mo2 22, P3 41, H8 0, CO's 3, Ar 8, Other 13

MO 133

-7.25

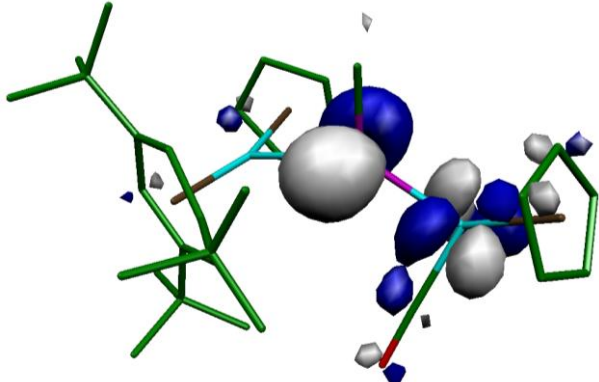
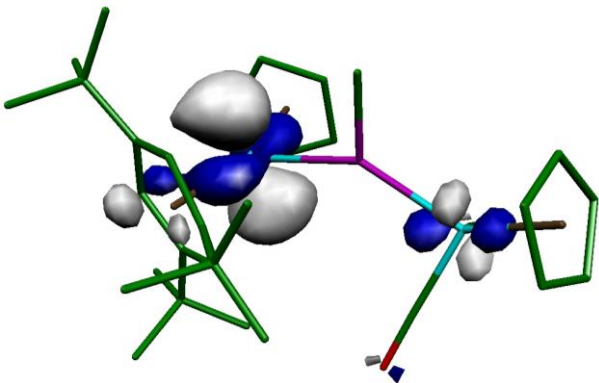
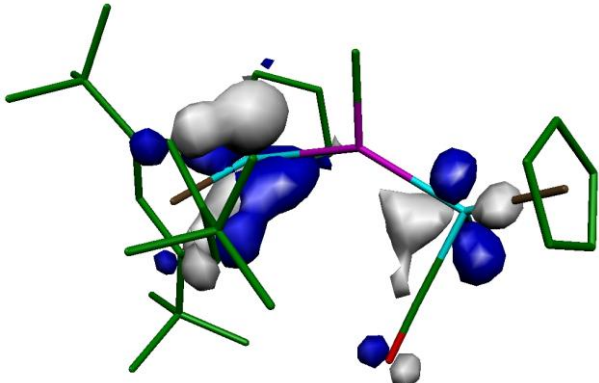
$\sigma_{\text{MoP}}$



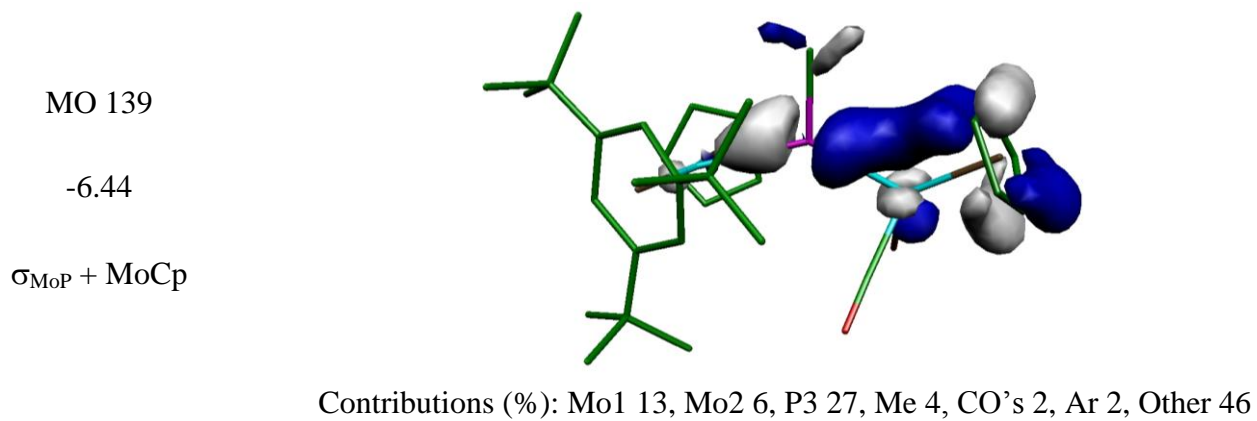
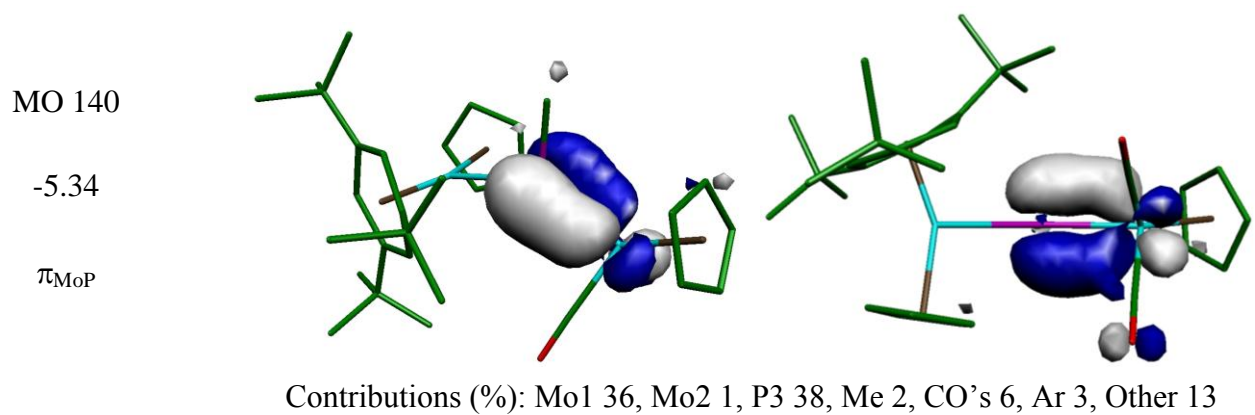
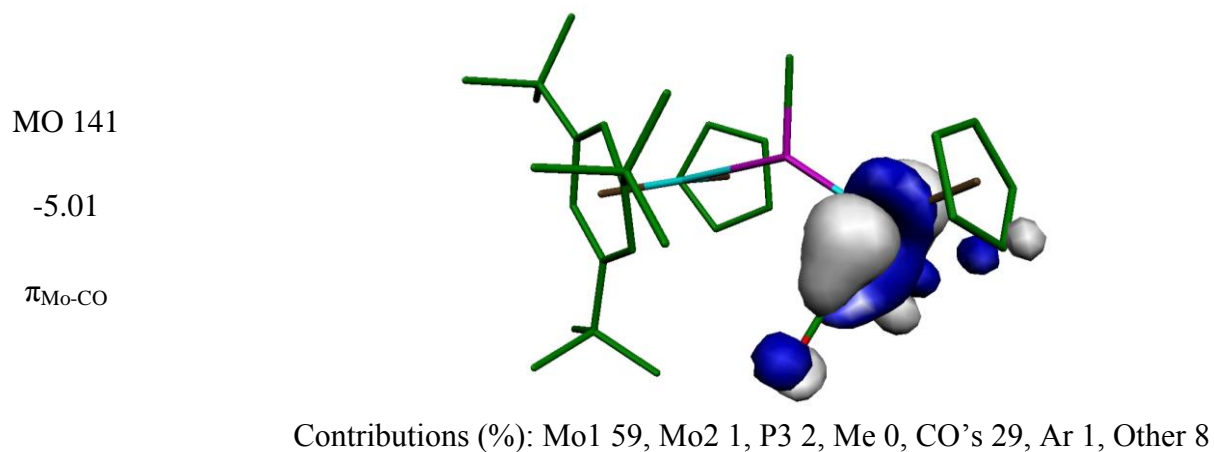
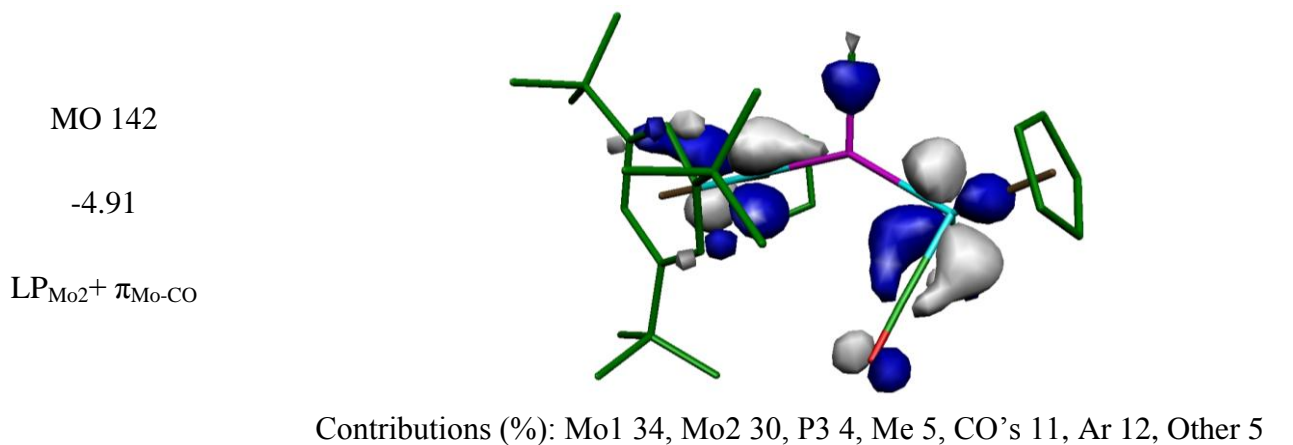
Contributions (%): Mo1 17, Mo2 18, P3 31, H8 0, CO's 1, Ar 5, Other 28

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**Table S6:** Molecular orbitals of *syn-3*.

OM	Energy (eV)	Assignment	Projection
LUMO 145	-1.64	$\pi^*_{\text{MoP}}$	
Contributions (%): Mo1 27, Mo2 3, P3 35, Me 2, CO's 14, Ar 5, Other 13			
HOMO 144	-4.44	$\text{LP}_{\text{Mo2}}$	
Contributions (%): Mo1 10, Mo2 64, P3 1, Me 0, CO's 4, Ar 14, Other 6			
MO 143	-4.68	$\text{Mo-Ar} + \text{LP}_{\text{Mo1}}$	
Contributions (%): Mo1 19, Mo2 46, P3 2, Me 0, CO's 6, Ar 20, Other 8			

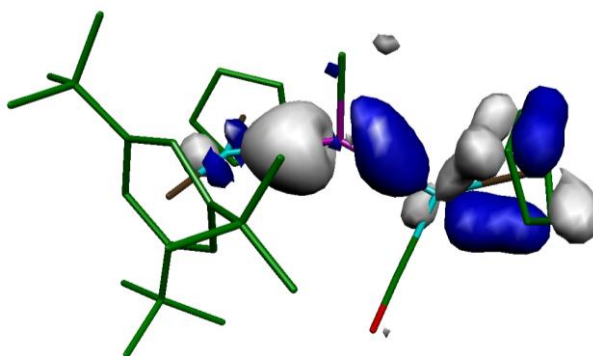




MO 136

-7.04

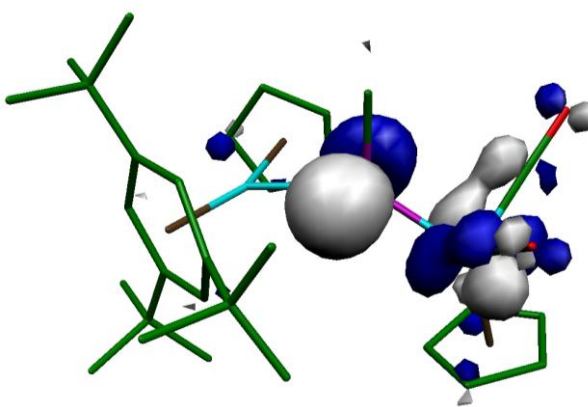
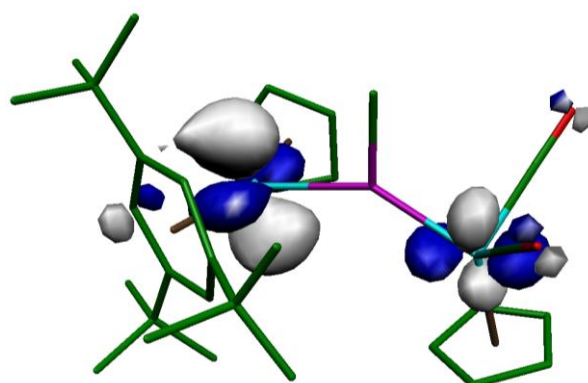
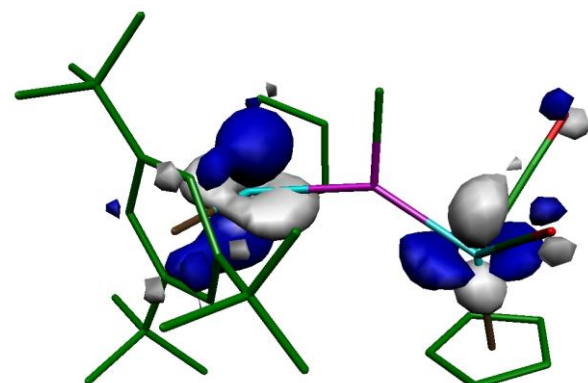
$\sigma_{\text{MoP}}$

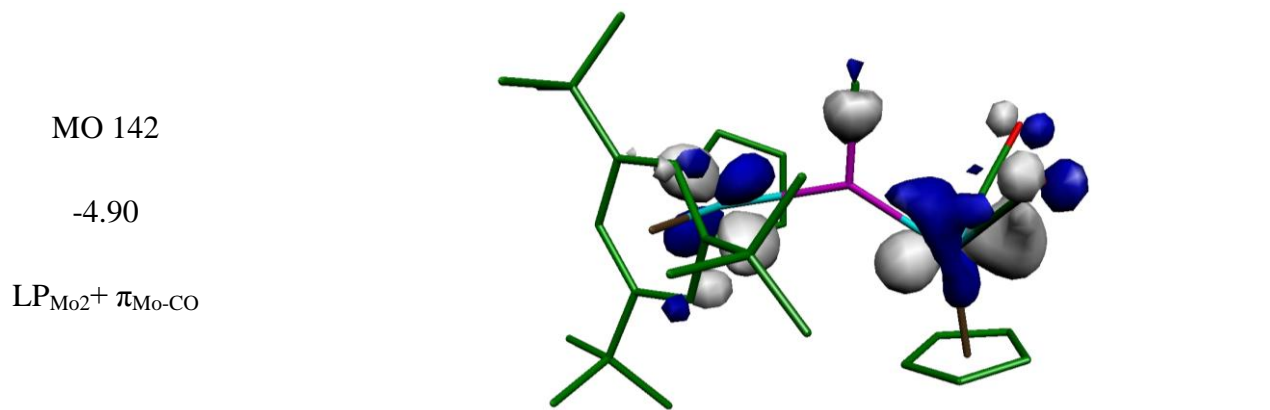


Contributions (%): Mo1 18, Mo2 15, P3 26, Me 3, CO's 2, Ar 4, Other 31

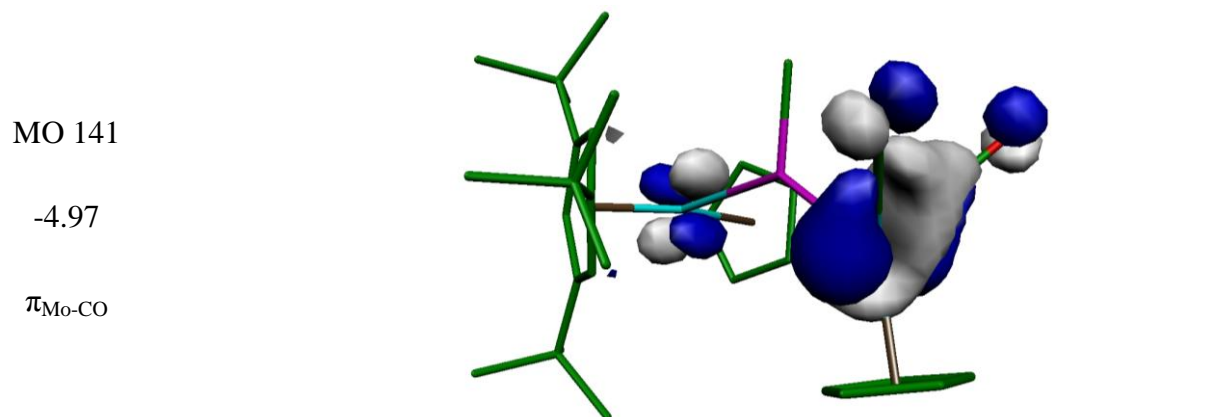
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**Table S7:** Molecular orbitals of *anti-3*.

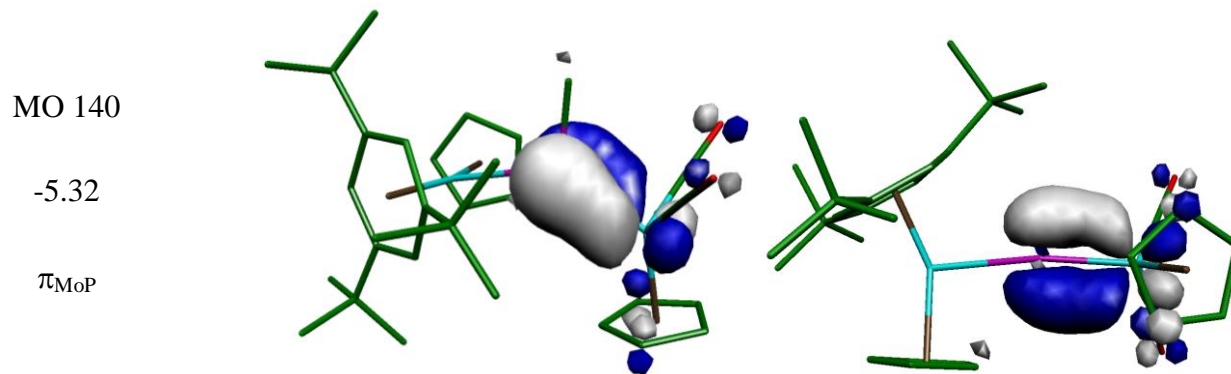
OM	Energy (eV)	Assignment	Projection
LUMO 145	-1.58	$\pi^*_{\text{MoP}}$	
Contributions (%): Mo1 29, Mo2 4, P3 34, Me 2, CO's 12, Ar 6, Other 13			
HOMO 144	-4.55	$\text{LP}_{\text{Mo2}} + \text{LP}_{\text{Mo1}}$	
Contributions (%): Mo1 19, Mo2 55, P3 1, Me 1, CO's 5, Ar 12, Other 6			
MO 143	-4.75	$\text{Mo-Ar} + \text{LP}_{\text{Mo1}}$	
Contributions (%): Mo1 24, Mo2 3, P3 1, Me 0, CO's 7, Ar 16, Other 8			



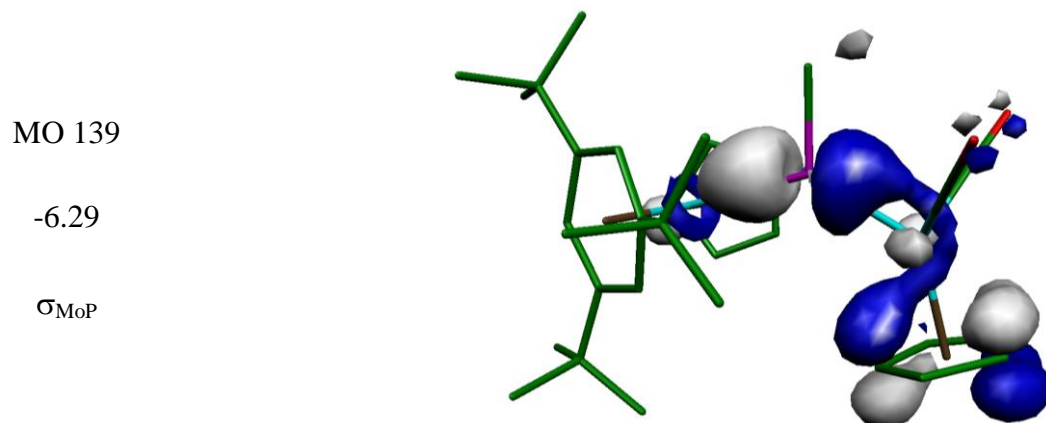
Contributions (%): Mo1 35, Mo2 26, P3 3, Me 5, CO's 13, Ar 11, Other 7



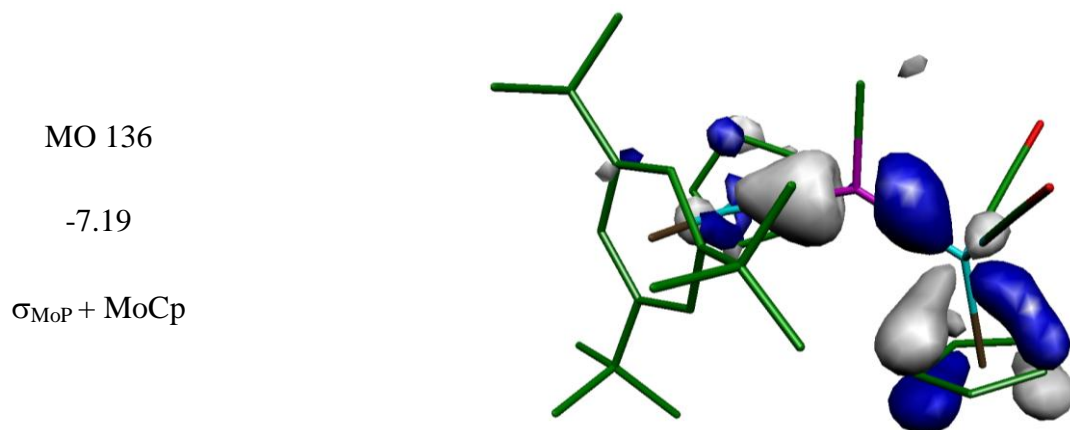
Contributions (%): Mo1 49, Mo2 14, P3 1, Me 0, CO's 23, Ar 6, Other 6



Contributions (%): Mo1 33, Mo2 2, P3 39, Me 2, CO's 6, Ar 4, Other 14



Contributions (%): Mo1 10, Mo2 12, P3 27, Me 2, CO's 4, Ar 3, Other 41



Contributions (%): Mo1 18, Mo2 12, P3 18, Me 2, CO's 1, Ar 5, Other 43

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**Table S8:** DFT/B3LYP-calculated stretching wavenumbers  $\nu(\text{cm}^{-1})$  and relative intensities for *syn* and *anti* isomers of compounds **2** and **3**.

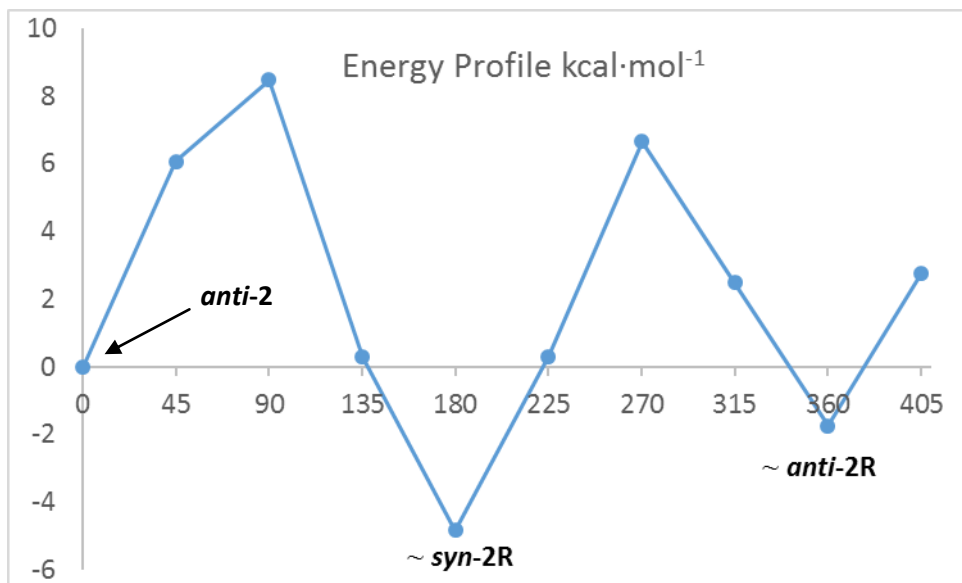
	<i>syn-2</i>	<i>syn-2R</i>	<i>anti-2</i>	<i>anti-2R</i>	<i>syn-3</i>	<i>anti-3</i>
$\nu_{\text{CO,symm.}}$	1999 (100)	1999 (100)	2023 (100)	2015 (100)	1997 (100)	2015 (100)
$\nu_{\text{CO,asymm.}}$	1944 (87)	1946 (75)	1970 (58)	1965 (61)	1938 (81)	1962 (61)

**Table S9:** DFT/B3LYP-calculated relative Gibbs Free Energies (Kcal/mol) in the gas phase.

	<i>syn-2</i>	<i>syn-2R</i>	<i>anti-2</i>	<i>anti-2R</i>	<i>syn-3</i>	<i>anti-3</i>	<b>5-mod</b>	<b>P-mod</b>	<b>7-mod</b>	<b>M1-mod</b>
$\Delta G_{298\text{K}}$	1.9	0	3.9	3.0	1.2	0	-2.3 <sup>a</sup>	6.5 <sup>b</sup>	-9.6 <sup>c</sup>	28.2 <sup>d</sup>

<sup>a</sup> Relative to *syn-2R* + HSnMe<sub>3</sub>. <sup>b</sup> Relative to *anti-3* + HSnMe<sub>3</sub>. <sup>c</sup> Calculated for the reaction *anti-3* + HSnMe<sub>3</sub> → **7-mod** + H<sub>2</sub>. <sup>d</sup> Relative to **1** + HSnMe<sub>3</sub>.

Energy profile for the rotation scan resulting from increasing the dihedral angle H8–P3–Mo1–C7 in *anti-2* by 45° steps.



Rotation	Energy (kcal/mol)
0 ( <i>anti-2</i> )	0.0
45	6.1
90	8.5
135	0.3
180 (~ <i>syn-2R</i> )	-4.8
225	0.3
270	6.7
315	2.5
360 (~ <i>anti-2R</i> )	-1.7
405	2.8

**Reference 42.** Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.02*, Gaussian, Inc., Wallingford, CT, 2004.