

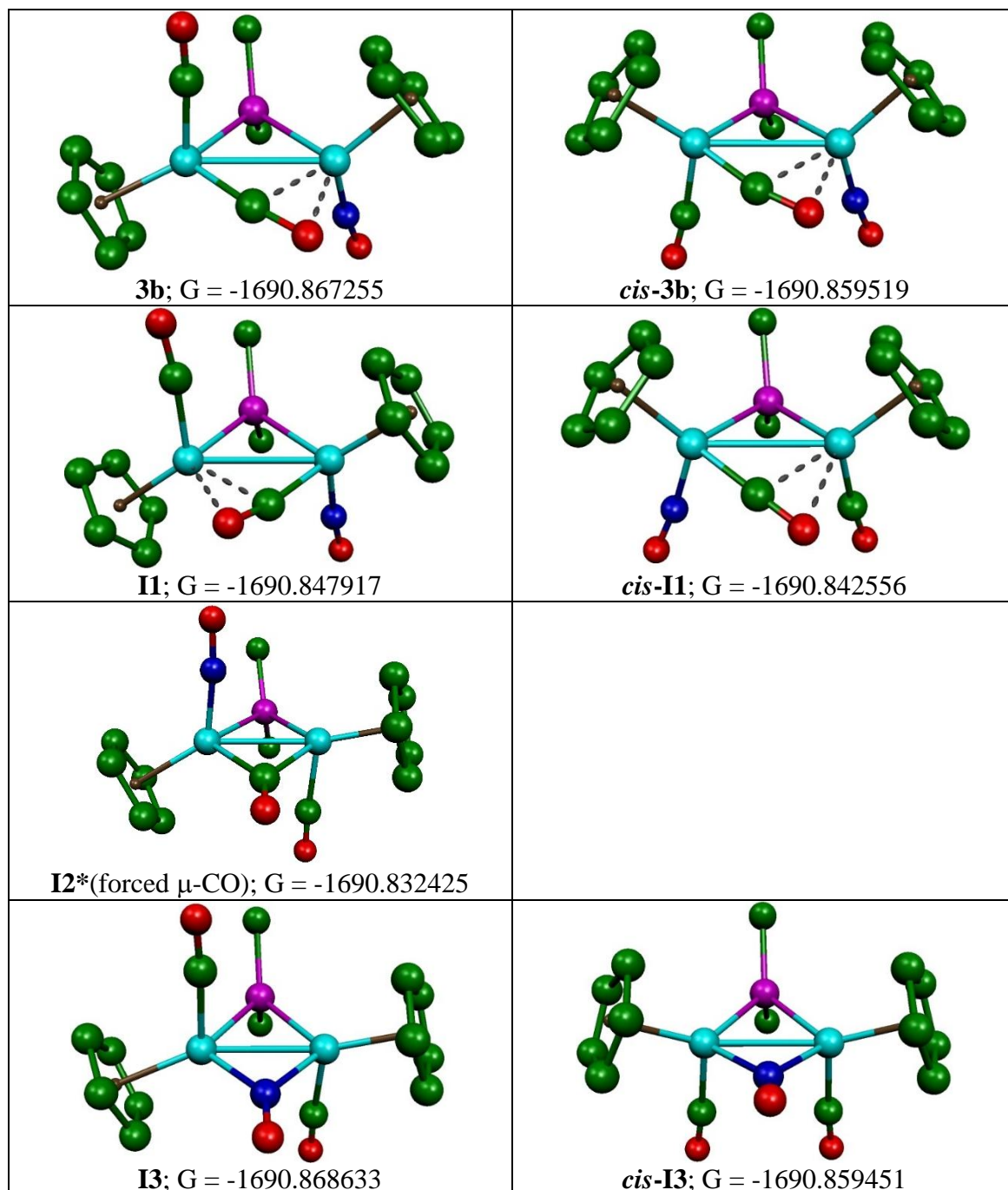
Electronic Supplementary Information

Terminal vs. Bridging Coordination of CO and NO Ligands after Decarbonylation of $[W_2Cp_2(\mu-PR_2)(CO)_3(NO)]$ Complexes (R = Ph, Cy). An Experimental and Computational Study.

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Table S1. DFT optimized structures for different isomers of compound **3b** (B3LYP // LANL2DZ, 6-31G*).



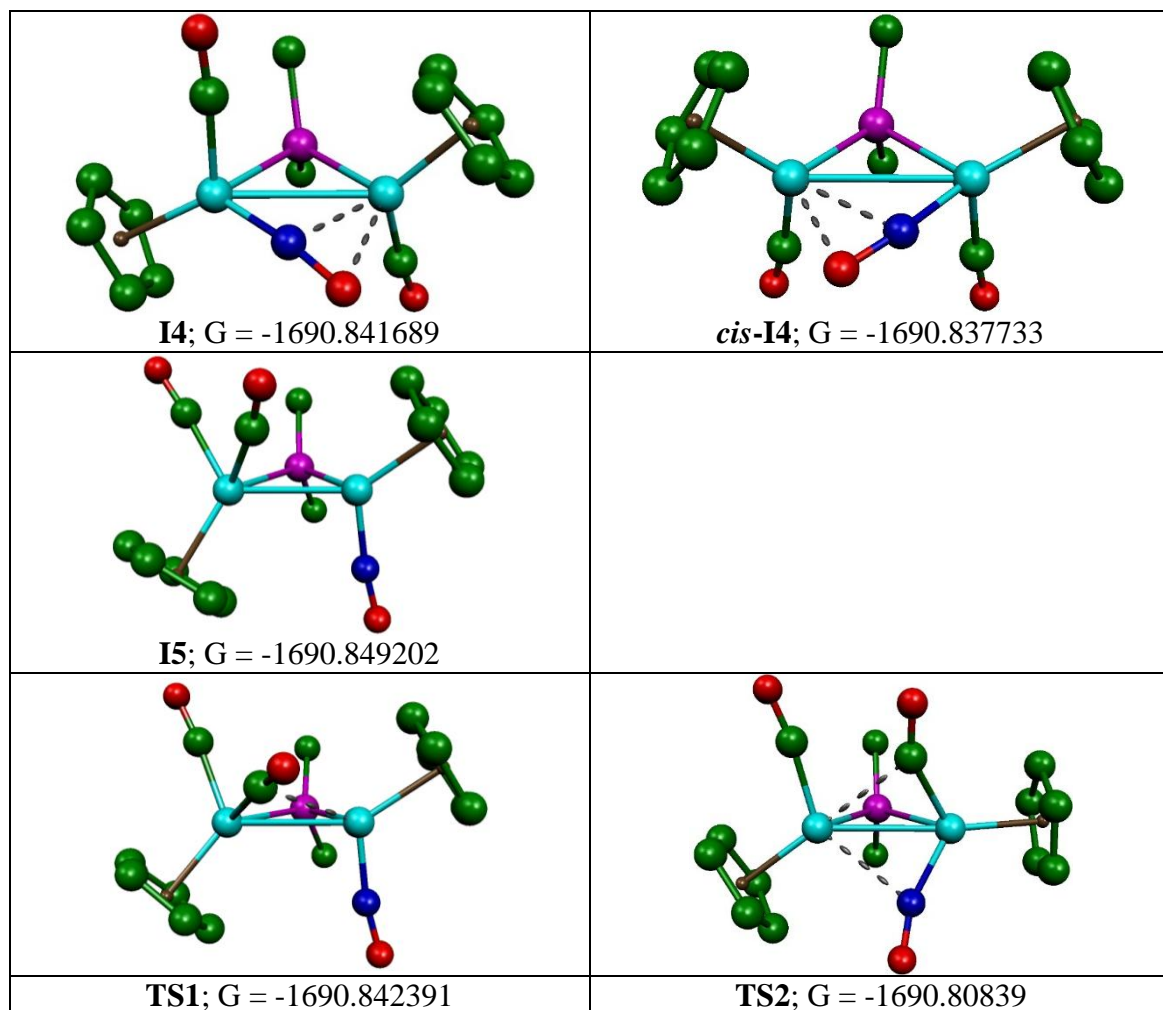


Table S2. Relative Gibbs Free Energies (kJ/mol) of DFT-optimized structures (B3LYP // LANL2DZ, 6-31G*).

	3b	<i>cis-3b</i>	I1	<i>cis-I1</i>	I2*	I3	<i>cis-I3</i>	I4	<i>cis-I4</i>	I5	TS1	TS2
ΔG	3.6	23.9	54.4	68.5	95.1	0	24.1	70.7	81.1	51.0	68.8	158.2

Table S3. DFT-optimized structures of compounds **3b** and **I3** with different functionals.

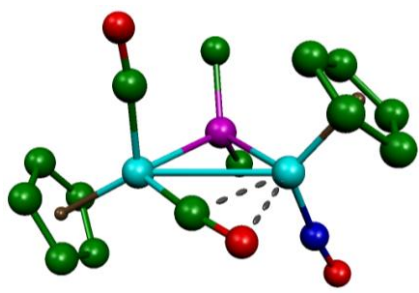
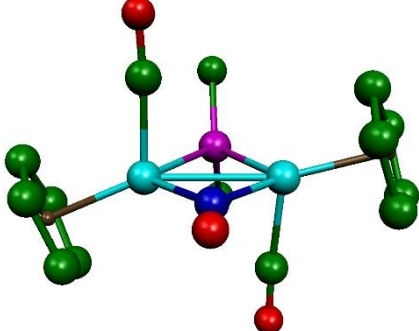
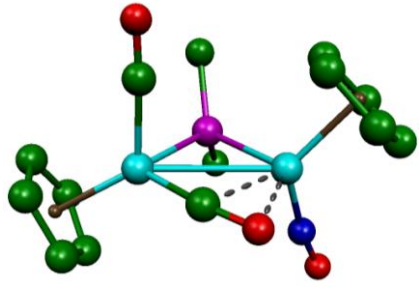
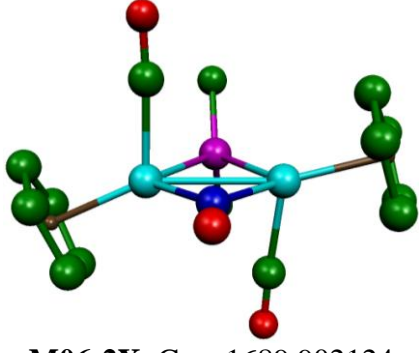
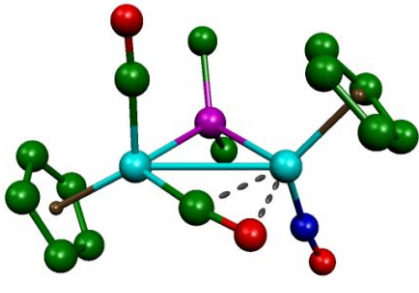
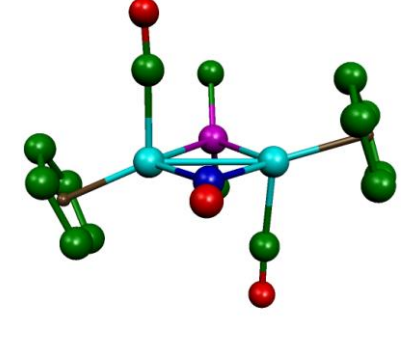
3b	I3
 <p>BP86; G = -1691.090487</p>	 <p>BP86; G = -1691.090414</p>
 <p>M06-2X; G = -1689.905297</p>	 <p>M06-2X; G = -1689.902124</p>
 <p>ωB97XD; G = -1690.499926</p>	 <p>ωB97XD; G = -1690.500702</p>

Table S4. Relative Gibbs Free Energies of compounds **3b** and **I3** (kJ/mol) computed with different DFT functionals.

	BP86	M06-2X	ωB97XD
$\Delta G_{I3 \rightarrow 3a}$	-0.2	-8.3	2.0

Table S5. DFT-optimized structures of compounds **3b** and **I2** (ω B97XD // SDD, 6-31G*).

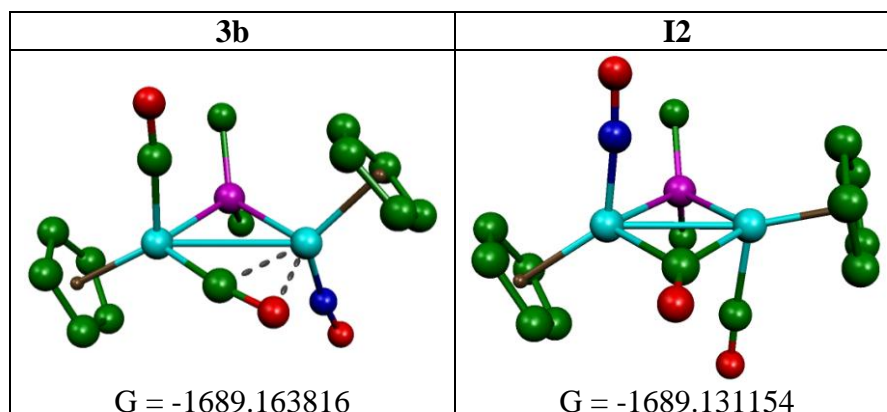
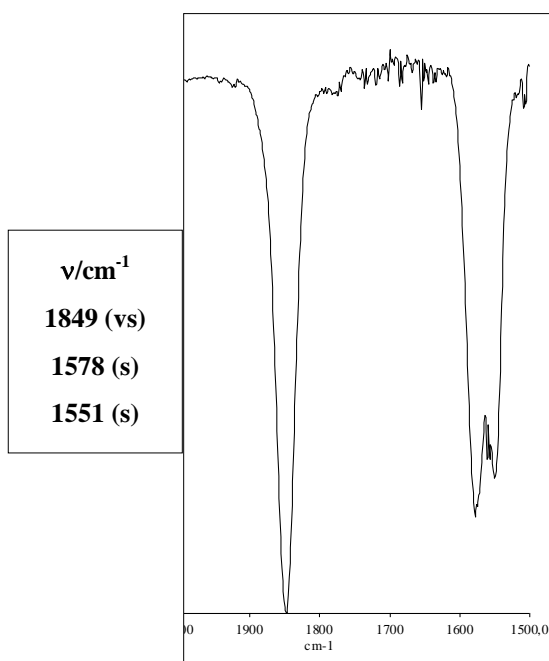
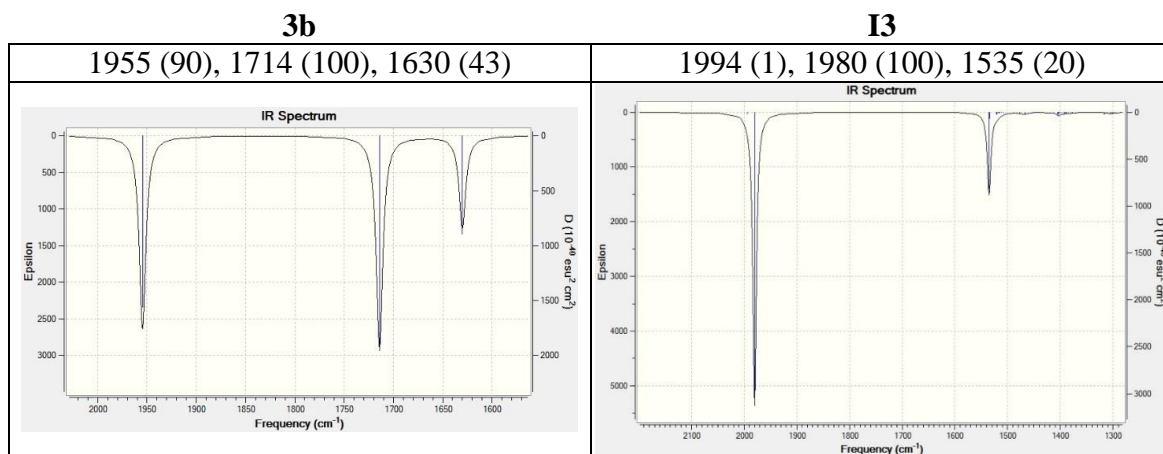


Table S6. Relative energies of compounds **3b** and **I2** ($\text{kJ}\cdot\text{mol}^{-1}$) (ω B97XD // SDD, 6-31G*).

$\Delta G_{3b \rightarrow I2}$	85.8
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Table S7. DFT-calculated stretching wavenumbers $\nu(\text{cm}^{-1})$ and relative intensities for isomers **3b** and **I3** (B3LYP // LANL2DZ, 6-31G*). The experimental spectrum of **3b** in dichloromethane solution is shown below.



Reference 49

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; 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.; and Pople, J. A.; *Gaussian 03, Revision B.02*; Gaussian, Inc.: Wallingford, CT, 2004.

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