

SUPPLEMENTARY MATERIAL

Table 1. Selected DFT calculated bond lengths [Å] and angles of $[W(CO)_5(py)]$, $[W(CO)_5(pyCN)]$ and $[W(CO)_5(piper)]$ compared with the symmetry-averaged experimental values. X-ray diffraction data from refs.¹⁻³

	$[W(CO)_5(py)]$			$[W(CO)_5(pyCN)]$		$[W(CO)_5(pip)]$		
	ADF BP	G98 B3LYP	Expt.	ADF BP	G98 B3LYP	ADF BP	G98 B3LYP	Expt.
W - N	2.295	2.338	2.272	2.296	2.330	2.346	2.397	2.315
W – C _{trans}	1.994	2.009	1.976	1.997	2.015	1.994	2.009	1.971
W – C _{cis}	2.047	2.065	2.017	2.049	2.069	2.046	2.067	2.045
N1-C2	1.356	1.353	1.349	1.358	1.352	1.500	1.495	1.495
C2-C3	1.391	1.396	1.395	1.389	1.388	1.531	1.533	1.526
C3-C4	1.396	1.400	1.386	1.405	1.402	1.534	1.535	1.529
(C-O) _{trans}	1.166	1.166	1.149	1.166	1.161	1.167	1.162	1.163
(C-O) _{cis}	1.162	1.161	1.150	1.162	1.156	1.164	1.158	1.145
C4-C (CN)	-	-	-	1.431	1.433	-	-	-
C-N (CN)	-	-	-	1.166	1.163	-	-	-
W- N1-C2	121.5	121.4	120.8	121.6	121.4	114.9	115.4	114.0
N1-C2-C3	123.2	123.4	122.3	123.6	123.5	113.3	113.1	112.6
C2-C3-C4	119.1	119.1	118.8	119.1	118.9	111.4	111.3	110.9
C _{trans} -W-C _{cis}	88.8	89.4	87.8	88.2	89.6	89.8	89.1	89.1
W-C _{cis} -O _{cis}	177.8	176.7	178.3	176.9	178.8	177.6	177.9	177.7

Table 2. DFT ADF/SAOP calculated one-electron energies and compositions of selected highest occupied and low-lying unoccupied molecular orbitals of [W(CO)₅(py)] (45°) expressed in terms of composing fragments.

MO	E (eV)	Prevailing Character	W	(CO) _{cis}	(CO) _{trans}	py
Unoccupied						
44a ₁	-2.59	d _W	30 (s); 35(d _{z2})	7	18	9
15a ₂	-2.59	d _W + CO	63 (d _{xy})	34		2
~	~					
42a ₁	-3.51	π CO + d _W	41 (d _{x2-y2})	53		4
23b ₁	-3.72	π CO + d _W	34 (d _{xz})	35	17	13
27b ₂	-3.72	π CO + d _W	37 (d _{yz})	41	16	3
41a ₁	-4.08	py+W	19(s); 3(d _{z2})	3	2	70
14a ₂	-4.91	π CO		98		
26b ₂	-5.05	π CO		36	62	
22b ₁	-5.04	π CO		35	64	
13a ₂	-5.84	π CO		80		18
25b ₂	-6.30	π CO	3 (p _y)	93	2	
21b ₁	-6.29	π CO	3 (p _x)	95		
12a ₂	-6.47	π py		16		83
40a ₁	-6.85	π CO	8 (p _z); 3(d _{z2})	85		2
20b ₁	-7.15	π py			3	96
Occupied						
19b ₁	-9.57	d _W + π CO	56 (d _{xz})	24	14	5
24b ₂	-9.62	d _W + π CO	59 (d _{yz})	27	15	
39 a ₁	-10.00	d _W + π CO	56 (d _{x2-y2})	43		
11a ₂	-11.70	py		1		98

Table 3. DFT ADF/SAOP calculated one-electron energies and compositions of selected highest occupied and low-lying unoccupied molecular orbitals of [W(CO)₅(py)] (0°) expressed in terms of composing fragments.

MO	E (eV)	Prevailing Character	W	(CO) _{cis}	(CO) _{trans}	py
Unoccupied						
49a ₁	-2.58	d _W	19(s); 40 (d _{z2})	6	21	9
48a ₁	-2.81	d _W	11(s); 41 (d _{x2-y2})	12	11	23
~	~					
10a ₂	-3.49	π CO + d _W	41 (d _{xy});	58		
23b ₁	-3.69	π CO + d _W	36 (d _{xz})	41	16	7
27b ₂	-3.84	π CO + d _W	37 (d _{yz})	46	12	4
46a ₁	-4.04	py+W	19(s); 3(d _{z2})	5		72
9a ₂	-4.91	π CO		98		
26b ₂	-4.97	π CO		28	69	
22b ₁	-5.05	π CO		35	63	
45a ₁	-5.99	π CO		98		
25b ₂	-6.30	π CO	3 (p _y)	93	2	
21b ₁	-6.33	π CO	3 (p _x)	95		
8a ₂	-6.47	π py				99
44a ₁	-6.85	π CO	8 (p _z); 3(d _{z2})	84		2
20b ₁	-7.12	π py			3	96
Occupied						
19b ₁	-9.59	d _W + π CO	57 (d _{xz})	24	15	2
24b ₂	-9.65	d _W + π CO	58 (d _{yz})	27	15	
7a ₂	-10.03	d _W + π CO	56 (d _{xy})	43		
6a ₂	-11.70	py		1		98

Table 4. DFT ADF/SAOP calculated one-electron energies and compositions of selected highest occupied and low-lying unoccupied molecular orbitals of [W(CO)₅(pyCN)] (0°) expressed in terms of composing fragments.

MO	E (eV)	Prevailing Character	W	(CO) _{cis}	(CO) _{tr}	pyC N
Unoccupied	-					
54a ₁	-2.64	d _W	28(d _{z2}); 18(d _{x2-y2});	10	18	25
52a ₁	-3.22	d _W	5(d _{z2}); 34(d _{x2-y2});	25	2	33
~	~					
10a ₂	-3.86	π CO + d _W	40(d _{xy})	56	1	
25b ₁	-3.95	π CO + d _W	34(d _{xz})	38	20	6
29b ₂	-4.24	π CO + d _W	36(d _{yz})	52		11
50a ₁	-4.28	pyCN	17(s); 3(d _{z2})	2	2	74
24b ₁	-4.91	π pyCN		7	1	90
28b ₂	-5.03	π CO	1(p _y); 11(d _{xy});	5	78	4
9a ₂	-5.22	π CO		98		
23b ₁	-5.46	π CO		35	63	
27b ₂	-5.48	π pyCN				98
49a ₁	-6.35	π CO		98		
22b ₁	-6.46	π CO	3(p _x)	95		
26b ₂	-6.69	π CO	3(p _y)	93	2	
48a ₁	-7.05	π CO	8(p _z); 3(d _{z2})	84		2
8a ₂	-7.09	π pyCN				99
21b ₁	-8.23	π pyCN	2(d _{xz})		3	96
Occupied						
25b ₂	-9.92	d _W + π CO	58(d _{yz})	27	15	-
20b ₁	-10.05	d _W + π CO	57(d _{xz})	24	15	2
7a ₂	-10.34	d _W + π CO	56(d _{xy})	43	-	-
6a ₂	-12.37	pyCN		1		98

Table 5. Comparison of selected low-lying singlet excitation energies of the 45° and 0° conformations of [W(CO)₅(pyCN)]. Selected transitions with oscillator strengths larger than 0.001 were calculated by G98/B3LYP TD-DFT. Extinction coeff. in M⁻¹cm⁻¹.

State	Composition (ADF/SAOP)	A		B		Expt.	Ext. coeff.
		Transition eV (nm)	Osc. str.	Transition eV (nm)	Osc. str.		
b ¹ A ₁	98% (20b ₁ ->21b ₁)	2.50 (496)	0.209	2.43 (509)	0.191	454 ^a	8680 ^b
a ¹ B ₁	81% (20b ₁ -> 44a ₁); 8%(25b ₂ -> 13a ₂) 8% (43a ₁ -> 22b ₁)	3.06 (405)	0.012	3.07 (404)	0.012	399 ^a	7280 ^b
a ¹ B ₂	79% (25b ₂ -> 44a ₁); 9% (20b ₁ -> 12a ₂)	3.15 (394)	0.013	3.10 (399)	0.009	355	

^a Obtained by gaussian fitting of the spectrum measured in methylcyclohexane.

^b Data from ref.⁴

Table 6. Selected TD-DFT calculated low-lying singlet excitation energies of [W(CO)₅(py)] (45°) with oscillator strength larger than 0.001. Experimental values obtained in isoctane. Data from ref.⁵

State	Composition (ADF/SAOP)	ADF/SAOP		G98/B3LYP		Expt.
		Transition eV (nm)	Osc. str.	Transition eV (nm)	Osc. str.	
a ¹ B ₁	55% (19b ₁ -> 40a ₁) 23%(24b ₂ -> 12a ₂)	2.90 (427)	0.008	3.08 (403)	0.011	382 ^a
b ¹ A ₁	98% (19b ₁ ->20b ₁)	2.70 (459)	0.124	3.13 (395)	0.135	355 ^a
a ¹ B ₂	83% (24b ₂ -> 44a ₁) 9% (24b ₂ -> 45a ₁)	3.04 (408)	0.009	3.18 (390)	0.012	

^a Overlapping absorption bands. The 355 nm is strongly solvatochromic. A shoulder at 440 nm (615 M⁻¹cm⁻¹) is attributed to a spin-forbidden triplet transition.

Table 7. TD-DFT calculated low-lying triplet excitation energies of [W(CO)₅(pyCN)] in the 45° conformation.

State	Composition (ADF/SAOP)	ADF/SAOP	G98/B3LYP
		Transition eV (nm)	Transition eV (nm)
a ³ A ₁	99% (20b ₁ ->21b ₁)	1.63 (760)	1.99 (621)
a ³ A ₂	99% (25b ₂ ->21b ₁)	1.72 (720)	2.19 (565)
a ³ B ₁	99% (43a ₁ -> 21b ₁)	2.07 (559)	2.57 (482)
a ³ B ₂	87% (20b ₁ -> 12a ₂); 12 (25b ₂ -> 44a ₁)	2.72 (456)	2.61 (474)

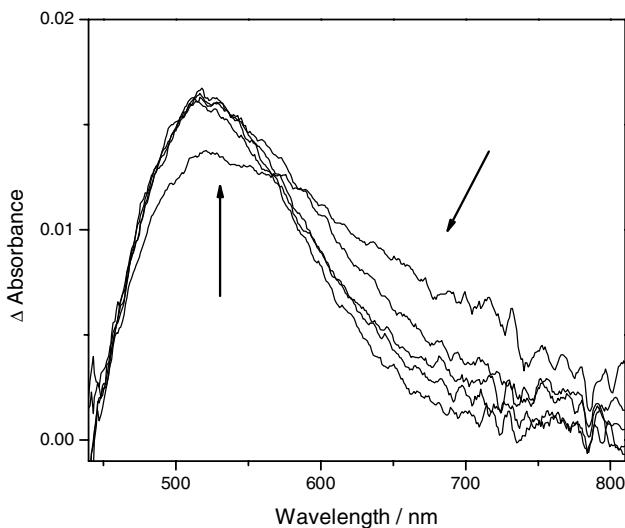


Figure 1. Time-resolved visible absorption spectra of $[\text{W}(\text{CO})_5(\text{pyCN})]$ measured in CH_3CN at 1, 2, 5, 10, and 40 ps after \sim fs, 390 nm excitation. The spectra evolve in the direction of the arrows, reflecting vibrational cooling.

(Previously, it was suggested⁶ that the early rise in intensity of excited-state absorption of $[\text{W}(\text{CO})_5(\text{pyCN})]$ and $[\text{W}(\text{CO})_5(\text{pyC(O)CH}_3)]$ is caused by intersystem crossing. This explanation seems unlikely in view of the results presented herein which indicate that this effect originates in vibrational cooling. Moreover, ISC is expected to occur within a few tens of femtoseconds.)

Time-resolved UV-Vis absorption spectra was measured using the experimental setup at the Institute of Molecular Chemistry, University of Amsterdam, that is described in ref.⁷ A \sim 130 fs, 390 nm pump pulse was generated by frequency doubling of the T:S laser output. White-light continuum probe pulses were generated by focusing the 800 nm fundamental in a sapphire plate. The solution was placed in a 2 mm fused silica cell.

References

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