Supporting Information for

The role of spin states in catalytic mechanism of the intra- and extradiol cleavage of catechols by O_2

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Coordinates of optimized structures

https://iochem.udg.edu:8443/browse/review-collection/100/205/e0158c795ca8e8683f8920f1

Table S1. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4H_2 ligand, obtained using S12h/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4H_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	17.34	15.71	39.42	31.82	20.49	27.80	31.91	14.91	23.55	11.93	32.28	1.30	1.07	-3.06
IS	11.21	9.19	30.28	26.21	15.77	23.42	40.53	2.89	14.43	-1.82	41.42	14.23	0.62	-16.81
HS	0.00	-0.99	16.56	10.75	6.33	29.80	19.84	3.01	12.37	-16.64	22.86	-8.10	-6.91	-31.63

Table S2. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4Me_2 ligand, obtained using S12h/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4Me_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	18.04	15.76	50.86	41.22	34.43	38.34	38.76	24.27	28.72	15.44	37.91	5.16	7.86	0.45
IS	11.48	9.70	56.30	30.15	21.54	30.75	23.15	9.94	15.90	2.09	46.16	16.30	5.53	-12.90
HS	0.00	-0.85	22.28	16.89	14.32	35.45	23.55	10.10	17.60	-12.89	25.38	-4.52	1.52	-27.88

Table S3. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4H_2 ligand, obtained using SSB-D/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4H_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	3.65	1.64	12.90	14.30	9.47	11.02	9.30	-4.43	2.52	-5.84	8.66	-15.25	-17.37	-19.40
IS	4.74	2.43	10.57	13.42	5.78	7.17	-0.18	-13.25	-5.93	-6.09	-0.11	-21.71	-22.90	-19.65
HS	0.00	-1.81	5.21	5.91	4.82	22.15	1.98	-12.81	-5.27	-15.81	4.02	-20.61	-22.57	-29.37

Table S4. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4Me_2 ligand, obtained using SSB-D/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4Me_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	2.49	0.02	21.77	23.40	21.56	20.70	13.80	1.89	5.46	-3.21	13.03	-12.21	-12.63	-16.77
IS	4.21	2.84	13.40	17.06	9.98	12.43	3.92	-7.51	-5.94	-2.84	3.15	-21.15	-17.00	-16.40
HS	0.00	-2.44	9.89	10.13	9.53	26.17	4.78	-7.16	-1.17	-12.92	5.46	-19.10	-17.87	-26.48

Table S5. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4H_2 ligand, obtained using M06-L/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4H_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	6.58	5.69	15.44	14.72	10.09	11.79	10.92	-3.08	4.86	-3.94	10.68	-20.78	-22.12	-18.08
IS	9.87	8.55	13.01	16.58	9.00	9.40	0.75	-11.89	-2.60	-7.08	1.27	-26.84	-26.82	-21.22
HS	0.00	-0.60	5.00	5.40	3.50	18.65	2.54	-11.96	-3.76	-20.35	5.01	-26.37	-26.91	-34.49

Table S6. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4Me_2 ligand, obtained using M06-L/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4Me_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	5.67	4.11	24.02	26.13	23.72	22.31	16.76	5.00	8.75	-1.45	14.87	-17.70	-16.73	-15.59
IS	9.72	9.36	15.21	22.01	14.60	16.68	5.82	-4.91	-1.95	-3.71	5.20	-25.67	-20.03	-17.85
HS	0.00	-1.07	10.89	10.96	9.75	23.17	6.27	-4.92	1.31	-17.04	7.39	-23.84	-20.98	-31.18

Table S7. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4H_2 ligand, obtained using MVS/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4H_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	10.13	9.17	8099.92	22.76	14.87	16.63	15.00	-0.42	7.37	3.11	12.59	-15.30	-17.18	-11.78
IS	10.42	9.74	18.59	22.60	12.47	12.04	3.56	-11.33	-1.43	-0.06	1.03	-22.82	-21.82	-14.95
HS	0.00	-0.21	11.22	8.64	6.04	24.04	5.94	-11.42	-3.16	-16.11	5.68	-22.38	-22.04	-31.00

Table S8. Electronic energies of stationary points in catechol dioxygenation mechanism, with LN_4Me_2 ligand, obtained using MVS/TZ2P//S12g/TZ2P level of theory, relative to the ground state of the initial complex (0).

L= LN_4Me_2	**First part of the reaction**						**Extradiol path**				**Intradiol path**			
structure	**0**	**1**	**2**	**TS_{23}**	**3**	**TS_{34}**	**TS_{45e}**	**5e**	**TS_{56e}**	**product**	**TS_{45i}**	**5i**	**TS_{56i}**	**product**
LS	8.79	7.81	37.85	35.92	32.02	29.63	20.45	7.47	13.86	4.30	16.71	-11.84	-13.12	-10.59
IS	10.01	11.86	21.41	26.92	16.66	20.80	7.42	-3.97	-0.01	2.52	5.41	-22.07	-19.87	-12.37
HS	0.00	-1.71	18.12	14.88	13.37	28.58	8.00	-3.88	1.99	-13.71	6.91	-19.58	-16.92	-28.60

Table S9. Selected average bond lengths (Å) of $[Fe^{III}(LN_4H_2)Cl_2]^+$, $[Fe^{III}(LN_4Me_2)Cl_2]^+$ and $[Fe^{III}(LN_4Me_2)Cat]^+$.

	Bond	Fe-N	Fe- N_{Pyr}	Fe-Cl
$[Fe^{III}(LN_4H_2)Cl_2]^+$	DFT	2.248	2.168	2.270
	X-ray	2.189	2.094	2.289
	Bond	Fe-N	Fe- N_{Pyr}	Fe-Cl
$[Fe^{III}(LN_4Me_2)Cl_2]^+$	DFT	2.284	2.165	2.268
	X-ray	2.228	2.116	2.248
	Bond	Fe-N	Fe- N_{Pyr}	Fe-O
$[Fe^{III}(LN_4Me_2)Cat]^+$	DFT	2.294	2.150	1.950
	X-ray	2.222	2.105	1.909