Electronic Supplementary Material (ESI) for Faraday Discussions.

SUPPORTING INFORMATION

Direct experimental evaluation of ligand-induced backbonding in nickel metallacyclic complexes

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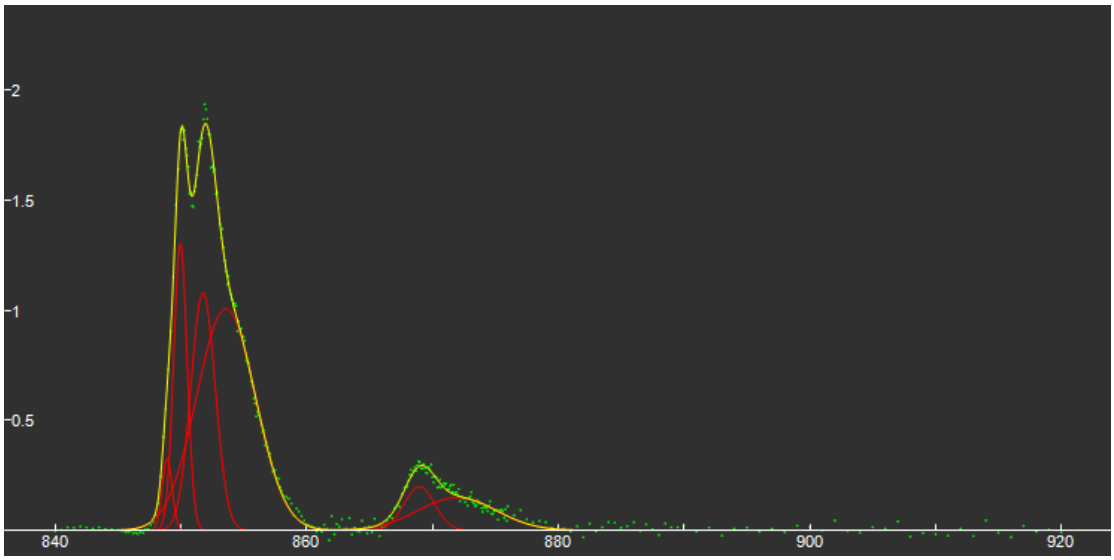
Contents

X-ray Absorption Spectroscopy – Peak Fitting

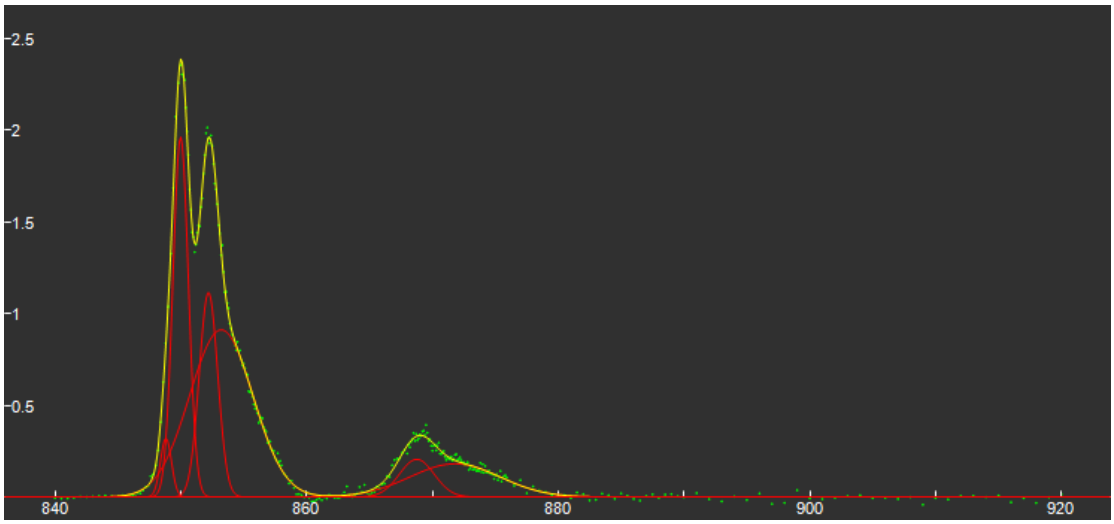
*SI 01. Simulated Ni L edge spectrum of **1**, spectra are normalized with Athena and its background subtracted with Fityk.*



*SI 02. Ni L edge pre-edge fit results for **1**.*

complex 1	gaussian	height	center	hwhm	area	FWHM
L_3 edge	1	0.328	848.909	0.464	0.324	0.927
	2	1.309	849.965	0.624	1.739	1.248
	3	1.082	851.768	1.136	2.618	2.272
	4	1.008	853.595	2.747	5.897	5.494
L_2 edge	5	0.199	868.965	1.430	0.605	2.860
	6	0.149	871.974	3.667	1.165	7.334

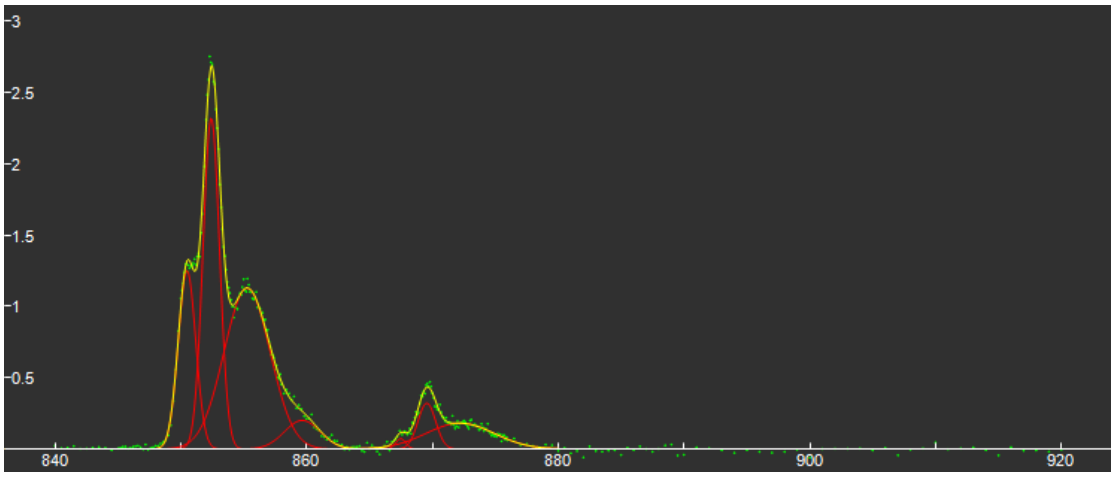
*SI 03. Simulated Ni L edge spectrum of **2**, spectra are normalized with Athena and its background subtracted with Fityk.*



*SI 04. Ni L edge pre-edge fit results for **2**.*

complex 2	gaussian	height	center	hwhm	area	FWHM
L_3 edge	1	0.321	848.820	0.514	0.352	1.028
	2	1.963	849.985	0.723	3.020	1.445
	3	1.116	852.201	0.863	2.050	1.725
	4	0.912	853.217	2.965	5.754	5.930
L_2 edge	5	0.206	868.762	1.631	0.714	3.261
	6	0.181	871.797	4.215	1.626	8.429

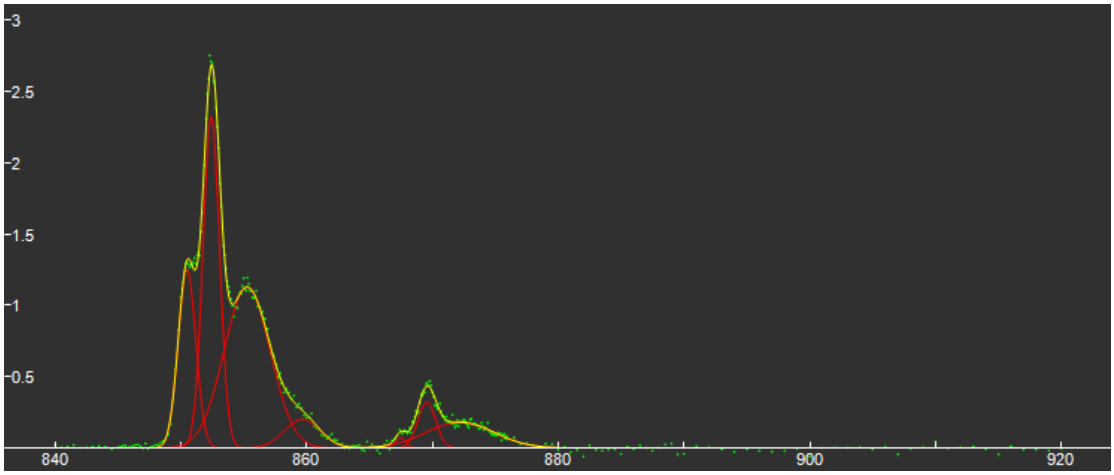
*SI 05. Simulated Ni L edge spectrum of **3**, spectra are normalized with Athena and its background subtracted with Fityk.*



*SI 06. Ni L edge pre-edge fit results for **3**.*

complex 3	**Gaussian**	**height**	**center**	**hwhm**	**area**	**FWHM**
L_3 edge	1	0.8401	849.4603	0.6646	1.1887	1.3293
	2	2.1918	851.5932	0.7861	3.6679	1.5721
	3	1.1171	854.4134	2.0235	4.8125	4.0471
	4	0.2488	858.3416	2.2268	1.1797	4.4536
L_2 edge	5	0.2836	868.7728	0.7438	0.4490	1.4876
	6	0.1448	871.7257	3.2767	1.0101	6.5535
	7	0.0623	866.6410	0.2594	0.0344	0.5188

*SI 07. Simulated Ni L edge spectrum of **4**, spectra are normalized with Athena and its background subtracted with Fityk.*



*SI 08. Ni L edge pre-edge fit results for **4**.*

complex 4	Gaussian	height	center	hwhm	area	FWHM
L_3 edge	1	1.251	850.495	0.818	2.178	1.636
	2	2.323	852.422	0.772	3.820	1.545
	3	1.128	855.271	2.154	5.172	4.308
	4	0.201	859.659	1.673	0.716	3.346
L_2 edge	5	0.073	867.482	0.468	0.072	0.936
	6	0.322	869.557	0.829	0.568	1.657
	7	0.181	872.205	3.195	1.233	6.390

Time-Dependent Density Functional Calculations

*SI 09. Molecular orbital descriptions for complex **1** from ground state DFT calculations.*

Complex 1		Ni character				Normalized Ni character		
Orbital	**Energy**	**Total**	**s**	**p**	**d**	**s**	**p**	**d**
76	-0.0106	34.90%	0.80%	30.90%	3.20%	2.29%	88.54%	9.17%
77	0.00891	10.70%	1.30%	7.20%	2.20%	12.15%	67.29%	20.56%
78	0.01894	6.60%	4.30%	1.20%	1.10%	65.15%	18.18%	16.67%
79	0.02251	15.80%	0.00%	0.90%	14.90%	0.00%	5.70%	94.30%
80	0.03369	16.00%	0.10%	12.50%	3.40%	0.63%	78.13%	21.25%
81	0.03514	12.90%	0.50%	7.20%	5.20%	3.88%	55.81%	40.31%
82	0.05266	15.60%	4.50%	8.80%	2.30%	28.85%	56.41%	14.74%

*SI 10. Acceptor orbital descriptions from L-edge TD-DFT calculation for complex **1**.*

Transition Energy	Contribution from MO acceptors				
849.078	MO #	76	77	79	
	Contribution	76.08%	6.70%	5.69%	
849.157	MO #	76	79	77	
	Contribution	64.69%	16.94%	5.16%	
849.208	MO #	79	76	80	
	Contribution	59.53%	12.32%	7.14%	
849.248	MO #	79	76	80	
	Contribution	56.74%	21.06%	6.75%	
850.26	MO #	77	76		
	Contribution	81.34%	8.76%		
850.574	MO #	78	81	80	82
	Contribution	57.78%	17.48%	5.07%	4.80%
850.726	MO #	78	82	77	81
	Contribution	69.97%	10.52%	5.12%	4.55%
850.803	MO #	78	82	77	
	Contribution	79.82%	7.74%	4.93%	
851.052	MO #	80	81	79	
	Contribution	65.70%	19.12%	9.76%	
850.439	MO #	81	80	78	
	Contribution	52.99%	15.00%	11.78%	
850.55	MO #	81	78	80	77
	Contribution	40.06%	20.89%	10.89%	4.54%

*SI 11. Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for **1**. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.*

		Weighted Average			Renormalized		
Photon E	**Intensity**	**Ni**	**pi ligand**	**Phosphine**	**Ni**	**pi ligand**	**Phosphine**
849.157	0.00948	25.80%	22.28%	38.70%	29.73%	25.67%	44.60%
849.078	0.00131	28.17%	19.57%	40.73%	31.84%	22.12%	46.04%
849.208	0.0225	14.85%	32.17%	31.97%	18.80%	40.73%	40.47%
849.248	0.0163	17.40%	32.33%	34.83%	20.57%	38.23%	41.19%
850.26	0.00302	11.76%	40.20%	38.14%	13.05%	44.62%	42.33%
850.439	0.0174	10.01%	10.43%	59.31%	12.55%	13.08%	74.37%
850.55	0.0175	12.03%	17.04%	68.19%	12.37%	17.52%	70.11%
850.574	0.0135	7.63%	11.32%	66.18%	8.96%	13.30%	77.74%
850.726	0.00308	7.39%	14.39%	68.39%	8.20%	15.95%	75.84%
850.803	0.00163	7.00%	14.16%	71.33%	7.57%	15.31%	77.12%
851.052	0.0011	14.52%	16.26%	63.80%	15.35%	17.19%	67.46%

*SI 12. Molecular orbital descriptions for complex **2** from ground state DFT calculations.*

Complex 2		Ni character				Normalized Ni character		
Orbital	**Energy**	**Total**	**s**	**p**	**d**	**s**	**p**	**d**
63	-0.00606	42.60%	0.00%	36.90%	5.70%	0.00%	0.87%	0.13%
64	0.01785	6.40%	5.60%	0.00%	0.80%	0.88%	0.00%	0.13%
65	0.03339	16.40%	0.00%	16.30%	0.10%	0.00%	0.99%	0.01%
66	0.03785	14.60%	1.30%	6.70%	6.60%	0.09%	0.46%	0.45%
67	0.04489	23.70%	0.10%	3.20%	20.40%	0.00%	0.14%	0.86%
68	0.05371	11.30%	0.50%	7.80%	3.00%	0.04%	0.69%	0.27%
69	0.05634	22.50%	12.00%	7.60%	2.90%	0.53%	0.34%	0.13%

*SI 13. Acceptor orbital descriptions from L-edge TD-DFT calculation for complex **2**.*

Orbital	Contribution from MO acceptors					
849.399	MO #	63	67			
	Contribution	86.78%	8.21%			
850.725	MO #	64	69			
	Contribution	90.17%	6.08%			
850.947	MO #	64	69			
	Contribution	85.66%	9.68%			
851.032	MO #	64	66			
	Contribution	82.10%	9.84%			
850.808	MO #	66	67			
	Contribution	78.47%	4.25%			
849.474	MO #	67	68	66		
	Contribution	70.25%	7.73%	4.81%		
849.481	MO #	67	63	68	66	63
	Contribution	62.09%	11.24%	6.24%	5.02%	4.88%

*SI 14. Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for **2**. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.*

		Weighted Average			Normalized		
Photon E	**Intensity**	**Ni**	**pi ligand**	**Phosphine**	**Ni**	**pi ligand**	**Phosphine**
849.399	0.00911	12.32%	4.90%	77.77%	12.97%	5.15%	81.88%
849.474	0.0247	4.97%	27.83%	49.98%	6.01%	33.62%	60.38%
849.481	0.0313	6.65%	24.95%	57.87%	7.43%	27.89%	64.68%
850.725	0.00495	1.41%	3.46%	91.37%	1.47%	3.60%	94.93%
850.808	0.0204	10.42%	7.76%	64.55%	12.60%	9.38%	78.02%
850.947	0.00246	1.67%	4.01%	89.66%	1.75%	4.20%	94.04%
851.032	0.00829	2.10%	2.90%	86.94%	2.28%	3.16%	94.56%

*SI 15. Molecular orbital descriptions for complex **3** from ground state DFT calculations.*

Complex 3		Ni character				Normalized Ni character		
Orbital	**Energy**	**Total**	**s**	**p**	**d**	**s**	**p**	**d**
91	-0.01633	37.10%	0.00%	31.00%	6.10%	0.00%	83.56%	16.44%
92	-0.00012	32.40%	0.40%	2.50%	29.50%	1.23%	7.72%	91.05%
93	0.00779	6.50%	3.90%	2.00%	0.60%	60.00%	30.77%	9.23%
94	0.02601	15.20%	0.80%	8.40%	6.00%	5.26%	55.26%	39.47%
95	0.03266	5.50%	0.30%	3.60%	1.60%	5.45%	65.45%	29.09%

*SI 16. Acceptor orbital descriptions from L-edge TD-DFT calculation for complex **3**.*

	Contribution from MO		
Orbital	**acceptors**		
849.722	MO #	91	
	Contribution	90.96%	
849.97	MO #	91	
	Contribution	93.40%	
850.056	MO #	91	
	Contribution	93.17%	
848.614	MO #	92	
	Contribution	86.17%	
848.712	MO #	92	
	Contribution	88.24%	
851.305	MO #	93	
	Contribution	90.41%	
851.727	MO #	93	94
	Contribution	82.99%	6.77%
851.446	MO #	94	95
	Contribution	69.51%	14.63%
851.525	MO #	94	95
	Contribution	6.11%	64.66%

*SI 17. Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for **3**. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.*

		Weighted Average			Normalized		
Photon E	**Intensity**	**Ni**	**pi ligand**	**Phosphine**	**Ni**	**pi ligand**	**Phosphine**
848.614	0.0356	27.92%	32.83%	54.22%	24.28%	28.56%	47.16%
848.712	0.0423	28.59%	33.62%	25.42%	32.63%	38.37%	29.01%
849.722	0.0135	34.65%	4.39%	54.36%	37.10%	4.70%	58.20%
849.97	0.00138	50.22%	39.66%	3.52%	53.77%	42.46%	3.77%
850.056	0.00605	34.56%	4.38%	54.22%	37.10%	4.70%	58.20%
851.305	0.00387	5.88%	2.53%	82.00%	6.50%	2.80%	90.70%
851.446	0.0158	11.37%	4.50%	68.27%	13.51%	5.34%	81.14%
851.525	0.0168	5.38%	3.70%	75.49%	6.36%	4.37%	89.26%
851.727	0.00406	6.42%	2.70%	80.64%	7.16%	3.00%	89.84%

SI 18. Complexes 4 TD-DFT calculation transitions final state acceptor Ni character contribution in MO, and normalized Ni character contribution are also provided.

Complex 4		**Ni character**				**Normalized Ni character**		
Orbital	**Energy**	**Total**	**s**	**p**	**d**	**s**	**p**	**d**
95	-0.01776	34.70%	0.00%	25.10%	9.60%	0.00%	72.33%	27.67%
96	-0.01219	34.30%	0.10%	5.60%	28.60%	0.29%	16.33%	83.38%
97	0.00781	5.40%	3.30%	1.60%	0.50%	61.11%	29.63%	9.26%
98	0.02325	12.90%	0.70%	6.60%	5.60%	5.43%	51.16%	43.41%
99	0.03099	5.40%	0.20%	4.00%	1.20%	3.70%	74.07%	22.22%

*SI 19. Acceptor orbital descriptions from L-edge TD-DFT calculation for complex **4**.*

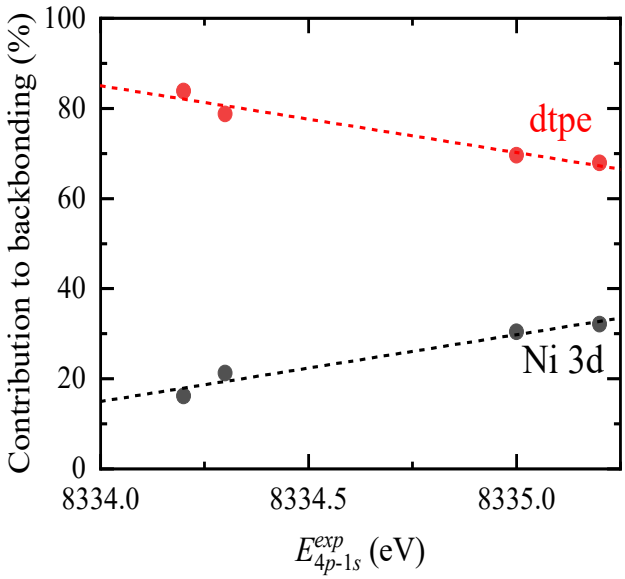
Orbital	Contribution from MO acceptors		
850.307	MO #	95	96
	Contribution	77.86%	17.20%
848.442	MO #	95	96
	Contribution	15.97%	76.35%
848.471	MO #	95	96
	Contribution	15.82%	76.40%
851.986	MO #	97	98
	Contribution	85.86%	7.05%
851.624	MO #	98	99
	Contribution	80.14%	9.54%
851.649	MO #	98	99
	Contribution	75.31%	9.20%

*SI 20. Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for **4**. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.*

		Weighted Average			Normalized		
Photon E	**Intensity**	**Ni**	**pi ligand**	**Phosphine**	**Ni**	**pi ligand**	**Phosphine**
848.442	0.0492	31.73%	28.39%	32.20%	34.37%	30.75%	34.88%
848.471	0.051	31.69%	28.39%	32.13%	34.37%	30.79%	34.84%
850.307	0.00884	32.92%	13.45%	48.69%	34.63%	14.15%	51.22%
851.624	0.0196	10.85%	2.17%	76.65%	12.10%	2.42%	85.48%
851.649	0.0169	10.21%	2.05%	72.25%	12.08%	2.42%	85.49%
851.986	0.00329	5.55%	0.34%	87.03%	5.97%	0.37%	93.66%

Additional Data

SI 21 Total contributions to backbonding from charge decomposition analysis (CDA). An increase in π acidity in the π ligand causes an overall increase in charge donation from both the metal centre and the diphosphine ligand (see SI 22), but the Ni 3d contribution is significantly greater with more π acidic ligands (such as in 3, 4).



SI 22 Calculated CDA-based charge donation from both the metal centre and the diphosphine ligand to π acidic ligands.

$EXP_{4p\leftarrow 1s}$(eV)	dtpe	Ni	Total	Ni 3d %	dtpe%
8334.2	0.217	0.042	0.2588	16.2	83.8
8334.3	0.296	0.080	0.37588	21.3	78.8
8335	0.291	0.127	0.41797	30.4	69.6
8335.2	0.336	0.159	0.49426	32.1	67.9

SI 23 Correlation of Ni L-edge peak intensities (experimental in black and TD-DFT in blue) with the energy of the Ni 4p←1s transition from Ni K-edge XAS. Top: contributions from direct Ni 3d backbonding (Peak A). Bottom: contributions including 3d/4p mixing (sum of peaks A & B) are shown on the right.