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The $n \rightarrow \pi^*$ interaction in metal complexes

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SUPPORTING INFORMATION

Computational Details

All electronic structure calculations were carried out with Gaussian09[1] at the B3LYP level of theory. The triple-ξ quality Def2-TZVPD basis set was employed for al atoms, including the associated pseudopotential for Pt. All optimized structures were characterized as true minima of the corresponding potential energy surfaces by vibrational analysis. Relative energies of conformers were calculated as the difference between the zero-point corrected electronic energies (ZPE).

Molecular electrostatic potential (MEP) maps were built on the electron density 0.001 au isosurface with GaussView.[2] The NBO analysis was done at the B3LYP/Def2-TZVPD level with the NBO3.1 program[3] included in Gaussian09.

Structural searches were performed in the Cambridge Structural Database[4] (CSD, version 5.38 (Nov. 2016) + 2 updates). Only structures with their 3D coordinates well defined, not disordered, not polymeric and with R < 10% were allowed in searches. CSD refcodes of selected examples are given throughout the text as six-letter codes (e.g. ABCDEF). The van der Waals radii used here were those proposed by Alvarez.[5]

References

(1) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(2) GaussView, version 5, R. Dennington, T. Keith and J. Millam, Semichem Inc., Shawnee Mission, KS, 2009.

(3) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

(4) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C., The Cambridge Structural Database. *Acta Crystallogr. Sect. B* **2016,** 72, 171-179.

(5) Alvarez, S., A cartography of the van der Waals territories. *Dalton Trans.* **2013,** 42, 8617-8636.

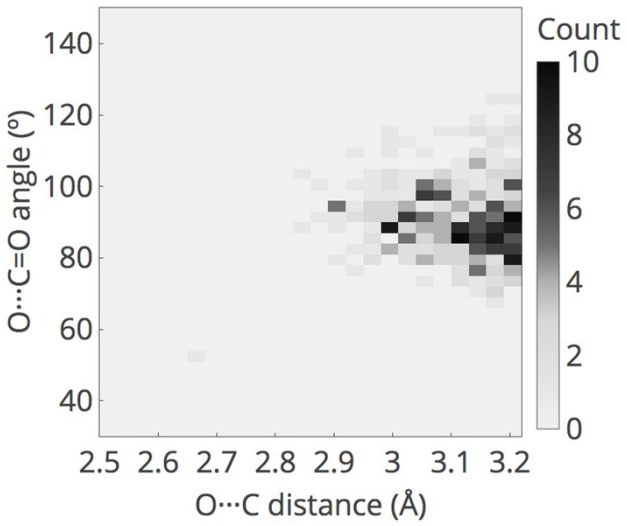

Figure S2. Heat maps of the O···C=O angle as a function of the intramolecular O···C contact distance in contacts of the type Metal-C=O···C=O(NonMetal).

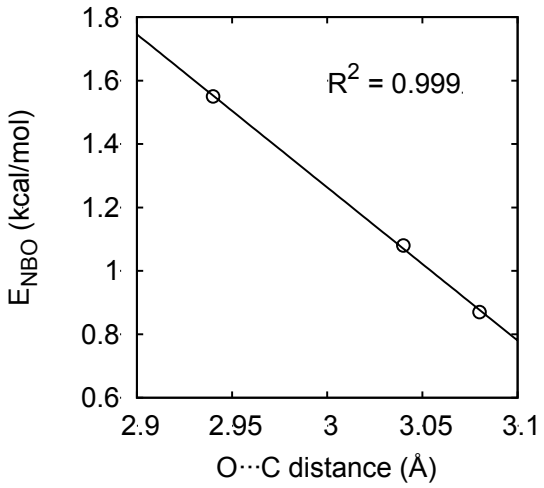

Figure S2. Linear dependence between the energy of the n → π* interaction and the donor-acceptor (O···C) distance for derivatives of the model molecule in Figure 3b.

Table S1. Cartesian coordinates of the fully optimized geometries of the model molecule (Fig. 3b) with different substitution patterns at the interacting and non-interacting units.

Int: **O**

Non-int: **H**

N	1.027993	0.231186	-0.134794
C	1.325128	1.549403	-0.106894
C	2.628235	2.001604	0.132836
C	3.620266	1.060277	0.335705
C	3.332911	-0.291975	0.289893
C	2.011406	-0.677554	0.040781
N	0.283410	2.423814	-0.333231
P	-1.284021	1.748054	-0.540230
Fe	-0.908666	-0.384298	-0.433144
P	-0.001778	-2.348004	-0.361224
N	1.649222	-2.007109	-0.054173
C	2.640577	-3.056570	0.137801
C	-2.548972	-0.889727	-0.885679
O	-3.576737	-1.220339	-1.264704
O	-1.044673	-0.482215	1.602517
C	-2.085193	-0.091416	2.248266
O	-3.100925	0.428218	1.801629
C	0.512046	3.862068	-0.317120
H	-1.730729	2.409565	-1.706815
H	-2.034358	2.481596	0.400217
H	0.086417	-3.264518	-1.433538
H	-0.293507	-3.284058	0.658979
H	2.852692	3.054928	0.163474
H	4.634843	1.385291	0.528892
H	4.107306	-1.025779	0.440140
H	-0.426764	4.369156	-0.528566
H	0.868423	4.201638	0.659246
H	1.236354	4.157785	-1.080506
H	2.156641	-4.023683	0.020068
H	3.443537	-2.986969	-0.600743
H	3.076424	-3.015442	1.139505
H	-1.993986	-0.262879	3.341167
H	-0.635106	-0.342836	-1.931635

Int: **S**

Non-int: **H**

N	1.218543	0.240076	-0.092248
C	1.513163	1.559301	-0.058314
C	2.790136	2.015623	0.289773
C	3.761602	1.078119	0.586927
C	3.481157	-0.275191	0.527013
C	2.186331	-0.665261	0.170117
N	0.496846	2.429445	-0.390435
P	-1.051942	1.751848	-0.707359
Fe	-0.678037	-0.383677	-0.577284
P	0.228929	-2.344014	-0.425405
N	1.836934	-1.996847	0.051358

C	2.811893	-3.042383	0.331078
C	-2.236672	-0.914599	-1.259939
O	-3.156576	-1.276024	-1.835423
O	-1.015369	-0.459774	1.441944
C	-2.091296	-0.229521	2.072722
S	-3.584859	0.235168	1.490350
C	0.720290	3.868727	-0.362343
H	-1.424950	2.418103	-1.895735
H	-1.862298	2.476509	0.189408
H	0.423588	-3.247119	-1.494609
H	-0.157105	-3.293730	0.549901
H	3.010643	3.069486	0.328374
H	4.755512	1.406604	0.863497
H	4.242059	-1.006264	0.744618
H	-0.194066	4.371922	-0.668883
H	0.978607	4.217142	0.641418
H	1.514831	4.160056	-1.053862
H	2.338765	-4.011801	0.190813
H	3.668661	-2.981118	-0.345219
H	3.169934	-2.986591	1.362212
H	-1.997560	-0.358123	3.160943
H	-0.245048	-0.330895	-2.032738

Int: **O**

Non-int: **CF_3**

C	-2.200284	-0.965468	-0.594853
N	-1.568487	0.120112	-0.096960
C	-1.923994	1.352520	-0.523962
C	-2.911886	1.533614	-1.498111
C	-3.532817	0.412216	-2.016111
C	-3.193574	-0.853076	-1.572708
Fe	-0.074521	-0.099335	1.294552
O	1.193554	-0.327784	-0.300848
C	2.378860	0.137185	-0.335378
O	2.975564	0.820660	0.479769
N	-1.270697	2.421627	0.054325
C	-1.579201	3.784930	-0.358052
N	-1.825116	-2.191218	-0.079562
C	-2.438333	-3.417991	-0.572110
P	-0.049991	2.069745	1.207110
P	-0.587705	-2.197313	1.102579
C	1.067856	-0.258001	2.645520
O	1.728412	-0.361508	3.573165
H	-0.407013	2.909452	2.285475
H	1.034103	2.827548	0.718144
H	-1.152303	-2.999343	2.118860
H	0.309583	-3.157129	0.578760
H	-3.180244	2.519406	-1.839935
H	-4.296316	0.526128	-2.775190
H	-3.682226	-1.726449	-1.971557
H	-0.961206	4.473599	0.213766
H	-1.365653	3.939091	-1.418812
H	-2.626944	4.030436	-0.166967
H	-2.010539	-4.263914	-0.038560
H	-3.517686	-3.419677	-0.400556
H	-2.247398	-3.558544	-1.638994
C	3.102335	-0.247680	-1.665071

H	-1.136444	0.020385	2.372870
F	4.385275	0.128455	-1.679104
F	3.071400	-1.580545	-1.880890
F	2.498808	0.341108	-2.724147

Int: **O**

Non-int: **CMe_3**

C	-3.261320	-0.764238	-1.573039
C	-2.247650	-0.925039	-0.622373
N	-1.594476	0.132814	-0.094739
C	-1.947430	1.384900	-0.461746
C	-2.955339	1.614779	-1.406083
C	-3.598479	0.521536	-1.955939
N	-1.873106	-2.173550	-0.165101
P	-0.620450	-2.234870	1.003425
Fe	-0.083916	-0.156848	1.268257
C	1.075450	-0.375105	2.596369
O	1.743776	-0.522823	3.513020
N	-1.271942	2.422068	0.145528
P	-0.018772	2.009750	1.248466
O	1.169226	-0.331044	-0.334352
C	2.376847	0.125798	-0.330547
C	3.173007	-0.178394	-1.630410
O	2.894141	0.760873	0.587791
C	-1.575765	3.802954	-0.203432
C	-2.512186	-3.372794	-0.688624
H	-0.330812	2.829435	2.356909
H	1.059617	2.764019	0.744173
H	-1.185346	-3.075581	1.989094
H	0.253652	-3.188780	0.429258
H	-3.222756	2.616430	-1.699235
H	-4.378493	0.673659	-2.691302
H	-3.768592	-1.616044	-1.994867
H	-0.938269	4.461750	0.382074
H	-1.385584	4.000168	-1.261904
H	-2.616567	4.050859	0.020957
H	-2.075677	-4.243819	-0.204798
H	-3.586290	-3.374311	-0.485023
H	-2.356111	-3.470390	-1.766170
H	-1.139178	-0.062042	2.364304
C	4.601962	0.359576	-1.514657
C	3.207270	-1.700120	-1.851774
C	2.457029	0.494440	-2.814389
H	3.764414	-1.939015	-2.761997
H	3.698302	-2.207185	-1.017577
H	2.198647	-2.101537	-1.948878
H	2.987947	0.285742	-3.747429
H	1.434019	0.130237	-2.908348
H	2.424065	1.579606	-2.686995
H	5.159206	0.146396	-2.431299
H	4.605402	1.437084	-1.349879
H	5.127708	-0.096945	-0.675749