Electronic Supplementary Information for Dalton Transactions

Supporting Information for

Theoretical characterization of a Ru N-Heterocyclic Carbene derivative of a polyoxometalate. Enhanced π-interaction in oxide supported TM-organic linkages.

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Table S1. Selected topological parameters of the analysis of the electron density distribution for the all studied carbene complexes. Values in a.u.[a]

	Fisher	**Ru-NHC**							**Schrock**
	4	**2_C**	**2_P**	**2_{Cl}**	**2_O**	**2_N**	**3**	**1**	**5**
M-C									
d (Å)	2.057	2.141	2.132	2.115	2.094	2.072	2.070	2.011	1.899
$\rho(r)$	.089	.096	.097	.106	.112	.114	.111	.128	.193
$\nabla^2\rho(r)$	.315	.254	.275	.226	.206	.269	.256	.310	.341
C_{carb}-N									
$\rho(r)$	-	.310	.310	.314	.320	.310	.320	.306	-
$\nabla^2\rho(r)$	-	-.820	-.820	-.822	-.851	-.810	-.861	-.788	-

[a] For **2_C**, **2_P**, and **2_N**, we report average values.

Table S2. Energy Decomposition Analysis of Ru-NHC, Fischer- (**4**), and Schrock- type (**5**) carbene complexes at BP86/TZP level. Energies in kcal.mol^{-1}and TM-$C_{carbene}$ distances in Å.[a]

	Fisher	**Ru-NHC**							**Schrock**
	4	**2_C**	**2_P**	**2_{Cl}**	**2_O**	**2_N**	**3**	**1**	**5**
d (Å)	2.057	2.141	2.132	2.115	2.094	2.072	2.070	2.011	1.899
ΔE_{int}	-48.1	-52.2	-53.4	-56.6	-114.7	-58.5	-58.1	-60.8	-129.5
ΔE_{steric}	+7.9	+8.5	+10.4	+23.2	-14.9	+16.5	+16.4	+61.0	+66.1
ΔE_{pauli}	109.6	144.6	155.8	182.1	152.8	174.6	176.6	268.8	248.4
ΔE_{elstat}	-101.7	-136.1	-145.4	-158.9	-167.7	-158.1	-160.2	-207.8	-182.3
	(65%)	(69%)	(69%)	(67%)	(63%)	(67%)	(68%)	(63%)	(48%)
ΔE_{orb}	-56	-60.6	-63.8	-79.7	-99.8	-76.5	-74.5	-121.8	-195.7
	(35%)	(31%)	(31%)	(33%)	(37%)	(33%)	(32%)	(37%)	(52%)

[a] For **2_C**, **2_P**, and **2_N**, we report average values. The values in parentheses give the percentage contribution to the total attractive energy

Table S3 Decomposition of ΔE_{orb} in terms of donation, back-donation and polarization for all studied carbenes.[a] Energies in kcal.mol^{-1}.[a]

	Fisher	**Ru-NHC**						
	4	**2_C**	**2_P**	**2_{Cl}**	**2_O**	**2_N**	**3**	**1**
$\Delta E_{orb.}$	-56.0	-60.6	-63.8	-79.8	-99.8	-76.5	-74.5	-121.8
ΔE_σ(L→TM)	-18.3	-24.3	-23.9	-33.3	-47.3	-31.6	-31.6	-32.8
	(69%)	(84%)	(78%)	(87%)	(90%)	(83%)	(85%)	(77%)
ΔE_π(TM→L)	-8.3 (31%)	-4.5	-6.8	-4.8	-5.4 (10%)	-6.6	-5.4 (15%)	-9.9
		(16%)	(22%)	(13%)		(17%)		(23%)
ΔE_{syn}	-6.9	-4.0	-4.7	-5.5	-8.0	-6.8	-6.8	-8.3
$\Delta E_{pol.}$	-27.1	-32.4	-32.3	-41.5	-41.3	-37.1	-37.0	-82.3
Δq_σ(L→TM)	0.25	0.38	0.30	0.33	1.61	0.32	0.31	0.25
Δq_π(TM→L)	0.11	0.06	0.12	0.06	0.03	0.09	0.06	0.12

[a] For **2_C**, **2_P**, and **2_N**, we report average values. The values in parentheses give the percentage contribution to the sum of σ-donation and π-backdonation terms.

Cartesian coordinates in Å:

(^{2}**1**) $[K(PW_9O_{34})2(cis\text{-}WO_2)(cis\text{-}RuLMe_2)]^{12-}$

W	1.362462	-3.659441	-0.241467
W	-1.544611	-2.944058	-1.952882
W	-1.466020	-2.900208	-5.762918
W	1.507169	-3.499620	-7.373733
W	4.771677	-4.266725	-5.488630
W	4.715935	-4.334955	-1.980272
W	1.793589	-6.951214	-2.087563
W	-1.174627	-6.234342	-3.875210
W	1.854265	-6.865498	-5.605337
W	0.000000	0.000000	-7.777383
Ru	0.000000	0.000000	-0.070080
P	1.567522	-3.780005	-3.796571
N	-2.592332	-0.746381	1.291277
N	-0.883807	-1.639524	2.369934
O	1.553972	-4.110649	1.491926
O	1.201615	-1.723703	-0.029227
O	-3.231850	-2.989445	-1.370088
O	-1.073094	-1.163670	-1.558328
O	-3.124113	-2.940014	-6.378028
O	1.781112	-3.856619	-9.097857
O	5.562365	-2.671162	-5.435647
O	5.913952	-5.138384	-6.578717
O	5.816177	-5.232917	-0.866972
O	5.478239	-2.722205	-1.923560
O	2.070863	-8.361073	-0.994631
O	-2.683350	-7.213897	-3.908171
O	2.180126	-8.258725	-6.706753
O	-1.115858	-0.779959	-8.918934
O	-0.618809	-3.595282	-0.365625
O	3.193748	-3.706645	-0.816723
O	1.200011	-5.540074	-0.863500
O	-1.676379	-2.519417	-3.844767
O	-1.529976	-4.888427	-2.553192
O	-0.465841	-3.551864	-7.283452
O	-1.477511	-4.859358	-5.160183
O	-0.950979	-1.126418	-6.083661
O	3.313057	-3.610736	-6.688103
O	1.344846	-5.452726	-6.807037
O	1.299311	-1.596858	-7.498531
O	5.433464	-4.873371	-3.721671
O	3.510530	-6.035101	-5.423959
O	3.442146	-6.080810	-2.127242
O	-0.141646	-7.231091	-2.519008
O	2.143287	-7.787634	-3.833526
O	-0.093509	-7.194699	-5.216313
O	0.904434	-3.155986	-2.512862
O	3.130944	-3.651156	-3.744398
O	1.169885	-5.329612	-3.838150
O	0.984282	-3.077404	-5.063042
C	-1.218643	-0.830983	1.296378
C	-3.179187	-1.778415	2.143546
C	-2.035373	-2.101035	3.109486
C	0.432768	-1.815216	2.924291
C	-3.420680	-0.243926	0.189058
K	0.000000	0.000000	-3.850342
H	-3.447616	-2.656258	1.520398
H	-4.091065	-1.403457	2.659431
H	-2.142518	-1.550748	4.098370
H	-1.953683	-3.181858	3.338066
H	0.644701	-2.888173	3.080854
H	0.540221	-1.236379	3.883679
H	1.164486	-1.475349	2.176951

H	-4.358145	0.153941	0.621161
H	-3.632634	-1.057707	-0.528324
H	-2.890770	0.583187	-0.300344
W	-1.362462	3.659441	-0.241467
W	1.544611	2.944058	-1.952882
W	1.466020	2.900208	-5.762918
W	-1.507169	3.499620	-7.373733
W	-4.771677	4.266725	-5.488630
W	-4.715935	4.334955	-1.980272
W	-1.793589	6.951214	-2.087563
W	1.174627	6.234342	-3.875210
W	-1.854265	6.865498	-5.605337
P	-1.567522	3.780005	-3.796571
N	2.592332	0.746381	1.291277
N	0.883807	1.639524	2.369934
O	-1.553972	4.110649	1.491926
O	-1.201615	1.723703	-0.029227
O	3.231850	2.989445	-1.370088
O	1.073094	1.163670	-1.558328
O	3.124113	2.940014	-6.378028
O	-1.781112	3.856619	-9.097857
O	-5.562365	2.671162	-5.435647
O	-5.913952	5.138384	-6.578717
O	-5.816177	5.232917	-0.866972
O	-5.478239	2.722205	-1.923560
O	-2.070863	8.361073	-0.994631
O	2.683350	7.213897	-3.908171
O	-2.180126	8.258725	-6.706753
O	1.115858	0.779959	-8.918934
O	0.618809	3.595282	-0.365625
O	-3.193748	3.706645	-0.816723
O	-1.200011	5.540074	-0.863500
O	1.676379	2.519417	-3.844767
O	1.529976	4.888427	-2.553192
O	0.465841	3.551864	-7.283452
O	1.477511	4.859358	-5.160183
O	0.950979	1.126418	-6.083661
O	-3.313057	3.610736	-6.688103
O	-1.344846	5.452726	-6.807037
O	-1.299311	1.596858	-7.498531
O	-5.433464	4.873371	-3.721671
O	-3.510530	6.035101	-5.423959
O	-3.442146	6.080810	-2.127242
O	0.141646	7.231091	-2.519008
O	-2.143287	7.787634	-3.833526
O	0.093509	7.194699	-5.216313
O	-0.904434	3.155986	-2.512862
O	-3.130944	3.651156	-3.744398
O	-1.169885	5.329612	-3.838150
O	-0.984282	3.077404	-5.063042
C	1.218643	0.830983	1.296378
C	3.179187	1.778415	2.143546
C	2.035373	2.101035	3.109486
C	-0.432768	1.815216	2.924291
C	3.420680	0.243926	0.189058
H	3.447616	2.656258	1.520398
H	4.091065	1.403457	2.659431
H	2.142518	1.550748	4.098370
H	1.953683	3.181858	3.338066
H	-0.644701	2.888173	3.080854
H	-0.540221	1.236379	3.883679
H	-1.164486	1.475349	2.176951
H	4.358145	-0.153941	0.621161
H	3.632634	1.057707	-0.528324
H	2.890770	-0.583187	-0.300344

(**3**) $[Cl_2Ru(LMe)(PH_3)(C(H)Ph)]$

Ru	19.768779	9.598368	16.969741
Cl	19.384166	10.122015	14.569199
Cl	19.780791	8.465248	19.120454
P	17.541958	10.405792	17.347551
C	21.430097	8.474951	16.437425
N	22.743723	8.667169	16.683587
C	23.589729	7.613948	16.092980
H	24.258589	7.186653	16.853317
H	24.207876	8.031215	15.282716
C	22.559928	6.597956	15.574980
H	22.709380	6.354175	14.513871
H	22.569651	5.660110	16.152812
N	21.286211	7.308491	15.773724
C	20.496013	11.108163	17.803579
H	20.687491	10.962325	18.887005
C	20.840143	12.445207	17.342339
C	20.662612	12.902862	16.013767
H	20.232400	12.217317	15.280580
C	21.043513	14.192644	15.657064
H	20.901159	14.531302	14.629424
C	21.613794	15.054250	16.604246
H	21.918268	16.061078	16.313578
C	21.793559	14.621847	17.923516
H	22.233843	15.290137	18.664273
C	21.406719	13.335365	18.288757
H	21.539769	12.992906	19.317068
H	17.237062	11.792603	17.236342
H	16.516316	9.936276	16.478003
H	16.886475	10.150170	18.591805
C	20.007613	6.701769	15.414066
H	19.336760	6.673730	16.286786
H	19.528045	7.258386	14.597036
H	20.188028	5.669180	15.092180
C	23.351186	9.805716	17.357073
H	23.220254	10.735353	16.785872
H	22.923538	9.932494	18.359736
H	24.424985	9.608538	17.459534

(**4**) $[Cr(CO)_5(C(OH)_2)]$

Cr	0.000000	0.000000	0.940148
C	0.000000	0.000000	2.856749
C	-1.369999	-1.344530	0.939495
C	1.369999	-1.344530	0.939495
C	1.369999	1.344530	0.939495
C	-1.369999	1.344530	0.939495
O	-2.199419	-2.155167	0.945878
O	2.199419	-2.155167	0.945878
O	2.199419	2.155167	0.945878
O	0.000000	0.000000	4.015617
O	-2.199419	2.155167	0.945878
C	0.000000	0.000000	-1.119634
O	0.000000	-1.063072	-1.925882
O	0.000000	1.063072	-1.925882
H	0.000000	-1.853113	-1.350361
H	0.000000	1.853113	-1.350361

(**5**) $[F_4W(C(CH_3)_2)]$

C	-0.416860	1.066061	0.000087
F	2.499223	1.092955	-0.421101
F	0.241233	-1.773182	0.420742
W	1.075413	-0.107686	0.000259

F	1.072994	-0.767416	-1.785120
F	1.717025	0.050144	1.784983
C	-0.324459	2.413392	0.690447
H	0.167723	3.146722	0.030971
H	-1.335634	2.781569	0.919925
H	0.251322	2.371628	1.624896
C	-1.703857	0.659739	-0.692801
H	-2.280429	-0.030453	-0.056000
H	-2.321041	1.551147	-0.880349
H	-1.524920	0.152127	-1.650384