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Supporting Information

Tuning steric and electronic effects in transition-metal β-diketiminate complexes

Chi Chen, Sarina M. Bellows, and Patrick L. Holland

Table 1. Crystal data of metal complexes

Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$L^{Me,iPr}ScCl_2(THF)$	86.77	2.107 2.175	116.9 117.8	0.694	Sc-Cl: 2.356 2.380	1
$L^{tBu,iPr}ScCl_2$	95.9	2.046 2.099	125.3 126.9	1.295	Sc-Cl: 2.353 2.326	2
$L^{Me,}$iPrScMe2(THF)	85.2	2.190 2.201	117.7 118.2	0.815	Sc-Cl: 2.209 2.245	2
$L^{tBu,iPr}ScMe_2$	92.2	2.103 2.145	124.5 127.5	1.262	Sc-Cl: 2.221 2.220	2
$L^{tBu,iPr}Sc(CH_2TMS)_2$	93.5	2.091 2.144	125.5 126.2	1.154	Sc-C: 2.228 2.203	2
$L^{Me,iPr}Sc(CH_2TMS)_2$	90.7	2.113 2.133	120.1 120.8	1.116	Sc-C: 2.244 2.194	2
$L^{Me,m\text{-}tBu}Sc(CH_2TMS)_2$	83.1	2.128 2.128	121.6 122.1	0.489	Sc-C: 2.210 2.215	3
$L^{Me,m\text{-}TIPP}Sc(CH_2SiMe_2Ph)_2$	84.9 ˚	2.127 2.123	120.4 ˚ 119.2 ˚	0.204	Sc-C: 2.203 2.202	3
$L^{Me,H}TiCl_2(THF)_2$	87.5 ˚	2.089 2.086	116.8 ˚ 117.1 ˚	0.224	Ti-Cl: 2.400 2.389	4
$L^{Me,iPr}TiCl_2(THF)$	88.4 ˚	2.030 2.089	115.7 ˚ 118.8 ˚	0.778	Ti-Cl: 2.342 2.327	5
$L^{Me,Mes}TiCl_2$	84.29 ˚	1.964 1.983	122.3 ˚ 121.4 ˚	0.150	Ti-Cl 2.295, 2.294	6
$L^{tBu,Mes}TiCl_2$	83.9 ˚	1.986 1.986	128.5 ˚ 128.5 ˚	0.000	Ti-Cl 2.296, 2.296	6
$L^{tBu,iPr}TiCl_2$	94.35 ˚	2.052 1.955	126.98 ˚ 123.70 ˚	1.069	Ti-Cl 2.306, 2.276	7
$L^{tBu,iPr}ZrCl_3$	82.72 ˚	2.302 2.100	128.2 ˚ 127.0 ˚	1.650	Zr-Cl: 2.381, 2.453 2.428	8
$L^{Me,iPr}ZrCl_3$	83.62 ˚	2.202 2.202	114.6 ˚ 114.6 ˚	0.820	Zr-Cl: 2.395, 2.395 2.339	9
$L^{Me,H}VCl_2(THF)_2$	90.93 ˚	2.023 2.030	116.3 ˚ 117.6 ˚	0.227	V-Cl: 2.359 2.365	4
$L^{Me,Me}VCl_2$	93.99 ˚	1.940 1.963	118.8 ˚ 120.5 ˚	0.528	V-Cl: 2.235 2.241	6
$[L^{Me,Et}V]_2$	88.69 ˚	2.066 2.041	115.84 ˚ 114.05 ˚	1.750	V-arene: 1.422 Two plane: 0 ˚	10
$[L^{Me,Me}V]_2$	88.73 ˚	2.057 2.034	115.98 ˚ 113.22 ˚	1.744	V-arene: 1.411 Two plane: 0 ˚	10
$[L^{Me,An}V]_2$	88.83 ˚	2.025 2.020	117.05 ˚ 117.01 ˚	1.796	V-arene: 1.744 Two Plane: 65.59 ˚	10
$L^{Me,Me}$Cr-Cp	91.43 ˚	2.018 2.015	118.88 ˚ 116.4 ˚	0.001	Cr-Cp 2.018	11
$L^{Me,Et}$Cr-Cp	90.4 ˚	2.028 2.026	118.9 ˚ 119.3 ˚	0.253	Cr-Cp 2.013	12
$L^{Me,iPr}$Cr-Cp	92.44 ˚	2.036 2.028	120.5 ˚ 118.6 ˚	0.130	Cr-Cp 2.016	13
$L^{Me,iPr}$Cr(Cl)(Cp)	89.9 ˚	2.036 2.036	117.3 ˚ 117.3 ˚	0.719	Cr-Cl 2.292 Cr-Cp 1.929	13
$L^{Me,Et}$Cr(Cl)(Cp)	90.3 ˚	2.022 2.016	118.0 ˚ 117.9 ˚	0.751	Cr-Cl 2.297 Cr-Cp 1.901	14
$L^{Me,Me}$Cr(Cl)(Cp)	90.5 ˚	2.019 2.018	117.7 ˚ 119.0 ˚	0.680	Cr-Cl 2.308 Cr-Cp 1.897	12
$L^{Me,H}$Cr(Cl)(Cp)	90.8 ˚	1.994 2.001	119.0 ˚ 119.2 ˚	0.087	Cr-Cl 2.345 Cr-Cp 1.917	15
$L^{Me,iPr/p\text{-}OMe}$Cr(Cl)(Cp)	89.5 ˚	2.007	118.7 ˚	0.676	Cr-Cr 2.305	16

		2.027	118.3 ˚		Cr-Cp 1.930	
Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$L^{Me,iPr}Cr(Me)(Cp)$	90.7 ˚	2.039 2.039	118.3 ˚ 118.8 ˚	0.702	Cr-Me 2.072 Cr-Cp 1.972	13
$L^{Me,Et}Cr(Me)(Cp)$	90.2 ˚	2.029 2.017	118.7 ˚ 118.3 ˚	0.699	Cr-Me 2.113 Cr-Cp 1.963	14
$L^{Me,Me}Cr(Me)(Cp)$	90.7 ˚	2.024 2.026	116.9 ˚ 117.6 ˚	0.65	Cr-Me 2.064 Cr-Cp 1.966	14
$L^{Me,Me}Cr(\mu\text{-}Cl)_2CrL\ (THF)_2$	89.77 ˚	2.063 2.059	117.3 ˚ 118.3 ˚	0.554	Two ligand plane 0.0	17
$L^{Me,iPr}Cr(\mu\text{-}Cl)_2CrL\ (THF)_2$	91.45 ˚	1.990 1.986	117.2 ˚ 115.9 ˚	0.668	Two ligand plane 0.0	18
$L^{tBu,iPr}Cr(\mu\text{-}Cl)_2CrL$	90.69 ˚	2.063 2.059	122.0 ˚ 122.2 ˚	0.060	Two ligand plane: 32.41	19
$[L^{tBu,iPr}FeH]_2$	95.33 ˚	1.989 2.022	127.22 ˚ 114.39 ˚	0.565	Two plane: 68.92 Fe-Fe: 2.624	20
$[L^{Me,iPr}FeH]_2$	95.06 ˚	1.978 1.987	117.9 ˚ 119.52 ˚	0.540	Two Plane:71.15 Fe-Fe: 2.464	21
$[^{Me}L^{Me,Me}FeH]_2$	90.8 ˚	1.925 1.932	118.56 ˚ 119.63 ˚	0.260	Two Plane:82.38 Fe-Fe: 2.501	22
$L^{tBu,iPr}FeH_2B(Et)_2$	97.35 ˚	1.971 1.969	127.8 ˚ 129.28 ˚	0.093	Fe-B: 2.232	23
$L^{Me,iPr}FeH_2B(Et)_2$	95.91 ˚	1.971 1.971	120.58 ˚ 120.58 ˚	0.000	Fe-B: 2.238	23
$L^{tBu,iPr}FeCl$	96.35 ˚	1.946 1.946	128.39 ˚ 128.39 ˚	0.000	Fe-Cl 2.172	24
$[L^{Me,iPr}FeCl]_2$	94.5 ˚	2.006 2.002	116.61 ˚ 116.72 ˚	0.441	Two plane 0 Fe-Cl: 2.405, 2.358	25
$L^{Me,iPr}FeCl_2Li(THF)_2$	93.22 ˚	2.021 2.006	120.27 ˚ 118.59 ˚	0.381	Fe-Cl; 2.338 2.324	24
$L^{Me,Me3}FeCl_2Li(THF)_2$	93.19 ˚	1.983 1.983	119.19 ˚ 119.19 ˚	0	Fe-Cl: 2.325 2.325	26
$L^{tBu,iPr}FeF$	95.67 ˚	1.961 1.961	127.95 ˚ 127.95 ˚	0	Fe-F: 1.808	21
$[L^{Me,iPr}FeF]_2$	93.28 ˚	2.016 2.008	119.91 ˚ 117.34 ˚	0.456	Fe-F: 1.976 1.977	21
$L^{tBu,iPr}FeF(tBuPy)$	97.8 ˚	2.007 2.015	124.8 ˚ 126.43 ˚	0.339	Fe-F: 1.87 Ligand/py: 87.55	21
$L^{Me,iPr}FeF(tBuPy)$	95 ˚	2.009 2.012	118.38 ˚ 119.53 ˚	0.294	Fe-F: 1.843 Ligand/Py: 88.07	21
$L^{tBu,iPr}Fe(tbuPy)NNFe(Py)L$	99.23 ˚ 97.33 ˚	2.005 2.000	123.02 ˚ 124.22 ˚ 124.76 ˚ 124.13 ˚	0.394 0.553	Fe-NN 1.790, 1.800 Fe-Py 2.079, 2.107 Ligand plane81.68	27
$L^{Me,iPr}Fe(tbuPy)NNFe(Py)L$	95.86 ˚ 95.86 ˚	2.005 1.993	118.59 ˚ 119.99 ˚ 118.59 ˚	0.250 0.250	Fe-NN Fe-Py Ligand plane 50.04	27
$[L^{tBu,iPr}Fe\text{-}AdN_3]_2$	98.84 ˚	2.018 2.043	123.88 ˚ 123.39 ˚	0.762	Ligand plane 0 Fe-N 2.013, 2.061	28
$[L^{Me,iPr}Fe\text{-}AdN_3]_2$	97.95 ˚	2.021 2.016	118.34 ˚ 117.40 ˚	0.753	Ligand plane 0 Fe-N2.003, 2.059	28
$L^{tBu,iPr}Fe\text{-}NNFeL$	96.01 ˚	1.965 1.970	129.11 ˚ 127.00 ˚	0.011 0.009	Two plane 87.18 Fe-N 1.77, 1.779	29
$L^{Me,iPr}Fe\text{-}NNFeL$	94.78 ˚	1.945 1.984	121.57 ˚ 118.66 ˚	0.046	Two plane 0 Fe-N 1.775	27
$[L^{tBu,iPr}Fe\text{-}NNFeL]K_2$	95.76 ˚	1.948 1.945	124.00 ˚ 124.60 ˚	0.29 0.111	Two plane 35.7 Fe-N 1.759, 1.770	29
$[L^{Me,iPr}Fe\text{-}NNFeL]K_2$	95.83 ˚	1.919 1.937	119.4 ˚ 119.68 ˚	0.004 0.072	Two plane 34.3 Fe-N 1.749, 1.754	27
$L^{tBu,iPr}Fe\text{-}(EtC{=}CHEt)$	94.16 ˚	1.988 1.990	127.53 ˚ 127.44 ˚	0.063	Fe-C 2.021	20
$L^{Me,iPr}Fe\text{-}(PhC{=}CHPh)$	94.44 ˚	1.980	120.17 ˚	0.133	Fe-C 2.017	30

		1.977	121.40 ˚			
Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$L^{tBu,iPr}$FeiPr	94.25 ˚	1.990 1.989	126.33 ˚ 128.11 ˚	0.065	Fe-C 2.055	31
$L^{Me,iPr}$FeiPr	92.78 ˚	1.983 1.983	119.84 ˚ 120.60 ˚	0.019	Fe-C 2.071	32
$L^{tBu,iPr}$Fe-(Ph-CCH)	96.16 ˚	1.975 2.005	123.65 ˚ 124.62 ˚	0.097	Fe-alkne 1.841	33
$L^{Me,iPr}$Fe-(Ph-CCH)	93.67 ˚	1.973 1.990	119.31 ˚ 118.57 ˚	0.008	Fe-alkyn 1.831	34
$[L^{Me,iPr}CoCl]_2$	96.47 ˚	1.972 1.971	116.50 ˚ 116.12 ˚	0.498	Co-Cl: 2.350 2.355	35
$L^{tBu,iPr}$CoCl	99.48 ˚	1.902	127.98 ˚	0	Co-Cl: 2.140	36
$L^{tBu,iPr}Co(Cl)_2Li(THF)_2$	99.42 ˚	1.968 1.961	124.78 ˚ 125.81 ˚	0.362	Co-Cl 2.294, 2.302	36
$L^{Me,iPr}Co(Cl)_2Li(THF)_2$	98.19 ˚	1.957 1.962	120.23 ˚ 120.38 ˚	0.314	Co-Cl 2.296, 2.294	37
$L^{tBu,iPr}$Co(alkyl)	97.68 ˚	1.950 1.960	125.04 ˚ 127.59 ˚	0.030	Co-C 2.011	38
$L^{Me,iPr}Co(CH_2TMS)$	95.6 ˚	1.948 1.946	119.7 ˚ 118.82 ˚	0.056	Co-C 1.999	39
$L^{Me,iPr}NiP_4NiL$	94.98 ˚	1.947 1.968	117.74 ˚ 116.94 ˚	0.184 0.184	Two plane 39.96 Ni-P: 2.217, 2.339, 2.195	40
$L^{Me,Et}NiP_4NiL$	96.44 ˚	1.931 1.928	119.86 ˚ 115.87 ˚	0.030 0.215	Two plane 51.24 Ni-P: 2.203, 2.329, 2.167	40
$L^{tBu,iPr}$NiCl	97.28 ˚	1.815 1.815	130.27 ˚ 130.27 ˚	0	Ni-Cl: 2.137	36
$[L^{Me,iPr}NiCl]_2$	93.66 ˚	1.938 1.946	117.11 ˚ 116.42 ˚	0.342	Two plane: 0 Ni-Cl:2.325, 2.350	41
$[L^{Me,Me}NiCl]_2$	94.7 ˚	1.915 1.913	117.88 ˚ 117.30 ˚	0.353	Two plane: 0 Ni-Cl: 2.300. 2.313	42
$L^{tBu,iPr}$NiCO	98.85 ˚	1.924 1.856	126.33 ˚ 129.40 ˚	0.017	Ni-C: 1.777	43
$L^{Me,iPr}$NiCO	96.41 ˚	1.917 1.868	119.89 ˚ 122.58 ˚	0.018	Ni-C: 1.770	44
$[L^{Me,Me}NiCO]_2$	95.0 ˚	1.927 1.913	114.95 ˚ 118.08 ˚	0.460	Ni-C: 1.759 2.079	45
${}^{Ph}L^{H,iPr}Cu\text{-}PPh_3$	96.17 ˚	1.956 1.954	116.74 ˚ 116.39 ˚	0.189	Cu-P: 2.165	46
${}^{Ph}L^{H,H}Cu(PPh_3)_2$	93.14 ˚	2.053 2.053	114.73 ˚	0	Cu-P: 2.292 2.292	46
${}^{H}L^{Me,Me}Cu(PPh_3)$	96.86 ˚	1.947 1.955	119.01 ˚ 119.70 ˚	0.131	Cu-P: 2.166	47
${}^{H}L^{Me,iPr}Cu(PPh_3)$	97.84 ˚	1.968 1.975	117.62 ˚ 118.05 ˚	0.210	Cu-P: 2.181	48
${}^{H}L^{Me,Me3}Cu(PPh_3)$	97.76 ˚	1.956 1.940	119.16 ˚ 119.04 ˚	0.177	Cu-P: 2.161	49
${}^{H}L^{CF3,m\text{-}CF3}Cu(PPh_3)_2$	94.65 ˚	2.093	119.75 ˚ 119.75 ˚	0	Cu-P: 2.295	50
$L^{Me,iPr/Et\text{-}pCN}Cu(OAc)$	96.73 ˚	1.901 1.895	119.39 ˚ 117.56 ˚	0.145	Cu-O: 2.032 2.011	51
$L^{Me,iPr/Me\text{-}pCN}Cu(OAc)$	96.26 ˚	1.905 2.004	119.56 ˚ 119.89 ˚	0.214	Cu-O: 2.034 2.004	51
$L^{Me,iPr\text{-}p\text{-}CN}Cu(OAc)$	96.79 ˚	1.902 1.898	119.86 ˚ 118.50 ˚	0.096	Cu-O: 2.015 2.002	51
$L^{Me,Et\text{-}p\text{-}CN}Cu(OAc)$	95.77 ˚	1.914 1.901	119.96 ˚ 121.37 ˚	0.156	Cu-O:2.006 2.032	51
${}^{CN}L^{Me,iPr}Cu(OAc)$	96.63 ˚	1.905 1.914	119.68 ˚ 120.45 ˚	0.246	Cu-O:2.012 2.000	52
$L^{Me,iPr}Cu(OAc)$	96.91 ˚	1.905 1.905	119.19 ˚ 119.19 ˚	0	Cu-O: 2.011 2.011	53

Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$^{CN}L^{H,iPr}Cu(OAc)$	94.79 ˚	1.944 1.944	116.9 ˚ 116.9 ˚	0.243	Cu-O: 2.028 2.028	54
$L^{Me,Et}Cu(OAc)$	96.90 ˚	1.921 1.920	120.18 ˚ 118.26 ˚	0.071	Cu-O: 2.021 2.034	53
$L^{Me,Me3}Cu(OAc)$	94.99 ˚	1.916 1.913	118.09 ˚ 119.00 ˚	0.403	Cu-O: 2.029 2.027	55
$L^{Me,Me}Cu(OAc)$	96.30 ˚	1.910 1.899	119.69 ˚ 119.48 ˚	0.285	Cu-O; 2.015 2.022	56
$[L^{Me,Et/iPr\text{-}pNO2}Cu(OH)]_2$	93.18 ˚	1.960 1.956	118.09 ˚ 115.32 ˚	0.179	Two Plane:0 Cu-O:1.928 1.942	51
$[L^{Me,Me}Cu(OH)]_2$	94.83 ˚	1.937 1.945	117.36 ˚ 117.61 ˚	0.335	Two Plane:0 Cu-O:1.923 1.914	57
$[L^{CF3,Me}Cu(OH)]_2$	95.28 ˚	1.940 1.943	122.69 ˚ 122.87 ˚	0.274 0.149	Two Plane:60.03 Cu-O:1.911 1.912	58
$[^{CN}L^{H,Me3}Cu(OH)]_2$	93.35 ˚	1.946 1.958 1.962	117.29 ˚ 117.62 ˚	0.586 0.532	Two Plane:11.34 Cu-O:1.904 1.922, 1.920	54
$[^{CN}L^{H,Et}Cu(OH)]_2$	93.63 ˚	1.943 1.955	115.44 ˚ 115.90 ˚	0.354	Two Plane:0 Cu-O:1.926 1.909	54
$[^{NO2}L^{H,Me3}Cu(OH)]_2$	94.34 ˚	1.933 1.941	117.42 ˚ 116.98 ˚	0.069	Two Plane:40.86 Cu-O:1.910 1.905	59
$L^{Me,Me}CuOtBu$	96.17 ˚	1.890 1.879	121.00 ˚ 121.34 ˚	0.246	Cu-O: 1.788	60
$L^{Me,Cl}CuOtBu$	96.26 ˚	1.884 1.890	122.04 ˚ 121.38 ˚	0.002	Cu-O: 1.785	61
$L^{Me,Me}Cu\text{-}CNXyl$	98.08 ˚	1.933 1.946	119.9 ˚ 119.74 ˚	0.144	Cu-C: 1.822	62
$L^{Me,iPr}Cu\text{-}CNXyl$	98.20 ˚	1.928 1.962	119.81 ˚ 120.13 ˚	0.342	Cu-C: 1.817	63
$L^{Me,Me3}Cu\text{-}CNXyl$	97.85 ˚	1.926 1.946	118.21 ˚ 119.65 ˚	0.097	Cu-C: 1.814	49
$^{CN}L^{H,iPr}Cu\text{-}(S)_2CuL$	97.53 ˚	1.920 1.910	115.39 ˚ 115.27 ˚	0.226	Two plane:0 Cu-S:2.199 2.209	64
$^{H}L^{Me,Et}Cu\text{-}(S)_2CuL$	99.30 ˚	1.907 1.910	118.43 ˚ 118.18 ˚	0.174	Two plane:0 Cu-S: 2.197 2.193	65
$^{H}L^{Me,Me}Cu\text{-}(S)_2CuL$	99.43 ˚	1.899 1.896	119.65 ˚ 119.17 ˚	0.280	Two plane:0 Cu-S:2.184 2.187	66
$^{H}L^{tBu,iPr}Cu\text{-}(S)_2CuL$	99.51 ˚	1.936 1.942	123.13 ˚ 122.73 ˚	0.037	Two plane:33.32 Cu-S:2.267 2.257	66
$^{Ph}L^{H,Et}Cu\text{-}(S)_2CuL$	96.92 ˚	1.911 1.909	116.96 ˚ 117.21 ˚	0.302	Two plane:0 Cu-S:2.195 2.194	66
$^{Ph}L^{H,iPr}Cu\text{-}(S)_2CuL$	96.95 ˚	1.913 1.905	116.70 ˚ 115.97 ˚	0.349	Two plane:0 Cu-S:2.198 2.205	66
$^{ArF}L^{H,Me}Cu\text{-}(S)_2CuL$	98.07 ˚	1.906 1.912	115.21 ˚ 117.26 ˚	0.002	Two plane:0 Cu-S:2.198 2.198	66
$^{ArF}L^{H,iPr}Cu\text{-}(S)_2CuL$	97.07 ˚	1.921 1.905	115.47 ˚ 116.00 ˚	0.271	Two plane: 0 Cu-S:2.194 2.206	66

Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$L^{Me,iPr}Cu(CO)$	99.42 ˚	1.921 1.917	118.57 ˚ 118.29 ˚	0.126	Cu-C: 1.784 C-O: 1.128	67
$L^{CF3,iPr}Cu(CO)$	98.99 ˚	1.932 1.940	122.69 ˚ 123.86 ˚	0.001	Cu-C: 1.793 C-O 1.129	67
$L^{CF3,Me}Cu\text{-}(NCCH_3)$	99.02 ˚	1.903 1.998	125.47 ˚ 122.07 ˚	0.026	Cu-N: 1.871	58
$^{ArF}L^{H,iPr}Cu\text{-}(NCCH_3)$	97.57 ˚	1.908 1.977	117.00 ˚ 118.94 ˚	0.068	Cu-N: 1.862	59
$^{NO2}L^{H,iPr}Cu\text{-}(NCCH_3)$	96.95 ˚	1.934 1.987	118.51 ˚ 117.74 ˚	0.306	Cu-N: 1.857	68
$L^{CF3/Me,iPr}Cu\text{-}(NCCH_3)$	99.04 ˚	1.934 1.931	122.91 ˚ 119.37 ˚	0.022	Cu-N: 1.866	67
$L^{CF3,iPr}Cu\text{-}(NCCH_3)$	98.98 ˚	1.940 1.935	124.74 ˚ 125.00 ˚	0.028	Cu-N 1.870	67
$L^{tBu,iPr}Cu\text{-}(NCCH_3)$	102.33 ˚	1.936 1.931	128.75 ˚ 127.68 ˚	0.046	Cu-N 1.946	69
$L^{Me,iPr}Cu\text{-}(NCCH_3)$	98. 98 ˚	1.940 1.942	118.94 ˚ 119.21 ˚	0.018	Cu-N 1.864	69
$^{Ph}L^{H,iPr}Cu\text{-}(NCCH_3)$	97.25 ˚	1.964 1.950	116.59 ˚ 118.46 ˚	0.142	Cu-N 1.860	69
$[^{Cl}L^{Me,Me}CuCl]_2$	94.67 ˚	1.919 1.922	119.58 ˚ 120.80 ˚	0.176	Two Plane:74.96 Cu-Cl 2.332 2.309	59
$[L^{Me,Et}CuCl]_2$	95.59 ˚	1.929 1.930	117.47 ˚ 118.67 ˚	0.258	Two Plane:0 Cu-Cl:2.327, 2.319	59
$L^{Me,iPr}CuCl$	97.22 ˚	1.869 1.871	122.05 ˚ 122.74 ˚	0.037	Cu-Cl: 2.126	70
$^{Cl}L^{Me,iPr}CuCl$	96.10 ˚	1.884 1.869	123.20 ˚ 122.25 ˚	0.035	Cu-Cl 2.123	63
$[L^{Me,Cl}CuCl]_2$	95.35 ˚	1.930 1.931	117.34 ˚ 119.9 ˚	0.377	Two Plane: 81.37 Cu-Cl: 2.307, 2.338	61
$L^{Me,m\text{-}CF3}Ru(Cl)(Benzene)$	88.27 ˚	2.103 2.115	117.49 ˚ 118.41 ˚	0.074	Ru-Cl:2.464 Ru-Benzene:1.714	71
$L^{CF3,Me}Ru(Cl)(Benzene)$	88.10 ˚	2.127 2.115	119.02 ˚ 120.74 ˚	0.624	Ru-Cl:2.463 Ru-Benzene: 1.673	71
$L^{CF3,m\text{-}CF3}Ru(Cl)(Benzene)$	87.77 ˚	2.108 2.106	120.44 ˚ 120.01 ˚	0.246	Ru-Cl: 2.414 Ru-Benzene: 1.703	71
$L^{Me,H}Ru(Cl)(Benzene)$	88.52 ˚	2.102 2.105	117.97 ˚ 118.34 ˚	0.048	Ru-Cl:2.461 Ru-Benzene: 1.689	71
$L^{Me,m\text{-}Me}Ru(Cl)(Benzene)$	88.21 ˚	2.098 2.091	117.53 ˚ 117.38 ˚	0.207	Ru-Cl:2.453 Ru-Benzene:1.683	72
$L^{Me,Me}Ru(Cl)(Benzene)$	86.56 ˚	2.099 2.099	116.80 ˚ 116.80 ˚	0.635	Ru-Cl: 2.521 Ru-Benzene:1.688	73
$L^{Me,Me}Ru(Cl)(Cp^*)$	87.51 ˚	2.089 2.075	114.98 ˚ 115.14 ˚	0.628	Ru-Cl: 2.461 Ru-Cp*:1.889	74
$L^{Me,m\text{-}Me}Ru(Cl)(Cp^*)$	87.83 ˚	2.050 2.051	116.43 ˚ 115.98 ˚	0.343	Ru-Cl:2.451 Ru-Cp*: 1.869	74
$L^{Me,m\text{-}CF3}Ru(Cl)(Cp^*)$	87.99 ˚	2.071 2.071	114.91 ˚ 115.46 ˚	0.004	Ru-Cl: 2.439 Ru-Cp*:1.864	74
$L^{CF3,\ m\text{-}Me}Ru(Cl)(Cp^*)$	90.18 ˚	2.069 2.055	118.55 ˚ 118.42 ˚	0.208	Ru-Cl: 2.431 Ru-Cp*: 1.886	74
$L^{CF3,m\text{-}CF3}Ru(Cl)(Cp^*)$	89.67 ˚	2.070 2.071	117.47 ˚ 118.21 ˚	0.179	Ru-Cl: 2.430 Ru-Cp*: 1.881	74
$L^{Me,Me}Ru(Cp^*)$	87.23 ˚	2.070 2.060	114.36 ˚ 113.70 ˚	0.001	Ru-Cp*:1.819	74
$L^{Me,m\text{-}Me}Ru(Cp^*)$	87.92 ˚	2.060 2.063	115.62 ˚ 115.29 ˚	0.079	Ru-Cp*: 1.809	74
$L^{Me,m\text{-}CF3}Ru(Cp^*)$	87.37 ˚	2.045 2.040	114.08 ˚ 114.07 ˚	0.043	Ru-Cp*:1.798	74

Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$L^{CF3,m\text{-}Me}Ru(Cp^*)$	90.08 ˚	2.050 2.050	116.95 ˚ 117.42 ˚	0.025	Ru-Cp*:1.824	74
$L^{CF3,m\text{-}CF3}Ru(Cp^*)$	89.55 ˚	2.055 2.056	116.09 ˚ 116.53 ˚	0.075	Ru-Cp*:1.827	74
$L^{Me,H}Ru(Cp^*)$	87.68 ˚	2.053 2.046	113.89 ˚ 113.74 ˚	0.006	Ru-Cp*: 1.800	75
$L^{Me,Me}$Ru-(Benzene)(OTf)	88.50 ˚	1.995 1.997	116.6 ˚ 116.00 ˚	0.087	Ru-Benzene: 1.705	73
$L^{Me,m\text{-}Me}$Ru-(Benzene)(OTf)	89.07 ˚	2.008 2.005	115.88 ˚ 116.55 ˚	0.110	Ru-Benzene: 1.703	72
$[L^{Me,H}Pd(\mu\text{-}OAc)]_2$	90.26 ˚ 91.56 ˚	1.989 1.989 1.985 1.994	120.35 ˚ 120.65 ˚ 121.11 ˚ 119.74 ˚	0.592 0.565	Pd-O: 2.061 2.054 2.062 2.054	76
$L^{Me,iPr}Pd(OAc)$	92.05 ˚	1.971 1.964	120.72 ˚ 122.18 ˚	0.034	Pd-O: 2.118 2.089	76
$[^{Cl}L^{Me,H}Pd(OAc)]_2$	87.41 ˚ 90.67 ˚	1.997 1.983 1.980 1.989	119.08 ˚ 121.12 ˚ 119.78 ˚ 120.13 ˚	0.886 0.488	Pd-O: 2.050 2.042	77
$[L^{Me,iPr}Pd(\mu\text{-}Cl)]_2$	91.78 ˚	2.023 2.013	118.65 ˚ 117.87 ˚	0.294	Two plane: 0 Pd-Cl: 2.366 2.354	78
$[L^{Me,m\text{-}CF3}Pd(\mu\text{-}Cl)]_2$	90.93 ˚	2.006 1.989	118.57 ˚ 118.97 ˚	0.468	Two Plane:0 Pd-Cl: 2.350, 2.352	78
$[L^{Me,H}Pd(\mu\text{-}Cl)]_2$	91.30 ˚	2.000 2.001	118.20 ˚ 120.61 ˚	0.473	Two Plane: 0 Pd-Cl: 2.342 2.356	77
$L^{Me,iPr}Pd(Cl)(Py)$	91.70 ˚	2.031 2.014	118.19 ˚ 116.65 ˚	0.178	Pd-Cl: 2.315 Pd-Py: 2.078	78
$L^{Me,m\text{-}CF3}Pd(Cl)(Py)$	90.08 ˚	2.026 2.013	119.46 ˚ 120.11 ˚	0.686	Pd-Cl: 2.302 Pd-Py: 2.039	78
$L^{Me,F5}Rh(COD)$	88.4 ˚	2.090 2.104	115.00 ˚ 114.64 ˚	0.450	Rh-alkene: 2.031 2.024	79
$L^{Me,Me}Rh(COD)$	89.21 ˚	2.095 2.095	114.18 ˚ 114.18 ˚	0	Rh-alkene: 2.043	80
$L^{Me,F5}Rh(CN\mathit{t}Bu)_2$	88.39 ˚	2.074 2.067	117.59 ˚ 116.61 ˚	0.204	Rh-C: 1.892 1.893	79
$L^{Me,Me}Rh(CN\mathit{t}Bu)_2$	90.38 ˚	2.067 2.073	116.80 ˚ 117.52 ˚	0.176	Rh-C: 1.905 1.895	79
$L^{Me,F5}Rh(CO)_2$	88.91 ˚	2.052 2.057	118.11 ˚ 117.66 ˚	0.121	Rh-C: 1.864 1.871	79
$L^{Me,p\text{-}Cl}Rh(CO)_2$	89.87 ˚	2.052 2.045	118.04 ˚ 116.45 ˚	0.000	Rh-C: 1.874 1.853	81
$L^{Me,iPr}Rh(CO)_2$	89.78 ˚	2.049 2.051	118.03 ˚ 117.23 ˚	0.066	Rh-C: 1.869 1.871	82

Table 2. Selected Reduction Potential on Substituents [a]

Complex	Ligand	Reduction potential[a] (V)	Reference
LRu(Cl)(η^5-Cp*)	$L^{Me,Me}$	0.39	74
	$L^{Me,m\text{-}Me}$	0.30	
	$L^{Me,m\text{-}CF3}$	0.56	
	$L^{CF3,m\text{-}Me}$	0.48	
	$L^{CF3,m\text{-}CF3}$	-0.25	
LRu(η^5-Cp*)	$L^{Me,Me}$	0.36	
	$L^{Me,m\text{-}Me}$	0.36	
	$L^{Me,m\text{-}CF3}$	0.16	
	$L^{CF3,m\text{-}Me}$	0.48	
	$L^{CF3,m\text{-}CF3}$	0.05	

[a] Conditions: in THF, 0.026 M $[Bu_4N]BArF$ as supporting electrolyte, potentials referenced to external Fc^+/Fc.

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