

**Supporting Information**  
**Tuning steric and electronic effects in transition-metal  $\beta$ -diketiminato complexes**  
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Table 1. Crystal data of metal complexes

Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C( $\beta$ )	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
$L^{\text{Me},i\text{Pr}}\text{ScCl}_2(\text{THF})$	86.77	2.107 2.175	116.9 117.8	0.694	Sc-Cl: 2.356 2.380	1
$L^{\text{tBu},i\text{Pr}}\text{ScCl}_2$	95.9	2.046 2.099	125.3 126.9	1.295	Sc-Cl: 2.353 2.326	2
$L^{\text{Me},i\text{Pr}}\text{ScMe}_2(\text{THF})$	85.2	2.190 2.201	117.7 118.2	0.815	Sc-Cl: 2.209 2.245	2
$L^{\text{tBu},i\text{Pr}}\text{ScMe}_2$	92.2	2.103 2.145	124.5 127.5	1.262	Sc-Cl: 2.221 2.220	2
$L^{\text{tBu},i\text{Pr}}\text{Sc}(\text{CH}_2\text{TMS})_2$	93.5	2.091 2.144	125.5 126.2	1.154	Sc-C: 2.228 2.203	2
$L^{\text{Me},i\text{Pr}}\text{Sc}(\text{CH}_2\text{TMS})_2$	90.7	2.113 2.133	120.1 120.8	1.116	Sc-C: 2.244 2.194	2
$L^{\text{Me},m\text{-tBu}}\text{Sc}(\text{CH}_2\text{TMS})_2$	83.1	2.128 2.128	121.6 122.1	0.489	Sc-C: 2.210 2.215	3
$L^{\text{Me},m\text{-tIPP}}\text{Sc}(\text{CH}_2\text{SiMe}_2\text{Ph})_2$	84.9 °	2.127 2.123	120.4 ° 119.2 °	0.204	Sc-C: 2.203 2.202	3
$L^{\text{Me},\text{H}}\text{TiCl}_2(\text{THF})_2$	87.5 °	2.089 2.086	116.8 ° 117.1 °	0.224	Ti-Cl: 2.400 2.389	4
$L^{\text{Me},i\text{Pr}}\text{TiCl}_2(\text{THF})$	88.4 °	2.030 2.089	115.7 ° 118.8 °	0.778	Ti-Cl: 2.342 2.327	5
$L^{\text{Me},\text{Mes}}\text{TiCl}_2$	84.29 °	1.964 1.983	122.3 ° 121.4 °	0.150	Ti-Cl 2.295, 2.294	6
$L^{\text{tBu},\text{Mes}}\text{TiCl}_2$	83.9 °	1.986 1.986	128.5 ° 128.5 °	0.000	Ti-Cl 2.296, 2.296	6
$L^{\text{tBu},i\text{Pr}}\text{TiCl}_2$	94.35 °	2.052 1.955	126.98 ° 123.70 °	1.069	Ti-Cl 2.306, 2.276	7
$L^{\text{tBu},i\text{Pr}}\text{ZrCl}_3$	82.72 °	2.302 2.100	128.2 ° 127.0 °	1.650	Zr-Cl: 2.381, 2.453 2.428	8
$L^{\text{Me},i\text{Pr}}\text{ZrCl}_3$	83.62 °	2.202 2.202	114.6 ° 114.6 °	0.820	Zr-Cl: 2.395, 2.395 2.339	9
$L^{\text{Me},\text{H}}\text{VCl}_2(\text{THF})_2$	90.93 °	2.023 2.030	116.3 ° 117.6 °	0.227	V-Cl: 2.359 2.365	4
$L^{\text{Me},\text{Me}}\text{VCl}_2$	93.99 °	1.940 1.963	118.8 ° 120.5 °	0.528	V-Cl: 2.235 2.241	6
$[L^{\text{Me},\text{Et}}\text{V}]_2$	88.69 °	2.066 2.041	115.84 ° 114.05 °	1.750	V-arene: 1.422 Two plane: 0 °	10
$[L^{\text{Me},\text{Me}}\text{V}]_2$	88.73 °	2.057 2.034	115.98 ° 113.22 °	1.744	V-arene: 1.411 Two plane: 0 °	10
$[L^{\text{Me},\text{An}}\text{V}]_2$	88.83 °	2.025 2.020	117.05 ° 117.01 °	1.796	V-arene: 1.744 Two Plane: 65.59 °	10
$L^{\text{Me},\text{Me}}\text{Cr-Cp}$	91.43 °	2.018 2.015	118.88 ° 116.4 °	0.001	Cr-Cp 2.018	11
$L^{\text{Me},\text{Et}}\text{Cr-Cp}$	90.4 °	2.028 2.026	118.9 ° 119.3 °	0.253	Cr-Cp 2.013	12
$L^{\text{Me},i\text{Pr}}\text{Cr-Cp}$	92.44 °	2.036 2.028	120.5 ° 118.6 °	0.130	Cr-Cp 2.016	13
$L^{\text{Me},i\text{Pr}}\text{Cr}(\text{Cl})(\text{Cp})$	89.9 °	2.036 2.036	117.3 ° 117.3 °	0.719	Cr-Cl 2.292 Cr-Cp 1.929	13
$L^{\text{Me},\text{Et}}\text{Cr}(\text{Cl})(\text{Cp})$	90.3 °	2.022 2.016	118.0 ° 117.9 °	0.751	Cr-Cl 2.297 Cr-Cp 1.901	14
$L^{\text{Me},\text{Me}}\text{Cr}(\text{Cl})(\text{Cp})$	90.5 °	2.019 2.018	117.7 ° 119.0 °	0.680	Cr-Cl 2.308 Cr-Cp 1.897	12
$L^{\text{Me},\text{H}}\text{Cr}(\text{Cl})(\text{Cp})$	90.8 °	1.994 2.001	119.0 ° 119.2 °	0.087	Cr-Cl 2.345 Cr-Cp 1.917	15
$L^{\text{Me},i\text{Pr}/p\text{-OMe}}\text{Cr}(\text{Cl})(\text{Cp})$	89.5 °	2.007	118.7 °	0.676	Cr-Cr 2.305	16

Complex	N-M-N	D(M-N) (Å)	C(aryl)-N-C(β)	Off plane (Å)	Cr-Cp 1.930 Selected Distance (Å) Or dihedral angle	ref
L <sup>Me,iPr</sup> 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 <sup>Me,Et</sup> 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 <sup>Me,Me</sup> 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 <sup>Me,Me</sup> Cr(μ-Cl) <sub>2</sub> CrL (THF) <sub>2</sub>	89.77 °	2.063 2.059	117.3 ° 118.3 °	0.554	Two ligand plane 0.0	17
L <sup>Me,iPr</sup> Cr(μ-Cl) <sub>2</sub> CrL (THF) <sub>2</sub>	91.45 °	1.990 1.986	117.2 ° 115.9 °	0.668	Two ligand plane 0.0	18
L <sup>tBu,iPr</sup> Cr(μ-Cl) <sub>2</sub> CrL	90.69 °	2.063 2.059	122.0 ° 122.2 °	0.060	Two ligand plane: 32.41	19
[L <sup>tBu,iPr</sup> FeH] <sub>2</sub>	95.33 °	1.989 2.022	127.22 ° 114.39 °	0.565	Two plane: 68.92 Fe-Fe: 2.624	20
[L <sup>Me,iPr</sup> FeH] <sub>2</sub>	95.06 °	1.978 1.987	117.9 ° 119.52 °	0.540	Two Plane:71.15 Fe-Fe: 2.464	21
[L <sup>Me,Me,Me</sup> FeH] <sub>2</sub>	90.8 °	1.925 1.932	118.56 ° 119.63 °	0.260	Two Plane:82.38 Fe-Fe: 2.501	22
L <sup>tBu,iPr</sup> FeH <sub>2</sub> B(Et) <sub>2</sub>	97.35 °	1.971 1.969	127.8 ° 129.28 °	0.093	Fe-B: 2.232	23
L <sup>Me,iPr</sup> FeH <sub>2</sub> B(Et) <sub>2</sub>	95.91 °	1.971 1.971	120.58 ° 120.58 °	0.000	Fe-B: 2.238	23
L <sup>tBu,iPr</sup> FeCl	96.35 °	1.946 1.946	128.39 ° 128.39 °	0.000	Fe-Cl 2.172	24
[L <sup>Me,iPr</sup> FeCl] <sub>2</sub>	94.5 °	2.006 2.002	116.61 ° 116.72 °	0.441	Two plane 0 Fe-Cl: 2.405, 2.358	25
L <sup>Me,iPr</sup> FeCl <sub>2</sub> Li(THF) <sub>2</sub>	93.22 °	2.021 2.006	120.27 ° 118.59 °	0.381	Fe-Cl; 2.338 2.324	24
L <sup>Me,Me<sub>3</sub></sup> FeCl <sub>2</sub> Li(THF) <sub>2</sub>	93.19 °	1.983 1.983	119.19 ° 119.19 °	0	Fe-Cl: 2.325 2.325	26
L <sup>tBu,iPr</sup> FeF	95.67 °	1.961 1.961	127.95 ° 127.95 °	0	Fe-F: 1.808	21
[L <sup>Me,iPr</sup> FeF] <sub>2</sub>	93.28 °	2.016 2.008	119.91 ° 117.34 °	0.456	Fe-F: 1.976 1.977	21
L <sup>tBu,iPr</sup> FeF(tBuPy)	97.8 °	2.007 2.015	124.8 ° 126.43 °	0.339	Fe-F: 1.87 Ligand/py: 87.55	21
L <sup>Me,iPr</sup> FeF(tBuPy)	95 °	2.009 2.012	118.38 ° 119.53 °	0.294	Fe-F: 1.843 Ligand/Py: 88.07	21
L <sup>tBu,iPr</sup> 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 plane 81.68	27
L <sup>Me,iPr</sup> 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 <sup>tBu,iPr</sup> Fe-AdN <sub>3</sub> ] <sub>2</sub>	98.84 °	2.018 2.043	123.88 ° 123.39 °	0.762	Ligand plane 0 Fe-N 2.013, 2.061	28
[L <sup>Me,iPr</sup> Fe-AdN <sub>3</sub> ] <sub>2</sub>	97.95 °	2.021 2.016	118.34 ° 117.40 °	0.753	Ligand plane 0 Fe-N 2.003, 2.059	28
L <sup>tBu,iPr</sup> Fe-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 <sup>Me,iPr</sup> Fe-NNFeL	94.78 °	1.945 1.984	121.57 ° 118.66 °	0.046	Two plane 0 Fe-N 1.775	27
[L <sup>tBu,iPr</sup> Fe-NNFeL]K <sub>2</sub>	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 <sup>Me,iPr</sup> Fe-NNFeL]K <sub>2</sub>	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 <sup>tBu,iPr</sup> Fe-(EtC=CHet)	94.16 °	1.988 1.990	127.53 ° 127.44 °	0.063	Fe-C 2.021	20
L <sup>Me,iPr</sup> Fe-(PhC=CHPh)	94.44 °	1.980	120.17 °	0.133	Fe-C 2.017	30

Complex	N-M-N	1.977 D(M-N) (Å)	121.40 ° C(aryl)-N-C(β)	Off plane (Å)	Selected Distance (Å) Or dihedral angle	ref
L <sup>tBu,iPr</sup> FeiPr	94.25 °	1.990 1.989	126.33 ° 128.11 °	0.065	Fe-C 2.055	31
L <sup>Me,iPr</sup> FeiPr	92.78 °	1.983 1.983	119.84 ° 120.60 °	0.019	Fe-C 2.071	32
L <sup>tBu,iPr</sup> Fe-(Ph-CCH)	96.16 °	1.975 2.005	123.65 ° 124.62 °	0.097	Fe-alkne 1.841	33
L <sup>Me,iPr</sup> Fe-(Ph-CCH)	93.67 °	1.973 1.990	119.31 ° 118.57 °	0.008	Fe-alkyn 1.831	34
[L <sup>Me,iPr</sup> CoCl] <sub>2</sub>	96.47 °	1.972 1.971	116.50 ° 116.12 °	0.498	Co-Cl: 2.350 2.355	35
L <sup>tBu,iPr</sup> CoCl	99.48 °	1.902	127.98 °	0	Co-Cl: 2.140	36
L <sup>tBu,iPr</sup> Co(Cl) <sub>2</sub> Li(THF) <sub>2</sub>	99.42 °	1.968 1.961	124.78 ° 125.81 °	0.362	Co-Cl 2.294, 2.302	36
L <sup>Me,iPr</sup> Co(Cl) <sub>2</sub> Li(THF) <sub>2</sub>	98.19 °	1.957 1.962	120.23 ° 120.38 °	0.314	Co-Cl 2.296, 2.294	37
L <sup>tBu,iPr</sup> Co(alkyl)	97.68 °	1.950 1.960	125.04 ° 127.59 °	0.030	Co-C 2.011	38
L <sup>Me,iPr</sup> Co(CH <sub>2</sub> TMS)	95.6 °	1.948 1.946	119.7 ° 118.82 °	0.056	Co-C 1.999	39
L <sup>Me,iPr</sup> NiP <sub>4</sub> NiL	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 <sup>Me,Et</sup> NiP <sub>4</sub> NiL	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 <sup>tBu,iPr</sup> NiCl	97.28 °	1.815 1.815	130.27 ° 130.27 °	0	Ni-Cl: 2.137	36
[L <sup>Me,iPr</sup> NiCl] <sub>2</sub>	93.66 °	1.938 1.946	117.11 ° 116.42 °	0.342	Two plane: 0 Ni-Cl: 2.325, 2.350	41
[L <sup>Me,Me</sup> NiCl] <sub>2</sub>	94.7 °	1.915 1.913	117.88 ° 117.30 °	0.353	Two plane: 0 Ni-Cl: 2.300, 2.313	42
L <sup>tBu,iPr</sup> NiCO	98.85 °	1.924 1.856	126.33 ° 129.40 °	0.017	Ni-C: 1.777	43
L <sup>Me,iPr</sup> NiCO	96.41 °	1.917 1.868	119.89 ° 122.58 °	0.018	Ni-C: 1.770	44
[L <sup>Me,Me</sup> NiCO] <sub>2</sub>	95.0 °	1.927 1.913	114.95 ° 118.08 °	0.460	Ni-C: 1.759 2.079	45
<sup>Ph</sup> L <sup>H,iPr</sup> Cu-PPh <sub>3</sub>	96.17 °	1.956 1.954	116.74 ° 116.39 °	0.189	Cu-P: 2.165	46
<sup>Ph</sup> L <sup>H,H</sup> Cu(PPh <sub>3</sub> ) <sub>2</sub>	93.14 °	2.053 2.053	114.73 °	0	Cu-P: 2.292 2.292	46
<sup>H</sup> L <sup>Me,Me</sup> Cu(PPh <sub>3</sub> )	96.86 °	1.947 1.955	119.01 ° 119.70 °	0.131	Cu-P: 2.166	47
<sup>H</sup> L <sup>Me,iPr</sup> Cu(PPh <sub>3</sub> )	97.84 °	1.968 1.975	117.62 ° 118.05 °	0.210	Cu-P: 2.181	48
<sup>H</sup> L <sup>Me,Me3</sup> Cu(PPh <sub>3</sub> )	97.76 °	1.956 1.940	119.16 ° 119.04 °	0.177	Cu-P: 2.161	49
<sup>H</sup> L <sup>CF3,m-CF3</sup> Cu(PPh <sub>3</sub> ) <sub>2</sub>	94.65 °	2.093	119.75 ° 119.75 °	0	Cu-P: 2.295	50
L <sup>Me,iPr/Et-pCN</sup> Cu(OAc)	96.73 °	1.901 1.895	119.39 ° 117.56 °	0.145	Cu-O: 2.032 2.011	51
L <sup>Me,iPr/Me-pCN</sup> Cu(OAc)	96.26 °	1.905 2.004	119.56 ° 119.89 °	0.214	Cu-O: 2.034 2.004	51
L <sup>Me,iPr-pCN</sup> Cu(OAc)	96.79 °	1.902 1.898	119.86 ° 118.50 °	0.096	Cu-O: 2.015 2.002	51
L <sup>Me,Et-pCN</sup> Cu(OAc)	95.77 °	1.914 1.901	119.96 ° 121.37 °	0.156	Cu-O: 2.006 2.032	51
<sup>CN</sup> L <sup>Me,iPr</sup> Cu(OAc)	96.63 °	1.905 1.914	119.68 ° 120.45 °	0.246	Cu-O: 2.012 2.000	52
L <sup>Me,iPr</sup> 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
<sup>CN</sup> L <sup>H,iPr</sup> Cu(OAc)	94.79 °	1.944 1.944	116.9 ° 116.9 °	0.243	Cu-O: 2.028 2.028	54
L <sup>Me,Et</sup> Cu(OAc)	96.90 °	1.921 1.920	120.18 ° 118.26 °	0.071	Cu-O: 2.021 2.034	53
L <sup>Me,Me3</sup> Cu(OAc)	94.99 °	1.916 1.913	118.09 ° 119.00 °	0.403	Cu-O: 2.029 2.027	55
L <sup>Me,Me</sup> Cu(OAc)	96.30 °	1.910 1.899	119.69 ° 119.48 °	0.285	Cu-O; 2.015 2.022	56
[L <sup>Me,Et/iPr-pNO2</sup> Cu(OH)] <sub>2</sub>	93.18 °	1.960 1.956	118.09 ° 115.32 °	0.179	Two Plane:0 Cu-O:1.928 1.942	51
[L <sup>Me,Me</sup> Cu(OH)] <sub>2</sub>	94.83 °	1.937 1.945	117.36 ° 117.61 °	0.335	Two Plane:0 Cu-O:1.923 1.914	57
[L <sup>CF3,Me</sup> Cu(OH)] <sub>2</sub>	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
[ <sup>CN</sup> L <sup>H,Me3</sup> Cu(OH)] <sub>2</sub>	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
[ <sup>CN</sup> L <sup>H,Et</sup> Cu(OH)] <sub>2</sub>	93.63 °	1.943 1.955	115.44 ° 115.90 °	0.354	Two Plane:0 Cu-O:1.926 1.909	54
[ <sup>NO2</sup> L <sup>H,Me3</sup> Cu(OH)] <sub>2</sub>	94.34 °	1.933 1.941	117.42 ° 116.98 °	0.069	Two Plane:40.86 Cu-O:1.910 1.905	59
L <sup>Me,Me</sup> CuOtBu	96.17 °	1.890 1.879	121.00 ° 121.34 °	0.246	Cu-O: 1.788	60
L <sup>Me,Cl</sup> CuOtBu	96.26 °	1.884 1.890	122.04 ° 121.38 °	0.002	Cu-O: 1.785	61
L <sup>Me,Me</sup> Cu-CNXYl	98.08 °	1.933 1.946	119.9 ° 119.74 °	0.144	Cu-C: 1.822	62
L <sup>Me,iPr</sup> Cu-CNXYl	98.20 °	1.928 1.962	119.81 ° 120.13 °	0.342	Cu-C: 1.817	63
L <sup>Me,Me3</sup> Cu-CNXYl	97.85 °	1.926 1.946	118.21 ° 119.65 °	0.097	Cu-C: 1.814	49
<sup>CN</sup> L <sup>H,iPr</sup> Cu-(S) <sub>2</sub> CuL	97.53 °	1.920 1.910	115.39 ° 115.27 °	0.226	Two plane:0 Cu-S:2.199 2.209	64
<sup>H</sup> L <sup>Me,Et</sup> Cu-(S) <sub>2</sub> CuL	99.30 °	1.907 1.910	118.43 ° 118.18 °	0.174	Two plane:0 Cu-S: 2.197 2.193	65
<sup>H</sup> L <sup>Me,Me</sup> Cu-(S) <sub>2</sub> CuL	99.43 °	1.899 1.896	119.65 ° 119.17 °	0.280	Two plane:0 Cu-S:2.184 2.187	66
<sup>H</sup> L <sup>tBu,iPr</sup> Cu-(S) <sub>2</sub> CuL	99.51 °	1.936 1.942	123.13 ° 122.73 °	0.037	Two plane:33.32 Cu-S:2.267 2.257	66
<sup>Ph</sup> L <sup>H,Et</sup> Cu-(S) <sub>2</sub> CuL	96.92 °	1.911 1.909	116.96 ° 117.21 °	0.302	Two plane:0 Cu-S:2.195 2.194	66
<sup>Ph</sup> L <sup>H,iPr</sup> Cu-(S) <sub>2</sub> CuL	96.95 °	1.913 1.905	116.70 ° 115.97 °	0.349	Two plane:0 Cu-S:2.198 2.205	66
<sup>ArF</sup> L <sup>H,Me</sup> Cu-(S) <sub>2</sub> CuL	98.07 °	1.906 1.912	115.21 ° 117.26 °	0.002	Two plane:0 Cu-S:2.198 2.198	66
<sup>ArF</sup> L <sup>H,iPr</sup> Cu-(S) <sub>2</sub> CuL	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
$L^{CF_3,IPr}Cu(CO)$	98.99 °	1.932 1.940	122.69 ° 123.86 °	0.001	Cu-C: 1.793 C-O 1.129	67
$L^{CF_3,Me}Cu-(NCCH_3)$	99.02 °	1.903 1.998	125.47 ° 122.07 °	0.026	Cu-N: 1.871	58
$^{ArF}L^{H,IPr}Cu-(NCCH_3)$	97.57 °	1.908 1.977	117.00 ° 118.94 °	0.068	Cu-N: 1.862	59
$^{NO_2}L^{H,IPr}Cu-(NCCH_3)$	96.95 °	1.934 1.987	118.51 ° 117.74 °	0.306	Cu-N: 1.857	68
$L^{CF_3/Me,IPr}Cu-(NCCH_3)$	99.04 °	1.934 1.931	122.91 ° 119.37 °	0.022	Cu-N: 1.866	67
$L^{CF_3,IPr}Cu-(NCCH_3)$	98.98 °	1.940 1.935	124.74 ° 125.00 °	0.028	Cu-N 1.870	67
$L^{tBu,IPr}Cu-(NCCH_3)$	102.33 °	1.936 1.931	128.75 ° 127.68 °	0.046	Cu-N 1.946	69
$L^{Me,IPr}Cu-(NCCH_3)$	98.98 °	1.940 1.942	118.94 ° 119.21 °	0.018	Cu-N 1.864	69
$^{Ph}L^{H,IPr}Cu-(NCCH_3)$	97.25 °	1.964 1.950	116.59 ° 118.46 °	0.142	Cu-N 1.860	69
$[L^{Cl,Me,Me}CuCl]_2$	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
$L^{Me,m-CF_3}Ru(Cl)(Benzene)$	88.27 °	2.103 2.115	117.49 ° 118.41 °	0.074	Ru-Cl:2.464 Ru-Benzene:1.714	71
$L^{CF_3,Me}Ru(Cl)(Benzene)$	88.10 °	2.127 2.115	119.02 ° 120.74 °	0.624	Ru-Cl:2.463 Ru-Benzene: 1.673	71
$L^{CF_3,m-CF_3}Ru(Cl)(Benzene)$	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
$L^{Me,m-Me}Ru(Cl)(Benzene)$	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
$L^{Me,m-Me}Ru(Cl)(Cp^*)$	87.83 °	2.050 2.051	116.43 ° 115.98 °	0.343	Ru-Cl:2.451 Ru-Cp*: 1.869	74
$L^{Me,m-CF_3}Ru(Cl)(Cp^*)$	87.99 °	2.071 2.071	114.91 ° 115.46 °	0.004	Ru-Cl: 2.439 Ru-Cp*:1.864	74
$L^{CF_3,m-Me}Ru(Cl)(Cp^*)$	90.18 °	2.069 2.055	118.55 ° 118.42 °	0.208	Ru-Cl: 2.431 Ru-Cp*: 1.886	74
$L^{CF_3,m-CF_3}Ru(Cl)(Cp^*)$	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
$L^{Me,m-Me}Ru(Cp^*)$	87.92 °	2.060 2.063	115.62 ° 115.29 °	0.079	Ru-Cp*: 1.809	74
$L^{Me,m-CF_3}Ru(Cp^*)$	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
$L^{CF_3, m-Me}Ru(Cp^*)$	90.08 °	2.050 2.050	116.95 ° 117.42 °	0.025	Ru-Cp*:1.824	74
$L^{CF_3, m-CF_3}Ru(Cp^*)$	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
$L^{Me, m-Me}Ru-(Benzene)(OTf)$	89.07 °	2.008 2.005	115.88 ° 116.55 °	0.110	Ru-Benzene: 1.703	72
$[L^{Me, H}Pd(\mu-OAc)]_2$	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
$[L^{Cl, Me, H}Pd(OAc)]_2$	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
$[L^{Me, iPr}Pd(\mu-Cl)]_2$	91.78 °	2.023 2.013	118.65 ° 117.87 °	0.294	Two plane: 0 Pd-Cl: 2.366 2.354	78
$[L^{Me, m-CF_3}Pd(\mu-Cl)]_2$	90.93 °	2.006 1.989	118.57 ° 118.97 °	0.468	Two Plane:0 Pd-Cl: 2.350, 2.352	78
$[L^{Me, H}Pd(\mu-Cl)]_2$	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
$L^{Me, m-CF_3}Pd(Cl)(Py)$	90.08 °	2.026 2.013	119.46 ° 120.11 °	0.686	Pd-Cl: 2.302 Pd-Py: 2.039	78
$L^{Me, F_5}Rh(COD)$	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
$L^{Me, F_5}Rh(CNtBu)_2$	88.39 °	2.074 2.067	117.59 ° 116.61 °	0.204	Rh-C: 1.892 1.893	79
$L^{Me, Me}Rh(CNtBu)_2$	90.38 °	2.067 2.073	116.80 ° 117.52 °	0.176	Rh-C: 1.905 1.895	79
$L^{Me, F_5}Rh(CO)_2$	88.91 °	2.052 2.057	118.11 ° 117.66 °	0.121	Rh-C: 1.864 1.871	79
$L^{Me, p-Cl}Rh(CO)_2$	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<sup>a</sup>

Complex	Ligand	Reduction potential <sup>a</sup> (V)	Reference
LRu(Cl)(η <sup>5</sup> -Cp <sup>*</sup> )	L <sup>Me,Me</sup>	0.39	74
	L <sup>Me,m-Me</sup>	0.30	
	L <sup>Me,m-CF<sub>3</sub></sup>	0.56	
	L <sup>CF<sub>3</sub>,m-Me</sup>	0.48	
	L <sup>CF<sub>3</sub>,m-CF<sub>3</sub></sup>	-0.25	
LRu(η <sup>5</sup> -Cp <sup>*</sup> )	L <sup>Me,Me</sup>	0.36	
	L <sup>Me,m-Me</sup>	0.36	
	L <sup>Me,m-CF<sub>3</sub></sup>	0.16	
	L <sup>CF<sub>3</sub>,m-Me</sup>	0.48	
	L <sup>CF<sub>3</sub>,m-CF<sub>3</sub></sup>	0.05	

<sup>a</sup> Conditions: in THF, 0.026 M [Bu<sub>4</sub>N]BARf as supporting electrolyte, potentials referenced to external Fc<sup>+</sup>/Fc.

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