Supplementary Material (ESI) for Dalton Transactions

Calibrating the Coordination Chemistry Tool Chest: Metrics of Bi- and Tridentate Ligands

David Aguilà, Esther Escribano, Saskia Speed, Daniel Talancón,
Luis Yermán, Santiago Alvarez*

Departament de Química Inorgànica, Universitat de Barcelona
Martí i Franquès 1-11, 08028 Barcelona

Electronic Supplementary Information

Table S1. Full results of the searches carried out for determining the bites of bidentate ligands. Average rigid bites (d), bite angles (a) and normalized bites (b) characteristic of bidentate ligands with donor atoms X and spacers S forming n-member chelate rings. Standard deviations given in parentheses. Number of crystallographically independent groups (CSD) from which the corresponding data were extracted, and restrictions on the R factor of the structures (when applied) are also given.

Ligand		X	S	n	d [a]	groups	α_S (°)	b_S	groups	α_L (°)	b_L	groups	R <
1	pyrazolato	N	-	3	1.38 (1)	63	40 (1)	0.68 (2)	2	38 (2)	0.65 (3)	61	-
2	O_2^{2-}	O	-	3	1.45 (5)	419	42 (2)	0.72 (3)	60	45 (1)	0.76 (2)	359	10%
	$R_2N\text{-}CR_2^-$	N,C	-	3	1.44 (3)	70	37 (2)	0.64 (3)	45	42 (2)	0.71 (3)	25	-
3	nitrato	O	N	4	2.13 (5)	1256	54 (5)	0.92 (7)	1097	53 (2)	0.89 (4)	159	10%
4	carboxylato	O	C	4	2.19 (2)	1292	57 (4)	0.96 (5)	1196	57 (2)	0.96 (4)	95	5%
5	triazenido	N	N	4	2.09 (3)	60	58 (4)	0.98 (5)	43	57 (1)	0.96 (1)	17	-
6	propanediolato	O	C	4	2.26 (2)	33	60 (5)	1.00 (7)	32				-
7	aminopyridine	N	C	4	2.22 (3)	344	61 (4)	1.02 (5)	165	60 (2)	1.00 (3)	179	10%
8	dichloromethane	Cl	C	4	2.89 (3)	10	63 (3)	1.05 (6)	10				-
9	amidinato	N	C	4	2.20 (3)	298	64 (2)	1.05 (3)	87	60 (2)	0.99 (3)	211	10%
10	carbonato	O	C	4	2.17 (3)	112	67 (3)	1.10 (5)	95	60 (2)	1.01 (2)	17	10%
11	sulfato	O	S	4	2.32 (5)	39	67 (3)	1.11 (5)	28	65 (2)	1.06 (6)	11	-
12	1,1-diaminoalkane	N	C	4	2.37 (4)	12	68 (2)	1.12 (3)	11	63 (-)	1.06 (-)	1	-
13	pyridinethiolato	S,N	C	4	2.54 (4)	254	68 (3)	1.13 (4)	145	65 (2)	1.08 (2)	109	10%
14	propanediyl	C	C	4	2.38 (12)	30	68 (1)	1.12 (2)	12	67 (6)	1.10 (9)	18	-
15	dppm-	P	C	4	2.70 (13)	12	71 (1)	1.17 (2)	3	63 (4)	1.04 (5)	6	-
16	dppm	P	C	4	2.72 (5)	426	72 (2)	1.18 (2)	359	67 (2)	1.10 (2)	67	10%
17	dithiocarbamates	S	C	4	2.87 (5)	942	74 (3)	1.20 (4)	561	69 (2)	1.14 (2)	381	5%
18	1,2-dimethoxyethane	O	C_2	5	2.66 (6)	129	75 (5)	1.21 (7)	49	71 (3)	1.16 (4)	80	-
19	dpasm	As	C	4	2.89 (3)	2	75 (1)	1.22 (2)	2				-
29	1,2-dichloroethane	Cl	C_2	5	3.39 (3)	11	76 (1)	1.23 (1)	11				-
21	pyrazolyl-pyridine	N	C_2	5	2.60 (5)	73	77 (3)	1.25 (4)	72	75	1.21	1	-
22	iminophosphinamidato	N	P	4	2.41 (2)	15	77 (1)	1.25 (1)	3	67 (2)	1.11 (4)	12	-
23	phosphinodimethylene	C	P	4	2.68 (6)	13	78 (2)	1.26 (3)	11	69 (4)	1.13 (6)	2	-
24	bipyridine	N	C_2	5	2.63 (4)	2967	78 (3)	1.26 (5)	2684	73 (2)	1.19 (4)	283	5%
25	phenanthroline	N	C_2	5	2.68 (4)	2348	78 (4)	1.26 (6)	2226	73 (3)	1.18 (4)	122	5%
26	4,5-diazafluoren-9-one	N	C_2	5	2.96 (7)	32	78 (4)	1.26 (5)	32				-
27	quinone	O	C_2	5	2.59 (6)	50	81 (3)	1.29 (4)	48	77 (2)	1.25 (2)	2	-
28	tropolonato [g]	O	C_2	5	2.55 (4)	51	80 (5)	1.29 (7)	35	71 (2)	1.16 (4)	16	-
29	dioximates	N	C_2	5	2.47 (3)	1074	81 (2)	1.30 (2)	1074				10%

30	C-bipyridine	N,C	C_2	5	2.64 (5)	22	81 (1)	1.29 (1)	22						-
31	biphosphinine	P	C_2	5	2.86 (6)	26	81 (3)	1.30 (4)	21	74 (1)	1.20	(1)	2		-
32	dithiophosphinato	S	P	4	3.20 (4)	50	82 (1)	1.31 (1)	25	79 (1)	1.27	(1)	25		10%
33	butanediyl	C	C_2	5	2.78 (11)	41	82 (2)	1.32 (2)	27	82 (6)	1.31	(8)	14		-
34	oxalato	O	C_2	5	2.60 (4)	803	83 (2)	1.32 (3)	503	75 (3)	1.21	(4)	300		10%
35	croconato	O	C_2	5	2.75 (6)	37	82 (3)	1.31 (4)	35	77 (7)	1.24	(1)	2		-
36	catecholato	O	C_2	5	2.58 (6)	503	83 (3)	1.32 (5)	317	78 (2)	1.26	(3)	186		10%
37	ethylenediamine	N	C_2	5	2.76 (9)	2291	83 (3)	1.33 (4)	2223	78 (2)	1.26	(3)	68		5%
38	diars	As	C_2	5	3.26 (6)	101	85 (1)	1.35 (2)	71	75 (4)	1.22	(5)	30		-
39	dpae	As	C_2	5	3.24 (6)	18	85 (1)	1.35 (1)	12	82 (1)	1.31	(1)	6		-
40	dppe	P	C_2	5	3.11 (9)	1592	86 (3)	1.36 (3)	1127	79 (2)	1.27	(3)	465		5%
41	dpp-benzene	P	C_2	5	3.10 (8)	141	86 (3)	1.36 (4)	113	78 (3)	1.26	(4)	28		-
42	diphosphinoethene	P	C_2	5	3.11 (9)	100	86 (2)	1.36 (3)	82	78 (3)	1.26	(4)	18		-
43	silanedithiolato	S	Si	4	3.33 (8)	3	88 (3)	1.39 (4)	2	87	1.38		1		-
44	dipyridylamine	N	CNC	6	2.87 (8)	662	88 (4)	1.39 (6)	638	81 (5)	1.30	(7)	24		10%
45	1,3,5-triazapenta-1,3-dienato	N	CNC	6	2.74 (14)	36	90 (4)	1.41 (4)	36				1		-
46	diselonolether	Se	C_2	5	3.54 (14)	9	88 (2)	1.40 (2)	8	80	1.28		1		-
47	biguanine	N	CNC	6	2.76 (11)	51	90 (2)	1.42 (2)	51						-
48	diketonato	O	C_3	6	2.84 (9)	1491	90 (4)	1.42 (4)	1218	82 (4)	1.32	(6)	273		5%
49	malonato	O	C_3	6	2.82 (6)	156	91 (2)	1.43 (3)	140	87 (2)	1.38	(3)	16		10%
50	propanediamine	N	C_3	6	2.93 (12)	326	91 (4)	1.42 (5)	323	90 (2)	1.42	(2)	3		10%
51	dithiolenes	S	C_2	5	3.15 (10)	738	91 (2)	1.43 (2)	575	81 (2)	1.30	(3)	163		5%
52	dithiooxalato	S	C_2	5	3.20 (8)	95	93 (2)	1.43 (3)	90	85 (3)	1.35	(4)	5		-
53	bispyrazolyl	N	NBN	6	2.94 (15)	52	90 (4)	1.42 (5)	37	83 (4)	1.32	(5)	15		-
54	distibanylbenzene	Sb	C_4	7	3.62 (16)	9	92 (3)	1.44 (3)					9		-
55	diselenolato	Se	C_2	5	3.39 (13)	21	91 (2)	1.43 (2)	17	84 (2)	1.34	(2)	4		-
56	binap	P	C_4	7	3.30 (11)	124	92 (3)	1.44 (3)	123	92	1.44		1		10%
57	butanediamine	N	C_4	7	2.91 (12)	9	93 (3)	1.45 (4)	9						-
58	dithiosquarato	S	C_2	5	3.43 (10)	22	93 (2)	1.45 (3)	22						-
59	dppp	P	C_3	6	3.32 (13)	360	93 (4)	1.45 (5)	328	87 (2)	1.38	(3)	32		10%
60	diselenosquarato	Se	C_2	5	3.56	1	94	1.46					1		-
61	diketiminate	N	C_3	6	2.91 (8)	500	94 (3)	1.46 (4)	392	87 (7)	1.38	(9)	108		10%
62	distibine	Sb	C_8	11	3.90 (12)	5	95 (1)	1.48 (1)	2	92 (1)	1.44	(2)	3		-
63	propanedithiolate	S	C_3	6	3.38 (12)	41	96 (3)	1.49 (4)	6	91 (7)	1.42	(8)	35		-

64	dppb	P	C_4	7	3.42 (11)	70	96 (3)	1.49 (4)	67	92 (1)	1.44 (1)	3	-
65	dpbx	P	C_4	7	3.59 (16)	35	100 (7)	1.54 (5)	35				-
66	dppf	P	$FeCp_2$	6	3.59 (21)	326	101 (8)	1.54 (7)	297	98(13)	1.50 (12)	29	10%
67	dppr	P	$RuCp_2$	6	3.55 (12)	6	101 (4)	1.54 (4)	6				-
68	squarato [e]	O	C_2	5	3.29 (4)	7		1.63 (1)	3		1.52 (1)	4	-
69	deltato	O	C_2	5	3.55								-
70	dpp-pentane	P	C_5	8	3.64 (23)	4	107 (10)	1.61 (11)	4				-
71	transphos	P	C_9	12	4.53 (28)	15	157 (23)	1.92 (12)	15				-
72	dppbp	P	C_{14}	17	4.69 (21)	36	177 (2)	1.999 (1)	17	167(17)	1.97 (11)	19	-

[a)] Standard deviation of the sample given in parenthesis. [c)] o-phenylene-bis(dimethylarsine). [e)] Data from structures as dinucleating ligand, no chelates found. [f)] Only trans-chelates found. All data from CSD version 5.30 + 2 updates.

Table S2. Geometric parameters of the chelate rings formed by bipyridine and related ligands. Standard deviations in parentheses.

	All Metals				Ru		
	β (º)	N-M-N (º)	Data Set	Ru-N (Å)	β (º)	N-M-N (º)	Data Set
bipy (**24**)	69 (2)	78 (4)	7109	2.07 (3)	69 (1)	78 (1)	1480
phen (**25**)	64 (1)	78 (4)	5299	2.09 (3)	65 (1)	79 (1)	261
pyrazolylpyridine (**21**)	59 (3)	78 (2)	8				
fluorenone (**26**)	45 (2)	78 (4)	41	2.14 (1)	49 (1)	81 (1)	5

Table S3.– Ranges of rigid bites (*d*) and bite angles (α) of some long-bite bidentate ligands with donor atoms D and spacers X.

Ligand	D	X	n	*d* (Å)	α (°)	Fragments
dppf (**66**)	P	$FeCp_2$	6	3.18 – 4.63	86 – 162	540
dppr (**67**)	P	$RuCp_2$	6	3.40 – 3.76	97 – 108	9
dppp-pentane (**70**)	P	C_5	8	3.38 – 3.86	97 – 117	5
xantphos (**83**)	P	C_2OC_2	8	3.40 – 4.52	99 – 159	69
bisbi (**84**)	P	C_6	9	3.52 – 4.56	100 – 165	14
acpy2 (**85**)	P	C_{14}	17	3.58 – 4.30	111 – 180	18
transphos (**71**)	P	C_9	12	3.57 – 4.84	105 – 177	21
dppbp **(86**)	N	C_8	11	4.41 – 4.85	169 – 179	10
diisocyanomenthane (**87**)	C	NC_5N	10	3.22 – 7.00	-	67
spanphos (**88**)	P	C_5O_2	12	3.50 – 4.60	96 – 174	6
89	P	$C_{14}O_2$	19	4.79	175	1
90 (n = 1)	P	C_8O_3	14	4.94	177	1
90 (n = 2)	P	$C_{10}O_4$	17	4.94	172	1
90 (n = 3)	P	$C_{12}O_5$	20	4.95	174	1

Table S4 – Parameters for ligands in bidentate and binucleating coordination modes.

				Bidentate		Binucleating			
	Ligand	D	X	*d* (Å)	D-X-D (º)	*d* (Å)	D-X-D (º)	Data Sets	R
1	pyrazolato	N	-	1.38 (1)		1.37 (3)		155	
3	nitrato	O	N	2.13 (5)	116 (3)	2.21 (8)	122 (2)	14	
4	carboxylato	O	C	2.19 (2)	121 (2)	2.24 (2)	125 (2)	1803	< 5%
5	triazenido	N	N	2.09 (3)	106 (3)	2.20 (3)	115 (2)	94	
7	aminopyridine	N	C	2.22 (3)	109 (2)	2.32 (3)	116 (2)	308	< 10%
9	amidinato	N	C	2.20 (3)	112 (2)	2.31 (3)	121 (2)	683	< 10%
10	carbonato	O	C	2.17 (3)	111 (2)	2.25 (1)	120 (2)	11	
11	sulfato	O	S	2.32 (5)	100 (3)	2.46 (2)	108 (2)	12	
13	pyridinethiolato	S,N	C	2.55 (4)	110 (3)	2.69 (5)	119 (4)	158	< 10%
16	dppm	P	C	2.72 (5)	95 (2)	3.04 (6)	112 (3)	1230	< 10%
17	dithiocarbamates	S	C	2.87 (5)	113 (3)	3.04 (6)	126 (5)	40	
19	dpasm	As	C	2.89 (3)	94 (2)	3.22 (8)	111 (4)	19	
23	phosphinodimethylene	C	P	2.68 (6)	100 (3)	2.85 (6)	108 (3)	38	
24	bipy	N	C_2	2.63 (4)	-	2.78 (8)	-	14	
32	dithiophosphinato	S	P	3.20 (4)	106 (3)	3.38 (5)	114 (3)	12	
37	ethylenediamine	N	C_2	2.76 (9)	-	3.3 (3)	-	3	
59	dppp	P	C_3	3.3 (1)	-	4.5 (2)	-	28	
64	dppb	P	C_4	3.4 (1)	-	5.1 (1)	-	7	
68	squarato	O	C_2		-	3.29 (4)	-	6	

All data from CSD version 5.30 + 2 updates.

Table S5 – Pyramidalities (Σ), average angle between DMD chelate rings (β) and normalized bites (*b*) for some common tridentate ligands with large (L) and small (S) transition metal ions, according to the classification of Figure 2. Standard deviations given in parentheses, and size of the data sets from which the parameters have been extracted are also given.

Abbreviaton	Ligand	β_L	β_S	Σ_L	Σ_S	b_L	b_S	Data Set L	Data Set S
Crown ligands (*only fac*)**:**									
Cp	η^5-cyclopentadienide			152 (7)	178 (8)			10000	10000
tach	triazacyclohexane (**91**) †	70 (1)	72 (1)	179 (4)	189 (6)	1.00(2)	1.05 (3)	28	41
ttch	trithiacyclohexane †		72 (-)		189 (-)		1.04 (-)		1
Ar	arene (C_6R_6)			187(13)	197 (9)			438	5348
tacn	triazacyclononane (**92**) †	79 (2)	83 (2)	228 (9)	246 (8)	1.23 (4)	1.31 (4)	219	911
chta	cyclohexanetriamine (**93**) †	85 (4)	87 (2)	264(19)	271 (9)	1.39 (8)	1.42 (4)	7	126
ttcn	trithiacyclononane (**95**) †	82 (3)	87 (2)	242(14)	262 (8)	1.29 (6)	1.38 (3)	20	257
tpcn	triphosphacyclononane (**94**) †		86 (1)		257 (1)		1.36 (1)		5
tacd	triazacyclodecane (**96**) †	-	84 (2)		264(13)		1.39 (5)		20
ttcd	trithiacyclodecane †	84 (-)	86 (1)	254 (-)	269 (6)	1.35 (-)	1.41 (2)	1	18
tpcd	triphosphacyclodecane †		87 (1)		262 (1)		1.38 (1)		3
toch	trisoxocyclohexane (**97**) †	82 (6)	88 (1)	244(27)	265 (6)	1.30(12)	1.40 (3)	17	19
tacdd	triazacyclododecane (**98**) †	81 (3)	80 (9)	246 (7)	292(16)	1.31 (3)	1.50 (6)	2	30
ttcdd	trithiacyclododecane * (**99**) †		78(11)		296(21)		1.51 (8)		7
tpcd	triphosphacyclododecane (**100**) †	88 (2)	84(8)	264 (7)	285(18)	1.47 (7)	1.51 (8)	13	12
Triskelion ligands (only *fac*)**:**									
tppm	$HC(PPh_2)_3$ (**101**)		76		216		1.18		1
tpm	tris(pyrazolyl)methane (**102**)	81 (2)	85 (2)	239 (2)	254 (6)	1.28 (4)	1.34 (3)	22	80
tpym	tris(pyridyl)methane (**103**) †	83 (1)	87 (2)	246 (3)	260 (7)	1.31 (2)	1.37 (3)	3	37
tpb	tris(pyrazolyl)borate (**104**)	82 (2)	86 (2)	244 (8)	265(10)	1.30 (4)	1.39 (4)	571	1082
timyb	tris(imidazol-2-ylidene)borate (**105**) †	-	88 (1)	-	271 (5)	-	1.42 (2)	-	12

taea	$RC(CH_2NR_2)_3$ (**106**)		82	88 (1)	246	264 (3)	1.31	1.39 (1)	1	20
tppe	tris(diphenylphosphinomethyl)ethane (**107**)		85 (2)	88 (1)	253 (7)	271 (7)	1.34 (3)	1.42 (3)	48	208
tpmb	tris(phosphinomethyl)borate (**108**) †		-	87 (2)	-	275 (8)	-	1.43 (3)	-	127
ttmb	tris(alkylthiomethyl)borate) (**109**)		84	85 (2)	250	277(12)	1.33	1.44 (5)	2	26
tip	tris(imidazolyl)phosphine (**110**)		82	85 (2)	244	279(10)	1.30	1.45 (4)	2	16
tpmo	tris(diphenylphosphine oxide)methane (**111**)		-	88 (1)	-	267 (1)	-	1.40 (1)	-	9
Clamp ligands (*mer* coordination)**:**										
	Bis(4'-phenyloxazolin-2'-yl)pyridine (**112**)			1 (1)				1.23 (4)		64
terpy	terpyridine (**113**)		10 (12)	3 (4)			1.13 (8)	1.25 (4)	62	916
dpzpy	dipyrazolylpyridine (**114**)		4	3 (3)			1.26 (x)	1.25 (4)	1	102
	NCN pincer (**115**) †		4 (3)	2 (3)	-	-	1.18 (2)	1.31 (2)	5	193
	PCP pincer †		-	17 (5)	-	-	-	1.32 (2)	-	146
	NCN pincer (*fac* coordination) †		54 (5)		-	-	1.16 (1)		5	
Ribbon ligands (both *fac* and *mer*)**:**										
dien	diethylenetriamine (**116**)	*fac*	83 (5)	84(7)	244(10)	260 (6)	1.25 (4)	1.32(4)	38	171
		mer	18 (5)	23 (4)	311(15)	329(11)	1.27(3)	1.32(4)	6	165
dptn	bis(aminopropyl)amine (**117**)	*fac*		-		297(18)	-	1.47 (4)	-	8
		mer				353 (8)	-	1.46 (3)	-	86
bpea	bis(pyridylethyl)amine (**118**)	*fac*	-	74(11)	-	299(12)	-	1.51 (2)	-	17
		mer	-	9 (8)	-	355 (6)	-	1.50 (7)	-	24

† Data from the CSD version 5.30 + 2 updates (February 2009); all other data from CSD version 5.29.