Supporting Information Available.

Table 1S. Selected bond angles (deg) for **5**·2CH_2Cl_2, **9**·C_6H_{14}, **11**OTf·Et_2O, and **13**OTf, and **14**PF_6·2MeCN·0.5Et_2O.

5		**9**		**11**		**13**		**14**	
N(2)–Ir(1)–N(1)	157.6(5)	N(2)–Ir(1)–N(1)	157.8(4)	N(2)–Ir(1)–N(1)	158.3(2)	N(2)–Ir(1)–N(1)	158.0(2)	N(2)–Ir(1)–N(1)	159.6(3)
C(1)–Ir(1)–N(1)	78.4(6)	C(1)–Ir(1)–N(1)	78.6(4)	C(1)–Ir(1)–N(1)	79.4(2)	C(1)–Ir(1)–N(1)	78.9(2)	N(4)–Ir(1)–N(1)	80.2(3)
C(1)–Ir(1)–N(2)	79.2(6)	C(1)–Ir(1)–N(2)	79.2(4)	C(1)–Ir(1)–N(2)	79.0(2)	C(1)–Ir(1)–N(2)	79.2(2)	N(4)–Ir(1)–N(2)	79.4(3)
C(2)–Ir(1)–N(3)	79.9(6)	C(2)–Ir(1)–N(3)	79.7(4)	C(2)–Ir(1)–N(3)	79.1(2)	C(2)–Ir(1)–N(3)	80.1(2)	C(2)–Ir(1)–N(3)	80.4(4)
C(1)–Ir(1)–N(3)	173.3(5)	C(1)–Ir(1)–N(3)	176.0(4)	C(1)–Ir(1)–N(3)	174.3(2)	C(1)–Ir(1)–N(3)	172.2(2)	N(4)–Ir(1)–N(3)	177.4(3)
C(2)–Ir(1)–C(1)	93.4(6)	C(2)–Ir(1)–C(1)	97.1(4)	C(2)–Ir(1)–N(6)	173.1(2)	C(2)–Ir(1)–C(1)	92.1(3)	C(2)–Ir(1)–Cl(1)	175.0(3)
C(2)–Ir(1)–Cl(1)	172.0(5)	C(2)–Ir(1)–Cl(1)	172.6(3)	Ir(1)–N(6)–C(34)	177.7(4)	C(2)–Ir(1)–N(6)	172.4(2)		
				N(6)–C(34)–C(35)	178.8(5)	Ir(1)–N(6)–C(44)	176.8(6)		
				C(2)–Ir(1)–C(1)	95.4(2)	N(6)–C(44)–C(45)	179.1(8)		

Table 2S. Selected torsion angles (deg) between planes for **5**·2CH_2Cl_2, **9**·C_6H_{14}, **11**OTf·Et_2O, **13**OTf, and **14**PF_6·2MeCN·0.5Et_2O,.

5		**9**		**11**		**13**		**14**	
Mebib [a]–mppy [b]	86.7(2)	Phbib [a]–ppy [b]	86.3(1)	Mebib [a]–ppy [b]	87.3(8)	Phbib [a]–ppy [b]	90.0(2)	Mebip [a]–ppy [b]	88.4(1)
Rings 1 [c]–2 [d]	1.7(5)	Rings 1 [c]–2 [d]	9.8(2)	Rings 1 [c]–2 [d]	4.7(1)	Rings 1 [c]–2 [d]	10.0(3)	Rings 1 [c]–2 [d]	6.7(3)
Rings 1 [c] –3 [e]	2.4(4)	Rings 1 [c]–3 [e]	14.9(2)	Rings 1 [c] –3 [e]	5.2(1)	Rings 1 [c] –3 [e]	12.1(3)	Rings 1 [c] –3 [e]	1.3(2)
Rings 2 [d] –3 [e]	4.1(6)	Rings 2 [d]–3 [e]	5.9(2)	Rings 2 [d] –3 [e]	2.4(2)	Rings 2 [d] –3 [e]	4.1(3)	Rings 2 [d] –3 [e]	6.8(3)
		Rings 1 [c]–4 [f]	66.4(2)			Rings 1 [c]–4 [f]	69.0(4)		
		Rings 3 [e]–5 [g]	65.7(2)			Rings 3 [e]–5 [g]	61.4(4)		

[a] Planes defined by N(1), N(2), N(4)–N(6), C(1), and C(3)–C(22) for **14**PF_6·2MeCN·0.5Et_2O; defined by N(1), N(2), N(4), N(5), C(1), and C(3)–C(23) for **5**·2CH_2Cl_2 and **11**OTf·Et_2O; defined by N(1), N(2), N(4), N(5), C(1), C(3)–C(8), C(15)–C(21), and C(28)–C(33) for **9**·C_6H_{14} and **13**OTf.

[b] Planes defined by N(3), C(2), and C(23)–C(32) for **14**PF_6·2MeCN·0.5Et_2O; defined by N(3), C(2), and C(24)–C(34) for **5**·2CH_2Cl_2; defined by N(3), C(2), and C(24)–C(33) for **11**OTf·Et_2O; defined by N(3), C(2), and C(34)–C(43) for **9**·C_6H_{14} and **13**OTf.

[c] Planes defined by N(1), N(5), C(1), C(3)–C(7), and C(9) for **14**PF_6·2MeCN·0.5Et_2O; defined by N(1), N(4), C(3)–C(8), and C(10) for **5**·2CH_2Cl_2 and **11**OTf·Et_2O; defined by N(1), N(4), C(3)–C(8), and C(15) for **9**·C_6H_{14} and **13**OTf.

[d] Planes defined by N(4) and C(10)–C(14) for **14**PF_6·2MeCN·0.5Et_2O, defined by C(1) and C(11)–C(15) for **9**·2CH_2Cl_2 and **11**OTf·Et_2O; defined by C(1) and C(16)–C(20) for **9**·C_6H_{14} and **13**OTf.

[e] Planes defined by N(2), N(6), C(15), and C(17)–C(22) for **14**PF_6·2MeCN·0.5Et_2O; defined by N(2), N(5), C(16), and C(18)–C(23) for **5**·2CH_2Cl_2 and **11**OTf·Et_2O; defined by N(2), N(5), C(21), and C(28)–C(33) for **9**·C_6H_{14} and **13**OTf.

[f] Planes defined by C(9)–C(14) fo **9**·C_6H_{14} and **13**OTf.

[g] Planes defined by C(22)–C(27) for **9**·C_6H_{14} and **13**OTf.

Table 3S. Excitation energy, oscillator strength (f), and major electronic configuration for Ir(Mebib)(mppy)Cl (**5**) with the X-ray structure. (Calculated at the B3PW91/LanL2DZ level) (HOMO is MO 145)

State	excitation energy	oscillator strength	major configuration and coefficient	
Triplet state				
1:	1.9659 eV		145 →146	0.69695
2:	2.2303 eV		144 →146	0.70169
3:	2.5710 eV		145 →147	0.66972
4:	2.7471 eV		143 →146	0.45792
5:	2.7741 eV		145 →148	0.51903
Singlet state				
1:	2.3407 eV	f=0.0285	145 →146	0.67899
2:	2.4900 eV	f=0.0740	144 →146	0.68478
3:	2.7308 eV	f=0.0053	145 →147	0.69117
4:	2.9390 eV	f=0.0009	144 →147	0.69852
5:	3.0404 eV	f=0.0060	143 →146	0.53982
		145 →148	-0.34659	
6:	3.0435 eV	f=0.0091	143 →146	0.37408
		145 →148	0.50979	
7:	3.2223 eV	f=0.0053	145 →148	-0.30226
		145 →149	0.62873	
8:	3.3666 eV	f=0.0065	144 →148	0.62165
9:	3.4141 eV	f=0.1911	142 →146	0.62572
10:	3.4282 eV	f=0.0175	144 →149	-0.60737
11:	3.4601 eV	f=0.0325	141 →146	0.55084
12:	3.5963 eV	f=0.0576	139 →146	0.48425
			140 →146	0.43794
13:	3.6461 eV	f=0.0338	143 →147	0.62341
14:	3.7003 eV	f=0.0117	139 →146	0.42798
			140 →146	-0.41912

Table 4S. Excitation energy, oscillator strength (f), and major electronic configuration for Ir(Mebib)(ppy)$(CH_3CN)^+$ (**11**) with the X-ray structure. (Calculated at the B3PW91/LanL2DZ level) (HOMO is MO 148)

State	excitation energy	oscillator strength	major configuration and coefficient	
Triplet state				
1:	2.6231 eV		148 ->149	0.62234
2:	2.9075 eV		148 ->150	0.49682
3:	2.9442 eV		147 ->149	0.67220
4:	3.1896 eV		148 ->152	0.45074
5:	3.1972 eV		148 ->150	0.39681
			148 ->151	-0.24382
			148 ->152	0.27203
Singlet state				
1:	3.1467 eV	f=0.0460	148 →149	0.67696
2:	3.2981 eV	f=0.0054	148 →150	0.68724
3:	3.4274 eV	f=0.2270	147 →149	0.65724
4:	3.5780 eV	f=0.0242	148 →152	0.59577
5:	3.6026 eV	f=0.0172	148 →151	0.61499
6:	3.6633 eV	f=0.0017	147 →150	0.69515
7:	3.7591 eV	f=0.0030	145 →149	0.59539
8:	3.9656 eV	f=0.0200	146 →149	0.49335
9:	3.9772 eV	f=0.0062	147 →151	0.65278
10:	4.0336 eV	f=0.0509	147 →152	0.50489
11:	4.1104 eV	f=0.0079	146 →150	0.59458
12:	4.1467 eV	f=0.0551	143 →149	0.41452
		144 →149	-0.37734	
13:	4.1657 eV	f=0.0353	145 →150	0.53489
14:	4.2298 eV	f=0.0020	145 →152	0.53234
15:	4.2771 eV	f=0.0683	143 →149	0.46954
		144 →149	0.26397	

Table 5S. Excitation energy, oscillator strength (f), and major electronic configuration for Ir(Mebip)(ppy)Cl^+ (**14**) with the X-ray structure. (Calculated at the B3PW91/LanL2DZ level) (HOMO is MO 141)

State	excitation energy	oscillator strength	major configuration and coefficient		
Triplet state					
1:	1.7211 eV		141 →142	0.70294	
2:	1.9866 eV		141 →143	0.68776	
3:	2.1107 eV		140 →142	0.70235	
4:	2.5676 eV		138 →142	0.52476	
5:	2.5841 eV		140 →143	0.69129	
Singlet state					
1:	1.8542 eV	f=0.0020	141 →142	0.68582	
2:	2.2494 eV	f=0.0079	141 →143	0.61992	
3:	2.5043 eV	f=0.0235	140 →142	0.59892	
4:	2.6819 eV	f=0.0173	140 →143	0.68852	
5:	2.8402 eV	f=0.0028	139 →142	0.56695	
6:	2.9626 eV	f=0.0003	137 →142	0.36130	
			138 →142	0.39858	
			139 →142	-0.35794	
7:	3.0424 eV	f=0.0059	137 →142	0.44826	
			138 →142	-0.40453	
8:	3.1342 eV	f=0.0258	141 →144	0.66343	
9:	3.1702 eV	f=0.0049	139 →143	0.62292	
10:	3.2289 eV	f=0.0060	136 →142	0.54085	
11:	3.2977 eV	f=0.0079	137 →143	0.40396	
			138 →143	0.39173	
12:	3.3764 eV	f=0.0153	134 →142	0.54684	
13:	3.4310 eV	f=0.0045	136 →143	0.59779	
14:	3.4400 eV	f=0.0399	136 →143	-0.26307	
			137 →143	-0.34105	
			138 →143	0.36795	
15:	3.5790 eV	f=0.1443	135 →142	0.58512	