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Synthesis and Characterization of Iridium(III) Complexes containing $(ppy)_2Ir$-unit and Nitrogen based Donor Ligands

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Abstract

The treatment of 4-dimethylamino pyridine (L^1) with 0.5 equivalent of $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ afforded the neutral yellow complex $[Ir(ppy)_2(L^1)Cl]$ (**1**) in 81% yield (ppyH = 2-phenylpyridine). When four equivalents of L^1 were reacted with an equivalent of $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ in the presence of NH_4PF_6 produced the yellow salt $[Ir(ppy)_2(L^1)_2]PF_6$ (**2**) in 96% yield. Dark brown crystals of $[(ppy)_2ClIr]_2(\mu\text{-}L^2)$ (**3**) with a bridging di(4-pyridyl) acetylene ligand (L^2) was isolated when $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ was treated with one equivalent of di(4-pyridyl) acetylene. Four iridium(III) complexes (**4**)-(**7**) of the type $[Ir(ppy)_2(N^N)]PF_6$ were prepared by reacting $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ with an appropriate bidentate ligand (N^N) in the molar ratio of 1:2 in the presence of NH_4PF_6; the products were isolated in good yields (**4**, 87%; **5**, 92%; **6**, 96%; **7**, 64%) as colored solids. All new complexes were characterized using a combination of

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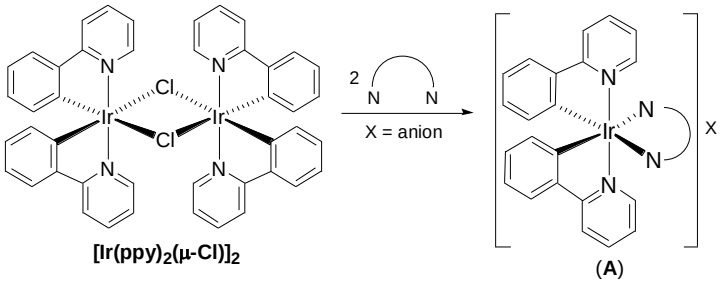
IR, NMR, mass spectrometry and elemental analysis. It is important to devise synthetic routes to cyclometallated Ir(III) complexes as they have shown interesting properties in the fields of cancer research, photovoltaic cells, *etc*.

Keywords: *Iridium-complexes, cyclometallation, polypyridine, N-donors, 2-phenylpyridine*

Introduction

Octahedral cyclometallated Ir(III) complexes of the type $[Ir(C^N)_2(N^N)]X$ (**A**) have shown applications in the fields of photovoltaic cells, chemo-sensors, light-emitting devices (LEDs) and phosphorescent dopants in organic light-emitting diodes (OLEDs) (Jing et al, 2024; Amouri, 2023; Yoon & Teets, 2022; Zhang & Ding, 2021). (**A**) can easily be prepared by reacting the $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ dimer with a bidentate ligand (N^N) in the presence a suitable anion X (Scheme 1) (Liao et al, 2021).



Scheme 1. Synthesis of complexes of the type (**A**)

Iridium(III) complexes of the type (**A**) possess important properties such as rigid configurational stability, high emissive quantum yields, long phosphorescence lifetime (in μs), and high electrochemical stability (Jing et al, 2024; Amouri, 2023). Luminescent Ir(III) polypyridine complexes are also candidates for biomolecular and cellular probes (Lo et al, 2011). Parameters such as water solubility, lipophilicity, cytotoxicity, cellular uptake, and intracellular localization could all be tuned by using various cyclometallated (C^N) and polypyridine (N^N) ligands (Zhang et al, 2021; Tan et al, 2021; Liao et al, 2021; Bolitho et al, 2020). Some of the basic and well-studied C^N and N^N ligand types (Lo et al, 2011; Tan et al, 2021) are given in Figures 1 and 2, respectively.

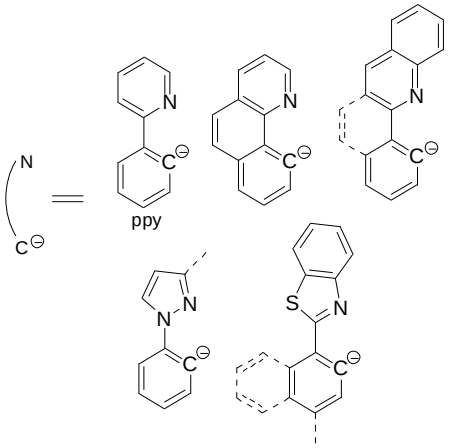


Figure 1. Common C^N ligand types

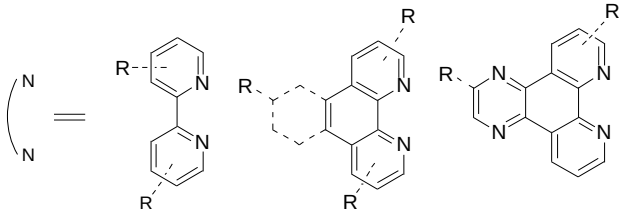


Figure 2. Common N^N ligand types; R = H or organic group

It is of interest to explore the chemistry of monodentate pyridine ligand (L^1), bridging pyridine ligand (L^2) and bulky bidentate bipyridine ligands (L^3 – L^6) with iridium(III) centers in order to prepare neutral complexes of the types $[Ir(ppy)_2(L^1)Cl]$ and $[(ppy)_2ClIr]_2(\mu\text{-}L^2)$, and salts of the type $[Ir(ppy)_2(N^N)]PF_6$, where ppy = 2-pyridylphenyl, L^1 = 4-dimethylamino pyridine (DMAP), L^2 = di(4-pyridyl) acetylene (DPA), and N^N = 6,6′-dimethyl-2,2′-bipyridine (L^3), 6,7-di(4-*tert*-butylphenyl)-5,8-diphenyl-1,12-diazatriphenylene (L^4), 3,4,5,6-tetraphenyl-2,2′-bipyridine (L^5), 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (L^6) (Figure 3). This research paper presents synthetic routes and characterization of those complexes.

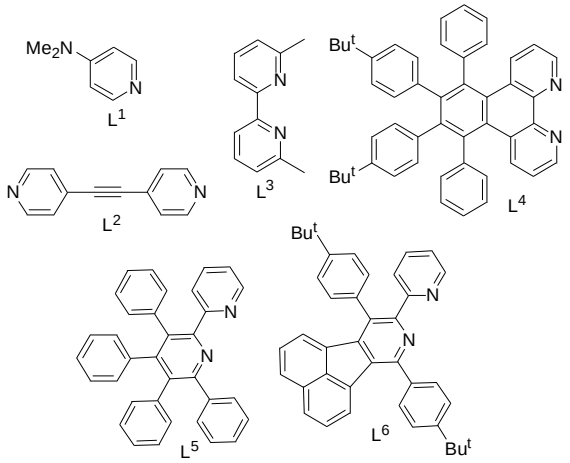


Figure 3. N^N ligands used in the present study.

Methodology

Elemental analysis was carried out on a Carlo Erba 1006 automatic analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. Mass spectral data were obtained using a micro-mass LCT electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters Premier spectrometer using α-cyano-4-hydroxy cinnamic acid matrix. NMR spectra were recorded on a DPX 400 spectrometer operating at 400.13 MHz for ^{1}H, and 100.62 MHz for ^{13}C, and were standardized with respect to TMS. Single-crystal analysis was performed on a Bruker SMART APEX CCD diffractometer using graphite monochromised Mo-Kα (λ = 0.71073Å) radiation and refinements were obtained using SHELXS software. 4-Dimethylamino pyridine (DMAP, L^1), and 6,6′-dimethyl-2,2′-bipyridine (L^3) were purchased from Aldrich. 6,7-Di(4-*tert*-butylphenyl)-5,8-diphenyl-1,12-diazatriphenylene (L^4), 3,4,5,6-tetraphenyl-2,2′-bipyridine (L^5), and 7,10-di(4-*tert*-butyl phenyl)-9-(2-pyridyl)-8-azafluoranthene (L^6) were prepared according to literature procedures (Perera, 2022; Ollangnier et al, 2008; Perera et al, 2010).

[IrCl(ppy)$_2$(L^1)] (**1**)

A suspension containing [Ir(ppy)$_2$(μ-Cl)]$_2$ (15 mg, 0.0139 mmol) and 4-dimethylamino pyridine (DMAP, L^1) (3.5 mg, 0.028 mmol) in chloroform (3 mL) was refluxed for 2.5 h to give a pale-yellow solution. It was concentrated to a very low volume and triturated with methanol

to give a yellow solid (15 mg, 81%). Found: C, 50.80; H, 4.11; N 7.90, calcd. (%) for $C_{29}H_{26}ClN_4Ir{\cdot}0.25CHCl_3$: C, 51.05; H, 3.84; N 8.14. Maldi (acetone, m/z): found: 623.1770; calcd. 623.1787 for $C_{29}H_{26}N_4Ir$, $[M\text{-}Cl]^+$. IR (neat): 2959, 1605, 1580, 1476, 1419, 1268, 1024, 830, 758, 730 and 705. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (d, 1H, ^{3}J(HH) 6.0 Hz, H^{DMAP}), 8.21 (d, 1H, ^{3}J(HH) 6.0 Hz), 7.90 (d, 1H, ^{3}J(HH) 8.0 Hz), 7.74 (t, 1H, ^{3}J(HH) 8.0 Hz), 7.72 (m, 2H, ^{3}J(HH) 7.5 Hz,), 7.57 (d, 1H, ^{3}J(HH) 8.0 Hz), 7.51 (d, 1H, ^{3}J(HH) 8.0 Hz), 7.17 (dt, 1H, ^{3}J(HH) 6.0, 7.3 Hz), 7.02 (t, 1H, ^{3}J(HH) 7.5 Hz), 6.85 (t, 1H, ^{3}J(HH) 7.5 Hz), 6.83-6.71 (m, 6H), 6.35-6.33 (m, 2H), 6.25 (d, 1H, ^{3}J(HH) 7.5 Hz) and 2.96 (s, 6H, NMe_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 149.2, 136.4, 136.2, 132.2, 131.4, 130.0, 129.4, 123.9, 123.8, 121.9, 121.5, 120.9, 120.6, 118.9, 117.9, 107.5 and 39.1.

$[Ir(ppy)_2(L^1)_2]PF_6$ (2)

A solution of NH_4PF_6 (10 mg, 0.061 mmol) in methanol (1 mL) was added to a suspension containing $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (15 mg, 0.0139 mmol) and 4-dimethylamino pyridine (L^1) (9 mg, 0.073 mmol) in chloroform (2 mL). The reaction mixture was refluxed for 2 h to give a bright yellow solution. It was concentrated to yield yellow crystals (24 mg, 96%). Found: C, 47.13; H, 4.08, calcd. (%) for $C_{36}H_{36}F_6IrN_6P{\cdot}0.25CHCl_3$: C, 47.33; H, 3.97. IR (neat): 2957, 1622, 1536, 1476, 1391, 1226, 835 and 762. ESI-MS (MeCN, m/z): found: 745.2599, calcd. 745.2631 for $C_{36}H_{36}N_6Ir$, $[M\text{-}PF_6]^+$. ^{1}H NMR (400 MHz, CD_3CN): δ 8.68 (d, 2H, ^{3}J(HH) 5.5 Hz, H^6), 7.99-7.88 (m, 8H, ^{3}J(HH) 7.0, 8.5 Hz, ^{4}J(HH) 1.5 Hz, H^7, H^3 & H^4), 7.59 (dd, 2H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.0 Hz, $H^{3'}$), 7.38 (m, 2H, ^{3}J(HH) 5.5 Hz, ^{4}J(HH) 1.5 Hz, H^5), 6.92-6.80 (m, 4H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.0 Hz, $H^{4'}$ & $H^{5'}$), 6.45 (m, 4H, ^{3}J(HH) 7.0 Hz, H^8) 6.33 (dd, 2H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.5 Hz, $H^{6'}$) and 2.95 (s, 6H, NMe_2). ^{13}C NMR (100 MHz, CD_3CN): δ 150.4 (4C, C^7), 149.3 (C^6), 138.3 (C^4), 132.1 ($C^{6'}$), 130.0 ($C^{5'/4'}$), 124.1 ($3'$), 123.2 (C^5), 121.9 ($C^{5'/4'}$), 119.3 (C^3) 107.9 (4C, C^8) and 38.4 (NMe_2).

$[IrCl(ppy)_2\{\mu\text{-di(4-pyridyl) acetylene}\}IrCl(ppy)_2]$ (3)

$[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (15 mg, 0.0139 mmol) and di(4-pyridyl) acetylene (DPA, L^2) (2.5 mg, 0.0138 mmol) were dissolved in chloroform (3 mL) and the solution was refluxed for 3 h to give a brown solution. It was concentrated to a low volume (ca. 1 mL) and methanol was added to

yield dark brown crystals (16 mg, 92%). Found: C, 49.73; H, 3.18; N 6.18, calcd. (%) for $C_{56}H_{40}Cl_2Ir_2N_6P{\cdot}1.0CHCl_3$: C, 49.90; H, 3.01; N 6.12. IR (neat): 3039, 2230, 1606, 1581, 1476, 1268, 1213, 1063, 1030, 834, 758 and 730. ESI-MS (dichloromethane, m/z): found: 1217.2235; calcd. 1217.2262 for $C_{56}H_{40}N_6ClIr_2$, $[M\text{-}Cl]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (d, 2H, ^{3}J(HH) 6.0 Hz, H^{DPA}), 8.05 (d, 2H, ^{3}J(HH) 6.0 Hz), 7.93 (d, 2H, ^{3}J(HH) 8.0 Hz), 7.81-7.67 (m, 6H), 7.59 (d, 2H, ^{3}J(HH) 7.5 Hz), 7.53 (d, 2H, ^{3}J(HH) 7.5 Hz), 7.19 (t, 2H, ^{3}J(HH) 7.3 Hz), 7.05 (t, 2H, ^{3}J(HH) 7.3 Hz), 6.91-6.74 (m, 12H), 6.35-6.29 (m, 4H), and 6.18 (d, 2H, ^{3}J(HH) 7.5 Hz).

$[Ir(ppy)_2(L^3)]PF_6$ (4)

A solution of NH_4PF_6 (10 mg, 0.061 mmol) in methanol (1 mL) was added to a suspension containing $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (15 mg, 0.0139 mmol) and 6,6′-dimethyl-2,2′-bipyridine (6 mg, 0.0279 mmol) in degassed dichloromethane (2 mL). The reaction mixture was refluxed for 2 h to give a pale-yellow solution which was concentrated to yield (**4**) as yellow crystals (20 mg, 87%). Found: C, 48.65; H, 3.24; N 6.47; calcd. (%) for $C_{34}H_{28}F_6IrN_4P$: C, 49.21; H, 3.40; N 6.75. IR (neat): 2954, 1606, 1580, 1478, 1458, 1438, 833, 779, 756 and 730. ESI-MS (MeCN, m/z): found: 685.1931; calcd. 685.1943 for $C_{34}H_{28}N_4Ir$, $[M\text{-}PF_6]^+$. ^{1}H NMR (400 MHz, CD_3CN): δ 8.28 (d, 2H, ^{3}J(HH) 8.0 Hz, $H^{3''}$), 8.07 (m, 2H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.5 Hz, H^3), 8.00 (t, 2H, ^{3}J(HH) 7.8 Hz, $H^{4''}$), 7.92-7.88 (m, 4H, ^{4}J(HH) 1.5 Hz, H^4 & H^6), 7.72 (dd, 2H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.2 Hz, $H^{3'}$), 7.34 (dd, 2H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 0.75 Hz, $H^{5''}$), 7.11 (dt, 2H, ^{3}J(HH) 5.8 Hz, ^{4}J(HH) 1.5 Hz, H^5), 6.96 (dt, 2H, ^{3}J(HH) 8.5 Hz, ^{4}J(HH) 1.2 Hz, $H^{4'}$), 6.77 (dt, 2H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.5 Hz, $H^{5'}$), 6.12 (dd, 2H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 0.75 Hz, $H^{6'}$) and 2.19 (s, 6H, Me). ^{13}C NMR (150 MHz, CD_3CN): δ 150.3 (C^6), 139.5 ($C^{4''}$), 138.5 (C^4), 131.5 ($C^{6'}$), 129.6 ($C^{5'}$), 128.4 ($C^{5''}$), 124.7 ($C^{3'}$), 123.2 (C^5), 122.6 ($C^{3''}$), 122.1 ($C^{4'}$), 119.7 (C^3) and 25.9 (Me).

$[Ir(ppy)_2(L^4)]PF_6$ (5)

A solution of NH_4PF_6 (10 mg, 0.061 mmol) in methanol (1 mL) was added to a suspension containing $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (15 mg, 0.0139 mmol) and 6,7-di(4-*tert*-butyl phenyl)-5,8-diphenyl-1,12-diazatriphenylene (L^4) (18 mg, 0.0279 mmol) in dichloromethane (2 mL). The reaction mixture was refluxed for 1 h to give a brown

solution. It was concentrated and triturated with methanol to yield yellow crystals (33 mg, 92%). Found: C, 63.47; H, 4.37; N 4.18, calcd. (%) for $C_{70}H_{58}F_6IrN_4P{\cdot}0.5CH_2Cl_2$: C, 63.43; H, 4.45; N 4.19. IR (neat): 2959, 1607, 1582 1477, 1437, 1268, 834, 756, 729 and 705. ESI-MS (MeCN, m/z): found: 1147.4323, calcd. 1147.4291 for $C_{70}H_{58}N_4Ir$, $[M\text{-}PF_6]^+$. ^{1}H NMR (600 MHz, CD_3CN): δ 8.07-8.04 (m, 4H, ^{4}J(HH) 1.1 Hz, $H^{4''}$ & $H^{6''}$), 7.95 (d, 2H, ^{3}J(HH) 7.9 Hz, H^3), 7.80 (m, 2H, ^{3}J(HH) 8.3 Hz, ^{4}J(HH) 1.5 Hz, H^4), 7.71 (d, br, 2H, ^{3}J(HH) 7.1 Hz, H^6), 7.21-7.13 (m, 10H, H^{Ph} & $H^{5''}$), 7.09-7.03 (m, 6H, H^{Ph}, H^5 & $H^{4'}$), 6.96 (dt, 2H, ^{3}J(HH) 7.5, ^{4}J(HH) 1.1 Hz, H^5), 6.88 (m, 4H, H^{Ar}), 6.57 (m, 4H, H^{Ar}), 6.37 (d, 2H, ^{3}J(HH) 7.1 Hz, $H^{6'}$) and 1.15 (s, 18H, CMe_3). ^{13}C NMR (150 MHz, CD_3CN): δ 149.1 ($C^{6''}$), 148.7(C^6), 138.6 ($C^{4''}$), 138.2 (C^4), 131.7 ($C^{6'}$), 131.5 (C^{Ph}), 130.9 (C^{Ph}), 130.8 ($C^{5'}$), 130.7 (C^{Ar}), 130.2 (C^8), 128.4 (C^{Ph}), 128.4 (C^{Ph}),124.7 (3′), 124.6 ($C^{5''}$), 123.5 (C^{Ar}), 123.4 (C^5), 122.6 ($C^{4'}$),119.6 (C^3) and 31.4 ($C\mathit{Me}_3$).

$[Ir(ppy)_2(L^5)]PF_6$ (6)

A solution of NH_4PF_6 (10 mg, 0.061 mmol) in methanol (1 mL) was added to a suspension containing $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (15 mg, 0.0139 mmol) and 3,4,5,6-tetraphenyl-2,2′-bipyridine (L^5) (14 mg, 0.030 mmol) in chloroform (2 mL). The reaction mixture was refluxed for 2 h to give a yellow-brown solution. It was concentrated and methanol was added to yield an orange solid (30 mg, 96%). Found: C, 58.38; H, 3.27; N 4.12, calcd. (%) for $C_{56}H_{40}F_6IrN_4P{\cdot}0.4CHCl_3$: C, 58.7; H, 3.53; N 3.64. IR (neat): 2962, 1606, 1476, 1425, 1362, 833, 756, 697 and 656. ESI-MS (MeCN, m/z): found: 961.2842, calcd. 961.2820 for $C_{56}H_{40}N_4Ir$, $[M\text{-}PF_6]^+$. ^{1}H NMR (400 MHz, CD_3CN): δ 8.05-7.94 (m, 4H), 7.87 (d, 1H, ^{3}J(HH) 8.0 Hz), 7.84 (d, 1H, ^{3}J(HH) 5.3 Hz), 7.70 (d, 1H, ^{3}J(HH) 5.8 Hz), 7.65 (dd, 1H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.0 Hz), 7.57 (dt, 1H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.0 Hz), 7.49 (dd, 1H, ^{3}J(HH) 6.0 Hz, ^{4}J(HH) 1.2 Hz), 7.33-7.16 (m, 8H), 7.10 (d, 1H, ^{3}J(HH) 8.5 Hz), 7.07-6.95 (m, 4H), 6.95-6.76 (m, 6H), 6.69 (t, 1H, ^{3}J(HH) 7.0 Hz), 6.58 (dt, 1H, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.2 Hz), 6.49 (d, 1H, ^{3}J(HH) 7.7 Hz), 6.41 (dt, 1H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.2 Hz), 6.34 (t, 2H, ^{3}J(HH) 7.8 Hz), 5.97 (d, 1H, ^{3}J(HH) 7.0 Hz) and 5.72 (d, 1H, ^{3}J(HH) 7.0 Hz). ^{13}C NMR (150 MHz, CD_3CN): δ 150.1, 149.8, 149.1, 138.8, 138.2, 137.2, 130.9, 130.8, 130.6, 130.4, 130.3, 130.0, 129.9, 129.8, 129.5, 129.0, 128.9, 129.87, 128.4, 127.4, 127.2, 127.1, 126.9, 126.9, 126.7, 126.6, 124.8, 124.6, 123.7, 122.7, 122.4, 120.4, 120.3 and 119.9.

$[Ir(ppy)_2(L^6)]PF_6$ (7)

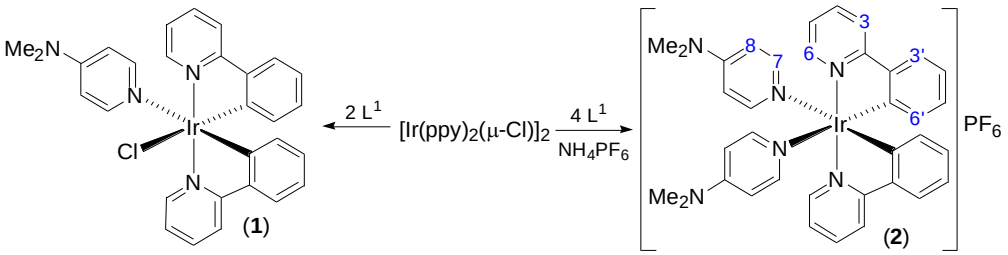
A solution of NH_4PF_6 (10 mg, 0.061 mmol) in methanol (1 mL) was added to a suspension containing $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (15 mg, 0.0139 mmol) and 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (L^6) (15 mg, 0.0275 mmol) in chloroform (2 mL). The reaction mixture was refluxed for 2 h to give a brownish red solution. It was concentrated and triturated with methanol to yield a red solid (21 mg, 64%). Found: C, 60.44; H, 4.24; N 4.46, calcd. (%) for $C_{62}H_{52}F_6IrN_4P{\cdot}0.5CHCl_3$: C, 60.05; H, 4.23; N 4.48. IR (neat): 2961, 1607, 1476, 1423, 1362, 1268, 832, 775, 756 and 655. ESI-MS (MeCN, m/z): found: 1045.3778, calcd. 1045.3821 for $C_{62}H_{52}N_4Ir$, $[M\text{-}PF_6]^+$. ^1H NMR (400 MHz, CD_3CN): δ 8.01 (d, 1H, $^3J(HH)$ 8.5 Hz), 7.93 (d, 1H, $^3J(HH)$ 5.5 Hz,), 7.89 (d, 1H, $^3J(HH)$ 8.0 Hz), 7.87-7.79 (m, 5H), 7.75-7.57 (m, 5H), 7.54-7.48 (m, 2H), 7.42 (d, 1H, $^3J(HH)$ 8.5 Hz), 7.34-7.27 (m, 1H), 7.24-7.18 (m, 4H), 7.12 (t, 1H, $^3J(HH)$ 6.0 Hz), 6.98 (d, 2H, $^3J(HH)$ 7.0 Hz), 6.95-6.87 (m, 2H, $^3J(HH)$ 7.0, 8.0 Hz), 6.86-6.79 (m, 2H, $^3J(HH)$ 7.5 Hz), 6.67 (t, 1H, $^3J(HH)$ 7.5 Hz), 6.49 (t, 1H, $^3J(HH)$ 7.5 Hz), 6.21 (d, br, 1H, $^3J(HH)$ 7.5 Hz), 6.11 (d, 1H, $^3J(HH)$ 7.5 Hz), 5.99 (d, 1H, $^3J(HH)$ 7.5 Hz), 5.78 (d, 1H, $^3J(HH)$ 7.5 Hz), 1.50 (s, 9H, CMe_3) and 1.38 (s, 9H, CMe_3). ^{13}C NMR (150 MHz, CD_3CN): δ149.9, 149.6, 149.3, 138.2, 137.5, 137.57, 130.9, 130.4, 129.6, 129.4, 129.1, 128.8, 128.4, 128.2, 127.8, 127.6, 127.4, 127.3, 126.5, 126.1, 125.4, 124.6, 124.4, 124.1, 122.9, 122.7, 122.5, 120.6, 119.7, 119.3, 33.7, 33.8, 31.0 and 30.9.

Results and Discussion

Treatment of DMAP (L^1) with 0.5 equivalent of the dimer $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ afforded the neutral yellow complex $[Ir(ppy)_2(L^1)Cl]$ (**1**) in 81% yield (Scheme 2). The complex (**1**) and other new complexes were characterized adequately by a combination of elemental analysis, IR, Mass, and NMR spectroscopy. The elemental analysis of (**1**) agrees with the proposed structure with the composition $C_{29}H_{26}ClN_4Ir$. Accurate mass spectral data of (**1**) showed a signal at 623.1770 for $C_{29}H_{26}N_4Ir$, $[M\text{-}Cl]^+$. The ^1H NMR spectrum of the unsymmetrical complex (**1**) is complicated, and a proton attached to carbon adjacent to nitrogen of the DMAP ligand appeared at 9.95 ppm, suggesting strong hydrogen bonding between H^{DMAP} and the chloride ligand (Kinzhalov, 2018). In the ^1H NMR spectrum of (**1**), a singlet was

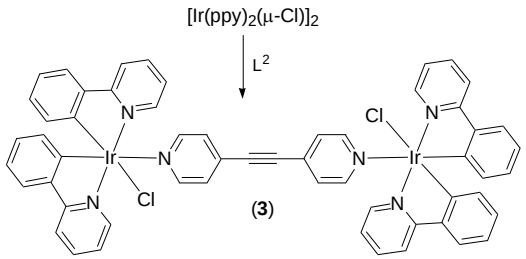
observed at 2.96 ppm for the six protons of the NMe_2 group, whilst its carbon-13 resonance was detected at 39.1 ppm.

When four equivalents of L^1 were reacted with an equivalent of $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ in the presence of NH_4PF_6 produced the yellow salt $[Ir(ppy)_2(L^1)_2]PF_6$ (**2**) in 96% yield (Scheme 2). The presence of two DMAP molecules was confirmed by the accurate mass spectral data at 745.2599 for $C_{36}H_{36}N_6Ir$, $[M\text{-}PF_6]^+$. The proton and carbon-13 chemical shifts of this symmetrical complex (**2**) were identified by ^{13}C-^1H-COSY experiments. The ^{13}C NMR data observed for C^3, C^4, C^5 and C^6 of the 2-pyridyl group are in good agreement with the values reported in the literature (Hii, et al, 1995; Perera, et al, 2010; Perera, 2022). The carbon-13 resonances at 150.4, 107.9 and 38.4 ppm were assigned for C^7, C^8 and C^{Me} of the two DMAP molecules.



Scheme 2. Synthesis of complexes (**1**) and (**2**) with atom labeling

Treatment of one equivalent of di(4-pyridyl) acetylene (DPA, L^2) with one equivalent of $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ gave dark brown crystals of (**3**) with the bridging ligand L^2 (Scheme 3).



Scheme 3. Synthesis of the complex (**3**)

Accurate mass spectral data of (**3**) showed a signal at 1217.2235 for $C_{56}H_{40}N_6ClIr$, $[M\text{-}Cl]^+$. The IR spectrum of (**3**) showed an IR band at 2230 cm^{-1} for the acetylene moiety. The complex (**3**) was not very soluble in common deuterated solvents; δ_H values were not resolved and a doublet at 9.90 with $^3J(HH)$ = 6.0 Hz was assigned to a proton attached to carbon adjacent to nitrogen of the DPA ligand.

Four iridium(III) complexes (**4**)-(**7**) of the type $[Ir(ppy)_2(N\text{^}N)]PF_6$ (Figure 4) were prepared by reacting $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ with an appropriate bidentate ligand (N^N) in the molar ratio of 1:2; the products were isolated in good yields (**4**, 87%; **5**, 92%; **6**, 96%; **7**, 64%) as colored solids.

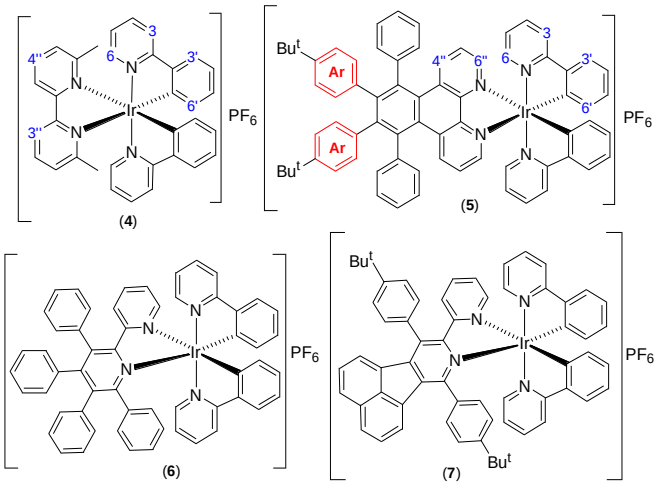


Figure 4. Structures of (**4**)-(**7**) and atom labeling for symmetrical complexes

The NMR data, elemental and mass spectral analyses of the complexes (**4**)-(**7**) are consistent with the proposed structures. Mass spectral data for complexes (**4**)-(**7**) indicated the presence of $[M\text{-}PF_6]^+$ ion. The complex (**4**) was characterized by X-ray crystallography (Figure 5).

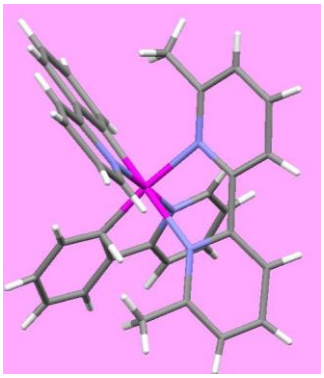


Figure 5. Molecular structure of the complex (**4**)

The proton and carbon-13 chemical shifts of the two symmetrical complexes (**4**) and (**5**) were assigned using H-H and C-H correlation spectroscopy. The ^{1}H NMR spectrum of (**4**) showed resonances at 8.28 (d, ^{3}J(HH) 8.0 Hz), 8.00 (t, ^{3}J(HH) 7.8 Hz) and 7.34 (dd, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 0.75 Hz) for H$^{3''}$, H$^{4''}$ and H$^{5''}$, respectively for the bipyridyl protons (Figure 6).

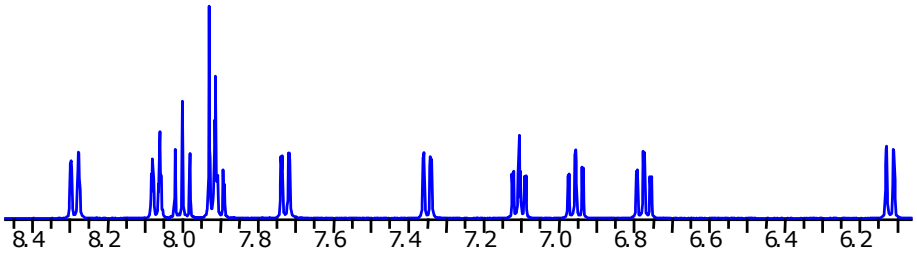


Figure 6. The aromatic region of the ^{1}H NMR spectrum of (**4**), δ_H in ppm

In the ^{1}H NMR spectrum of (**5**), the peaks for the aryl groups showed a second order NMR pattern (Figure 7) with multiplets centered at 6.88 (4H m), 6.57 (4H), and a singlet at 1.15 (18H) ppm for the *tert*-butyl protons.

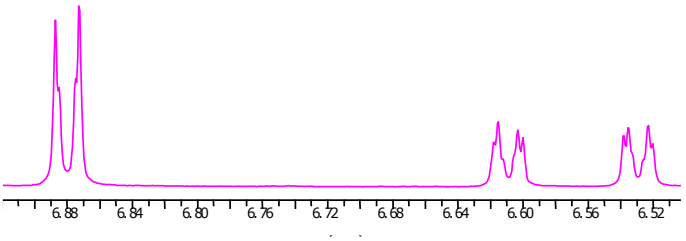


Figure 7. Second order NMR pattern of the aryl groups of (**5**), δ_H in ppm

In the ^{1}H NMR spectrum of (**7**), *tert*-butyl protons appeared as singlets at 1.38 (9H) and 1.50 (9H) ppm whilst the corresponding carbon-13 resonances appeared at 30.9 and 31.0 ppm.

Conclusions

The chemistry of monodentate pyridine ligand (L^1), bridging pyridine ligand (L^2), and bulky bidentate bipyridine ligands (L^3 – L^6) with the dimer $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ was explored. Synthetic routes to complexes of the type $[Ir(ppy)_2(L)Cl]$, $[Ir(ppy)_2(L)_2]PF_6$, $[Ir(ppy)_2(N\text{^}N)]PF_6$ and $[(ppy)_2ClIr]_2(\mu\text{-}L)$ have been devised.

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