

Iridium(III) and rhodium(III) cyclometalated complexes containing sulfur and selenium donor ligands

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Abstract

Treatment of $[M(\text{Buppy})_2\text{Cl}]_2$ ($M = \text{Ir}$ (**1**), Rh (**2**); $\text{BuppyH} = 2-(4'\text{-tert-butylphenyl})\text{pyridine}$) with $\text{Na}(\text{Et}_2\text{NCS}_2)$, $\text{K}[\text{S}_2\text{P}(\text{OMe})_2]$, and $\text{K}[\text{N}(\text{Ph}_2\text{PS})_2]$ afforded monomeric $[\text{Ir}(\text{Buppy})_2(\text{S}^{\wedge}\text{S})]$ ($\text{S}^{\wedge}\text{S} = \text{Et}_2\text{NCS}_2$ (**3**), $\text{S}_2\text{P}(\text{OMe})_2$ (**4**), $\text{N}(\text{PPh}_2\text{S})_2$ (**5**)) and $[\text{Rh}(\text{Buppy})_2(\text{S}^{\wedge}\text{S})]$ ($\text{S}^{\wedge}\text{S} = \text{Et}_2\text{NCS}_2$ (**6**), $\text{S}_2\text{P}(\text{OMe})_2$ (**7**), $\text{N}(\text{PPh}_2\text{S})_2$ (**8**)), respectively. Reaction of **1** with $\text{Na}[\text{N}(\text{PPh}_2\text{Se})_2]$ gave $[\text{Ir}(\text{Buppy})_2\{\text{N}(\text{PPh}_2\text{Se})_2\}]$ (**9**). The crystal structures of **3**, **4**, **7**, and **8** have been determined. Treatment of **1** or **2** with AgOTf ($\text{OTf} = \text{triflate}$) followed by reaction with KSCN gave dinuclear $[\{\text{M}(\text{Buppy})_2\}_2(\mu\text{-SCN})_2]$ ($M = \text{Ir}$ (**10**), Rh (**11**)), in which the SCN^- ligands bind to the two metal centers in a $\mu\text{-S,N}$ fashion. Interaction of **1** and **2** with $[\text{Et}_4\text{N}]_2[\text{WQ}_4]$ gave trinuclear heterometallic complexes $[\{\text{Ir}(\text{Buppy})_2\}_2(\mu\text{-WQ}_4)]$ ($Q = \text{S}$ (**12**), Se (**13**)) and $[\{\text{Rh}(\text{Buppy})_2\}_2(\mu\text{-WQ}_4)]$ ($Q = \text{S}$ (**14**), Se (**15**)), respectively. Hydrolysis of **12** led to formation of $[\{\text{Ir}(\text{Buppy})_2\}_2\{\text{W}(\text{O})(\mu\text{-S})_2(\mu_3\text{-S})\}]$ (**16**) that has been characterized by X-ray diffraction. © 2004 Elsevier B.V. All rights reserved.

Keywords: Iridium(III); Rhodium(III); Cyclometalated complex; Sulfur ligands

1. Introduction

Luminescent complexes containing d^6 transition metal centers have attracted much attention due to their potential applications to photocatalysis [1–3]. While extensive works have been done on $\text{Ru}(\text{II})$ and $\text{Os}(\text{II})$ complexes with polyimine ligands [1–3], the isoelectronic $\text{Ir}(\text{III})$ analogues have received relatively less attention [4]. Recently, there is an increasing interest in the synthesis and photophysical studies of $\text{Ir}(\text{III})$ complexes with cyclometalated ligands, notably 2-phenylpyridine (ppy) [5–12], which have found applications as phosphors in organic light emitting diodes (OLEDs) [13–16], sensors [17,18], and luminescent labels for biomolecules [19].

Mononuclear $\text{Ir}(\text{III})$ bis-cyclometalated complexes are generally synthesized from dinuclear $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$. Substitution of $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ with bidentate O,O or N,O ligands $L^{\wedge}L$ afforded $[\text{Ir}(\text{ppy})_2(L^{\wedge}L)]$, which have been employed as dopants for OLEDs [13] and sensors for singlet oxygen [18]. However, $\text{Ir}(\text{III})$ cyclometalated complexes with chalcogen donor ligands have not been well explored. Our interest in dithiolate ligands such as dithiocarbamate [20] is stimulated by the fact that these ligands are capable of stabilizing metal ions in unusual oxidation states. For example, $[\text{Ir}(\text{R}_2\text{NCS}_2)_3]$ can be oxidized reversibly to $[\text{Ir}(\text{R}_2\text{NCS}_2)_3]^+$ [21]. Also of interest are the tetrathio(seleno)tungstate(VII) anions $[\text{WQ}_4]^{2-}$ ($Q = \text{S}$ [22] or Se [23]) that binds to metal ions to give heterometallic clusters. $\text{W}(\text{Mo})/\text{M}/\text{S}(\text{Se})$ ($M = \text{Cu}$, Ag , Au and Pd) clusters are known to exhibit rich structural chemistry and non-linear optical properties [22,23]. In this paper, we report on the syntheses and crystal structures of cyclometalated $\text{Ir}(\text{III})$ and $\text{Rh}(\text{III})$ complexes

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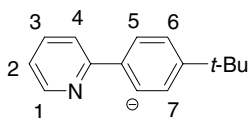
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containing bidentate sulfur ligands and tetrathio(sele-
no)tungstate(VI) $[WQ_4]^{2-}$ (Q = S, Se).

2. Experimental

2.1. General information

Solvents were purified by standard procedures and distilled prior to use. The ligand 2-(4'-*tert*-butylphenyl)pyridine (BuppyH) was prepared by Pd-catalyzed cross-coupling of 4-*tert*-butylphenylboronic acid and 2-bromopyridine according to a literature method [24]. The atom labeling scheme for Buppy⁻ is shown below



$[M(\text{Buppy})_2\text{Cl}]_2$ (M = Ir (**1**), Rh (**2**)) were synthesized by reactions of BuppyH with IrCl_3 and RhCl_3 , respectively, in alcohols as described elsewhere [25]. $\text{K}[\text{N}(\text{Ph}_2\text{PQ})_2]$ (Q = S [26] or Se [27]) and $[\text{Et}_4\text{N}]_2[\text{WQ}_4]$ (Q = S [28] or Se [29]) were synthesized according to literature methods. Other reagents were obtained from commercial sources and used as received.

NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P , respectively. Chemical shifts (δ , ppm) were referenced to SiMe_4 (^1H) and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

2.2. $[\text{Ir}(\text{Buppy})_2(\text{S}^\wedge\text{S})]$ ($\text{S}^\wedge\text{S} = \text{Et}_2\text{NCS}_2$ (**3**), $\text{S}_2\text{P}(\text{OMe})_2$ (**4**), $\text{N}(\text{PPh}_2\text{S})_2$ (**5**))

To a solution of **1** (ca. 0.04 mmol) in methanol (20 ml) was added the $\text{M}[\text{S}^\wedge\text{S}]$ (M = Na for Et_2NCS_2 , K for $\text{S}_2\text{P}(\text{OMe})_2$ and $\text{N}(\text{SPh}_2)_2$; 0.04 mmol) and the mixture was stirred at room temperature for 3 h. The solvent was pumped off, and the residue was washed with methanol and Et_2O and then extracted with CH_2Cl_2 . Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$ at room temperature in air afforded the yellow crystalline product.

3: Yield: 25 mg (53%). Anal. Calc. for $\text{C}_{35}\text{H}_{42}\text{N}_3\text{S}_2\text{Ir} \cdot \text{H}_2\text{O}$: C, 54.54; H, 5.58; N, 5.45. Found: C, 54.45; H, 5.34; N, 5.19%. ^1H NMR (CDCl_3): δ 1.03 (s, 18H, *t*-Bu), 1.21–1.27 (m, 6H, CH_2CH_3), 3.46–3.50 (m, 2H, CH_2CH_3), 3.85–3.90 (m, 2H, CH_2CH_3), 6.36 (d, 2H, $J = 2$ Hz, H^1), 6.81 (dd, 2H, $J_1 = 2$ Hz, $J_2 = 8$ Hz, H^2),

7.19 (t, 2H, $J = 7$ Hz, H^6), 7.46 (d, 2H, $J = 8$ Hz, H^3), 7.68–7.81 (m, 4H, H^4 and H^5), 9.63 (d, 2H, $J = 5.6$ Hz, H^7). MS (FAB): m/z 761 (M^+).

4: Yield: 30 mg (63%). Anal. Calc. for $\text{C}_{32}\text{H}_{38}\text{N}_2\text{S}_2\text{O}_2\text{PIr}$: C, 49.92; H, 4.97; N, 3.64. Found: C, 49.91; H, 5.03; N, 3.59%. ^1H NMR (CDCl_3): δ 1.03 (s, 18H, *t*-Bu), 3.63 (s, 3H, CH_3O), 3.68 (s, 3H, CH_3O), 6.29 (d, 2H, $J = 2$ Hz, H^1), 6.84 (dd, 2H, $J_1 = 2$ Hz, $J_2 = 6.6$ Hz, H^2), 7.21 (t, 2H, $J = 7.3$ Hz, H^6), 7.45 (d, 2H, $J = 8.2$ Hz, H^3), 7.71–7.82 (m, 4H, H^4 and H^5), 9.70 (d, 2H, $J = 6.2$ Hz, H^7). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 104.75 (s). MS (FAB): m/z 770 (M^+).

5: Yield (65%). Anal. Calc. for $\text{C}_{54}\text{H}_{52}\text{N}_3\text{P}_2\text{S}_2\text{Ir} \cdot \text{H}_2\text{O}$: C, 60.06; H, 5.00; N, 3.89. Found: C, 60.55; H, 4.84; N, 3.70%. ^1H NMR (CDCl_3): δ 0.95 (s, 18H, *t*-Bu), 5.94 (d, $J = 2$ Hz, 2H, H^1), 6.28 (t, 2H, $J = 14.6$ Hz, H^6), 6.84 (dd, 2H, $J_1 = 2$ Hz, $J_2 = 8$ Hz, H^2), 6.97–7.02 (m, 4H, phenyl protons), 7.24 (t, 2H, $J = 1.6$ Hz, H^3), 7.34–7.72 (m, 10H, phenyl protons), 7.63–7.72 (m, 6H, phenyl protons), 8.00–8.07 (m, 4H, H^4 and H^5), 9.12 (d, 2H, $J = 5.8$ Hz, H^7). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 28.45 (s). MS (FAB): m/z 1061 (M^+).

2.3. $[\text{Rh}(\text{Buppy})_2(\text{S}^\wedge\text{S})]$ ($\text{S}^\wedge\text{S} = \text{Et}_2\text{NCS}_2$ (**6**), $\text{S}_2\text{P}(\text{OMe})_2$ (**7**), $\text{N}(\text{PPh}_2\text{S})_2$ (**8**))

These complexes were prepared similarly as for the Ir analogues using **2** in place of **1**, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$.

6: Yield: 23 mg (38%). Anal. Calc. for $\text{C}_{35}\text{H}_{42}\text{N}_3\text{S}_2\text{Rh}$: C, 62.58; H, 6.30; N, 6.26. Found: C, 62.50; H, 6.32; N, 6.14%. ^1H NMR (CDCl_3): δ 1.05 (s, 18H, *t*-Bu), 1.23–1.28 (m, 6H, CH_2CH_3), 3.62–3.66 (m, 2H, CH_2CH_3), 4.02–4.09 (m, 2H, CH_2CH_3), 6.33 (s, 2H, H^1), 6.86 (dd, 2H, $J_1 = 2$ Hz, $J_2 = 8$ Hz, H^2), 7.19–7.24 (m, 2H, H^6), 7.49 (d, 2H, $J = 8$ Hz, H^3), 7.79 (d, 4H, $J = 6$ Hz, H^4 and H^5), 9.56 (d, 2H, $J = 7$ Hz, H^7). MS (FAB): m/z 671 (M^+).

7: Yield: 30 mg (49%). Anal. Calc. for $\text{C}_{32}\text{H}_{38}\text{N}_2\text{S}_2\text{O}_2\text{PRh} \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 55.73; H, 5.66; N, 4.06. Found: C, 55.97; H, 5.39; N, 4.10%. ^1H NMR (CDCl_3): δ 1.03 (s, 18H, *t*-Bu), 3.63 (s, 3H, CH_3O), 3.68 (s, 3H, CH_3O), 6.26 (s, 2H, H^1), 6.91 (d, 2H, $J = 7$ Hz, H^2), 7.24 (t, 2H, $J = 6$ Hz, H^6), 7.50 (d, 2H, $J = 8$ Hz, H^3), 7.79–7.84 (m, 4H, H^4 and H^5), 9.65 (d, 2H, $J = 6$ Hz, H^7). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 103.88. MS (FAB): m/z 680 (M^+).

8: Yield: 71 mg (75%). Anal. Calc. for $\text{C}_{54}\text{H}_{52}\text{N}_3\text{P}_2\text{S}_2\text{Rh}$: C, 66.73; H, 5.39; N, 4.32. Found: C, 66.58; H, 5.37; N, 4.10%. ^1H NMR (CDCl_3): δ 0.97 (s, 18H, *t*-Bu), 5.93 (s, 2H, H^1), 6.33 (t, 2H, $J = 7.0$ Hz, H^6), 6.88 (d, 2H, $J = 10$ Hz, H^2), 6.97 (m, 4H, phenyl protons), 7.33–7.51 (m, 10H, phenyl protons), 7.64–7.71 (m, 6H, phenyl protons), 8.04–8.12 (m, 4H, H^4 and H^5), 8.78 (d, 2H, $J = 5.8$ Hz, H^7). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 34.80. MS (FAB): m/z 1065 (M^+).

2.4. $[Ir(\text{Buppy})_2\{N(\text{Ph}_2\text{PSe})_2\}]$ (**9**)

To a solution of **1** (50 mg, 0.039 mmol) in MeOH (20 ml) were added 2 equiv. of $K[N(\text{Ph}_2\text{PSe})_2]$ (0.077 mmol) and the mixture was stirred at room temperature overnight. The solvent was pumped off and the residue was washed with Et_2O . Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ gave the yellow crystalline product. Yield: 31 mg (69%). Anal. Calc. for $\text{C}_{54}\text{H}_{52}\text{N}_3\text{P}_2\text{Se}_2\text{Ir}$: C, 55.29; H, 4.64; N, 3.59. Found: C, 55.79; H, 4.75; N, 3.43%. ^1H NMR (CDCl_3): δ 0.95 (s, 18H, *t*-Bu), 5.96 (s, 2H, H^1), 6.25 (t, 2H, $J = 6.7$ Hz, H^6), 6.83 (d, 2H, $J = 8$ Hz, H^2), 7.01–7.06 (m, 4H, phenyl protons), 7.35–7.43 (m, 12H, H^3 and phenyl protons), 7.64–8.01 (m, 6H, phenyl protons), 8.01–8.08 (m, 4H, H^4 and H^5), 9.20 (d, 2H, $J = 5.4$ Hz, H^7). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 16.72 (s). MS (FAB): m/z 1155 (M^+).

2.5. $[\{M(\text{Buppy})_2\}_2(\mu\text{-SCN})_2]$ ($M = \text{Ir}$ (**10**), Rh (**11**))

To a solution of **1** (40 mg, 0.031 mmol) in MeOH (20 ml) was added $\text{Ag}(\text{OTf})$ ($\text{OTf} = \text{triflate}$, 0.062 mmol) and the mixture was stirred at room temperature for 1 h and filtered. To the red filtrate was added KSCN (10 mg, 0.062 mmol) and the mixture was stirred for 3 h and evaporated to dryness by a rotavapor. The residue was washed with hexane and Et_2O , and then extracted with CH_2Cl_2 . Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ gave yellow crystals. Yield: 15 mg (34%). Complex **11** was prepared by a similar procedure, employing **2** (34 mg) instead of **1**. Yield: 19 mg (41%).

10: Anal. Calc. for $\text{C}_{62}\text{H}_{64}\text{N}_6\text{S}_2\text{Ir}_2 \cdot \frac{1}{3}\text{hexane}$: C, 56.09; H, 5.05; N, 6.13. Found: C, 56.15; H, 5.01; N, 6.07%. ^1H NMR (CDCl_3): δ 1.01 (s, 18H, *t*-Bu), 1.05 (s, 18H, *t*-Bu), 6.12 (d, 4H, $J = 12.6$ Hz, H^1), 6.86 (dd, 2H, $J_1 = 1.8$ Hz, $J_2 = 7.8$ Hz, H^2), 6.78 (dd, 2H, $J_1 = 1.8$ Hz, $J_2 = 7.8$ Hz, $\text{H}^{2'}$), 7.04 (t, 4H, $J = 7.2$ Hz, H^6), 7.32–7.42 (m, 4H, H^3), 7.71–7.82 (m, 8H, H^4 and H^5), 9.14 (d, 2H, $J = 5.4$ Hz, H^7), 9.88 (d, 2H, $J = 5.4$ Hz, $\text{H}^{7'}$). IR (KBr, cm^{-1}): 2132 (s) [$\nu(\text{C}\equiv\text{N})$]. MS (FAB): m/z 1341 (M^+).

11: Anal. Calc. for $\text{C}_{62}\text{H}_{64}\text{N}_6\text{S}_2\text{Rh}_2$: C, 64.02; H, 5.54; N, 7.22. Found: C, 63.87; H, 5.15; N, 7.12%. ^1H NMR (CDCl_3): δ 1.03 (s, 36H, *t*-Bu), 5.30 (s, 4H, H^1), 6.26 (d, 4H, $J = 2$ Hz, H^2), 6.90 (t, 4H, $J = 7.8$ Hz, H^6), 7.48 (d, 4H, $J = 2$ Hz, H^3), 7.79–7.87 (m, 8H, H^4 and H^5), 9.64 (d, 4H, $J = 5.4$ Hz, H^7). IR (KBr, cm^{-1}): 2129 (s) [$\nu(\text{C}\equiv\text{N})$]. MS (FAB): m/z 1163 (M^+).

2.6. $[\{Ir(\text{Buppy})_2\}_2(\text{WQ}_4)]$ ($Q = \text{S}$ (**12**), Se (**13**))

To a solution of **1** (0.036 mmol) in CH_2Cl_2 (20 ml) was added 1 equiv. of $[\text{Et}_4\text{N}]_2[\text{WQ}_4]$ (0.036 mmol) and the mixture was stirred at room temperature overnight. The solvent was pumped off and the residue was washed with hexane and Et_2O and then extracted with CH_2Cl_2 .

Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$ afforded orange (**12**, yield: 37%) or red crystals (**13**, yield: 43%).

12: Despite two attempts, we were not able to obtain satisfactory elemental analyses. The compound has been characterized by NMR spectroscopy and mass spectrometry. ^1H NMR (CDCl_3): δ 1.05 (s, 36H, *t*-Bu), 6.39 (d, 4H, $J = 1.8$ Hz, H^1), 6.99 (t, 8H, $J = 15$ Hz, H^2), 7.55–7.63 (m, 8H, H^3 and H^5), 7.73 (d, 4H, $J = 7.8$ Hz, H^4), 9.01 (d, 4H, $J = 6$ Hz, H^7). MS (FAB): m/z 1539 ($\text{M}^+ + 1$).

13: Anal. Calc. for $\text{C}_{60}\text{H}_{64}\text{N}_4\text{Se}_4\text{WIr}_2$: C, 41.69; H, 3.70; N, 3.24. Found: C, 41.56; H, 3.74; N, 3.09%. ^1H NMR (CDCl_3): δ 1.04 (s, 36H, *t*-Bu), 6.37 (d, 4H, $J = 1.8$ Hz, H^1), 6.91–6.97 (m, 8H, H^2 and H^6), 7.53–7.61 (m, 8H, H^3 and H^5), 7.72 (d, 4H, $J = 8.2$ Hz, H^4), 9.18 (d, 4H, $J = 6$ Hz, H^7). MS (FAB): m/z 1727 (M^+).

2.7. $[\{Rh(\text{Buppy})_2\}_2(\text{WQ}_4)]$ ($Q = \text{S}$ (**14**), Se (**15**))

These were prepared similarly as for **12** and **13**, respectively, using **2** instead of **1**. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ gave yellow (**14**, yield: 40%) or red (**15**, yield: 45%) crystals.

14: Anal. Calc. for $\text{C}_{60}\text{H}_{64}\text{N}_4\text{S}_4\text{WRh}_2 \cdot \text{H}_2\text{O}$: C, 52.28; H, 4.79; N, 4.07. Found: C, 52.23; H, 4.64; N, 4.01%. ^1H NMR (CDCl_3): δ 1.03 (s, 36H, *t*-Bu), 6.30 (s, 4H, H^1), 6.85–7.05 (m, 8H, H^2 and H^6), 7.55 (d, 4H, $J = 4$ Hz, H^3), 7.61–7.72 (m, 8H, H^4 and H^5), 8.92 (d, 4H, $J = 5.6$ Hz, H^7). MS (FAB): m/z 1359 (M^+).

15: Anal. Calc. for $\text{C}_{60}\text{H}_{64}\text{N}_4\text{Se}_4\text{WRh}_2$: C, 46.04; H, 4.21; N, 3.58. Found: C, 46.19; H, 4.15; N, 3.53%. ^1H NMR (CDCl_3): δ 1.04 (s, 36H, *t*-Bu), 6.31 (s, 4H, H^1), 6.85–7.00 (m, 8H, H^2 and H^6), 7.53 (d, 4H, $J = 8.2$ Hz, H^3), 7.60–7.72 (m, 8H, H^4 and H^5), 9.04 (d, 4H, $J = 5.8$ Hz, H^7). MS (FAB): m/z 1546 (M^+).

2.8. $[\{Ir(\text{Buppy})_2\}_2\{WO(\mu\text{-S})_2(\mu_3\text{-S})\}]$ (**16**)

Complex **12** was dissolved in CH_2Cl_2 and was left to stand in air at -10 °C for ca. 1 month. The yellow crystals formed were collected and washed with hexanes. Yield: 10%. Anal. Calc. for $\text{C}_{60}\text{H}_{64}\text{N}_4\text{OS}_3\text{-WIr}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 45.60; H, 4.14; N, 3.49. Found: C, 45.12; H, 4.11; N, 3.44%. ^1H NMR (CDCl_3): δ 1.03 (s, 36H, *t*-Bu), 6.33 (s, 4H, H^1), 6.81–7.04 (m, 8H, H^2 and H^6), 7.53 (m, 4H, H^3), 7.69 (d, 8H, H^4), 9.07 (d, 4H, H^7). IR (KBr, cm^{-1}): 881 [$\nu(\text{W}=\text{O})$]. MS (FAB): m/z 1522 ($\text{M}^+ + 1$).

2.9. X-ray crystallography

Crystallographic data and experimental details for complexes **3**, **4**, $7 \cdot 4\text{CH}_2\text{Cl}_2$, and **8** are summarized in Table 1 and those for **10**· C_6H_{14} , **11**· $\text{C}_6\text{H}_{14} \cdot 2\text{H}_2\text{O}$, **15**· $2\text{C}_6\text{H}_{14}$, and **16**· $4\text{CH}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$ in Table 2. Intensity data of all complexes were collected on a Bruker

Table 1

Crystallographic data and experimental details for [Ir(Buppy)₂(Et₂NCS₂)] (**3**), [Ir(Buppy)₂{S₂P(OMe)₂}] (**4**), [Rh(Buppy)₂{S₂P(OMe)₂}]·4CH₂Cl₂ (**7**·4CH₂Cl₂), and [Rh(Buppy)₂{N(SPh)₂}] (**8**)

	3	4	7 ·4CH ₂ Cl ₂	8
Empirical formula	C ₃₂ H ₃₈ IrN ₂ O ₂ PS ₂	C ₃₅ H ₄₂ Ir N ₃ S ₂	C ₃₃ H ₄₀ Cl ₂ N ₂ O ₂ RhS ₂	C ₅₄ H ₅₂ N ₃ P ₂ RhS ₂
Formula weight	769.98	761.08	765.57	971.96
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.101(1)	11.269(1)	9.6198(4)	11.2789(6)
<i>b</i> (Å)	11.477(1)	20.186(2)	12.1914(5)	17.2900(9)
<i>c</i> (Å)	16.296(2)	15.984(1)	16.3629(7)	24.476(1)
α (°)	107.96(1)		91.390(1)	
β (°)	94.45(1)	107.42(1)	104.004(1)	101.088(1)
γ (°)	113.11(1)		111.713(1)	
<i>V</i> (Å ³)	1609.8(4)	3469.2(5)	1716.0(1)	4681.1(4)
<i>Z</i>	2	4	2	4
ρ_{calc} (g cm ⁻³)	1.588	1.457	1.482	1.387
Temp (K)	298	298	100	100
<i>F</i> (000)	768	1528	788	2016
μ (Mo K α) (mm ⁻¹)	4.369	4.006	0.854	0.562
Reflection collected	9865	20,672	10,232	28,191
Independent reflection	6915	7949	7548	10,991
<i>R</i> _{int}	0.052	0.020	0.0117	0.0340
Goodness-of-fit	2.17	1.03	1.040	1.024
<i>R</i> 1, ^a <i>wR</i> 2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.063, 0.072 ^c	0.024, 0.030 ^c	0.0266, 0.0689	0.0354, 0.0779
<i>R</i> 1, ^a <i>wR</i> 2 ^b (all data)			0.0283, 0.0700	0.0482, 0.0829

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)|^2]}{[\sum w|F_o|^2]^{1/2}}$$

$$^c R_w = \frac{[\sum w(|F_o| - |F_c|)^2]}{[\sum w|F_o|^2]^{1/2}}$$

Table 2

Crystallographic data and experimental details for [Ir(Buppy)₂]₂(μ -SCN)₂·C₆H₁₄ (**10**·C₆H₁₄), [Rh(Buppy)₂]₂(μ -SCN)₂·C₆H₁₄·2H₂O (**11**·C₆H₁₄·2H₂O), [Rh(Buppy)₂]₂(μ -WSe₄)·2C₆H₁₄ (**15**·2C₆H₁₄), and [Ir(Buppy)₂]₂{WO(μ -S)₂(μ_3 -S)}·4CH₂Cl₂·0.5H₂O (**16**·4CH₂Cl₂·0.5H₂O)

	10 ·C ₆ H ₁₄	11 ·C ₆ H ₁₄ ·2H ₂ O	15 ·2C ₆ H ₁₄	16 ·4CH ₂ Cl ₂ ·0.5H ₂ O
Empirical formula	C ₇₄ H ₉₂ Ir ₂ N ₆ S ₂	C ₇₄ H ₉₆ N ₆ O ₂ Rh ₂ S ₂	C ₇₂ H ₉₂ N ₄ Rh ₂ Se ₄ W	C ₆₄ H ₇₃ Cl ₈ Ir ₂ N ₄ O _{1.5} S ₃ W
Formula weight	1514.06	1371.51	1719.01	1870.29
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.2267(6)	13.223(5)	12.002(2)	15.42(1)
<i>b</i> (Å)	22.7050(11)	22.775(8)	17.420(2)	15.67(1)
<i>c</i> (Å)	11.1233(5)	11.125(4)	18.182(3)	15.70(1)
α (°)			72.298(3)	62.49(1)
β (°)	93.875(1)	94.848(7)	83.184(3)	84.29(1)
γ (°)			78.694(3)	83.43(1)
<i>U</i> (Å ³)	3332.8(3)	3341.0(2)	3544.1(8)	3550(1)
<i>Z</i>	2	2	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.509	1.363	1.611	1.749
<i>T</i> (K)	98(2)	100(2)	100(2)	100(2)
<i>F</i> (000)	1528	1440	1704	1818
μ (mm ⁻¹)	4.098	0.607	4.175	5.786
Reflection collected	20,011	20,347	17,780	21,098
Independent reflection	7754	7883	12,250	15,503
<i>R</i> _{int}	0.0333	0.0707	0.0807	0.0770
Goodness-of-fit	1.042	0.992	0.904	0.882
<i>R</i> 1, ^a <i>wR</i> 2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0299, 0.0717	0.0629, 0.1501	0.0614, 0.1079	0.0573, 0.0884
<i>R</i> 1, ^a <i>wR</i> 2 ^b (all data)	0.0377, 0.0749	0.1105, 0.1730	0.1000, 0.1346	0.1032, 0.1503

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)|^2]}{[\sum w|F_o|^2]^{1/2}}$$

SMART APEX 1000 area-detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.70173$ Å). The structures were solved by direct methods and

refined by full-matrix least-squares analyses on *F*². Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their calculated positions. Calcula-

tions were performed using the TEXSAN [30] (for **3** and **4**) and SHELXTL [31] (for other complexes) crystallographic software packages.

3. Results and discussion

3.1. Cyclometalated complexes containing sulfur donor ligands

Dinuclear $[M(\text{Buppy})_2\text{Cl}]_2$ ($M = \text{Ir}$ **1**, Rh **2**) were synthesized by refluxing IrCl_3 and RhCl_3 with 2-(4'-*tert*-butylphenyl)pyridine (BuppyH) in alcohol, respectively [25]. As expected, treatment of $[M(\text{Buppy})_2\text{Cl}]_2$ with bidentate sulfur ligands resulted in cleavage of the chloro bridges and formation of mononuclear complexes. Scheme 1 summarizes the reactions of **1** and **2** with sulfur and selenium donor ligands. Treatment of **1** with $\text{NaS}_2\text{CNEt}_2$, $\text{K}[\text{S}_2\text{P}(\text{OEt})_2]$, and $\text{K}[\text{N}(\text{PPh}_2\text{S})_2]$ led to formation of $[\text{Ir}(\text{Buppy})_2(\text{S}^{\wedge}\text{S})]$ ($\text{S}^{\wedge}\text{S} = \text{Et}_2\text{NCS}_2$ (**3**), $\text{PS}_2(\text{OMe})_2$ (**4**), $\text{N}(\text{PPh}_2\text{S})_2$ (**5**)). The corresponding Rh (III) complexes $[\text{Rh}(\text{Buppy})_2(\text{S}^{\wedge}\text{S})]$ ($\text{S}^{\wedge}\text{S} = \text{Et}_2\text{NCS}_2$ (**6**), $\text{S}_2\text{P}(\text{OMe})_2$ (**7**), $\text{N}(\text{PPh}_2\text{S})_2$ (**8**)) were prepared similarly from **2** and $\text{Na}[\text{S}^{\wedge}\text{S}]$ or $\text{K}[\text{S}^{\wedge}\text{S}]$. The Ir diselenide complex $[\text{Ir}(\text{Buppy})_2\{\text{N}(\text{PPh}_2\text{Se})_2\}]$ (**9**) was prepared from **1** and $\text{K}[\text{N}(\text{PPh}_2\text{Se})_2]$. These complexes are soluble in most organic solvents except hexanes, and are stable in both the solid state and solution. They have been fully characterized by spectroscopic methods and elemental analyses. The ^{31}P chemical shifts for complexes **4** (δ 104.8) and **7** (δ 103.9) and **5** (δ 28.45) and **8** (δ 34.80) are typical for dithiophosphate [32] and imidodiphosphinosulfide [33] complexes, respectively. The ^{31}P resonance

for **9** was observed at δ 16.72 that is more upfield than that for the sulfide analogue **5**.

The solid-state structures of **3**, **4**, **7** and **8** have been unambiguously established by X-ray crystallography. The corresponding crystal structures are shown in Figs. 1–4. Selected metrical parameters for these complexes are compiled in Table 3 for comparison. In each of these complexes, the geometry around the metal is distorted octahedral with two mutually *trans* pyridyl groups and the sulfur atoms being opposite to the phenyl rings. The average Ir–C (2.012(2) Å for **3** and 2.024(2) Å for **4**) and Ir–N (2.052(1) Å for **3** and 2.054(2) Å for **4**) distances are normal by comparison with other Ir(III) bis-ppy complexes [9a,9b,9c]. The average Ir–S distances for **3** (2.478(2) Å) and **4** (2.532(2) Å) are longer than that in $[\text{Ir}(\text{Et}_2\text{NCS}_2)_3]$ (2.367(3) Å) [34] due to *trans* influence of the phenyl groups. The average Rh–C (1.995(2) Å for **7** and 2.003(1) Å for **8**) and Rh–N distances (2.046(2) and 2.054(1) Å, respectively) are normal [35]. The Rh–S

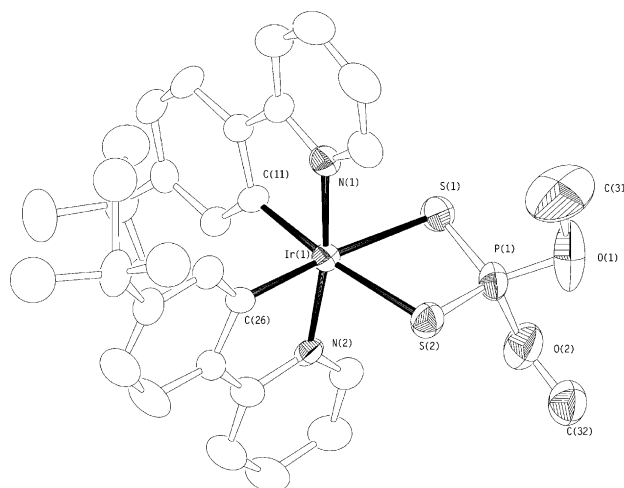


Fig. 1. Perspective view of $[\text{Ir}(\text{Buppy})_2(\text{Et}_2\text{NCS}_2)]$ (**3**).

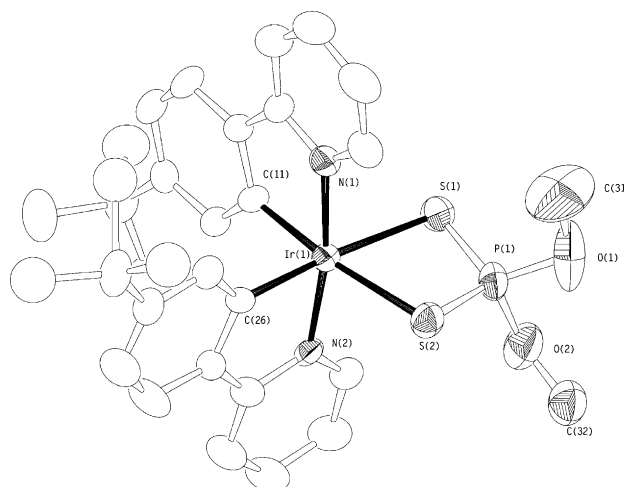
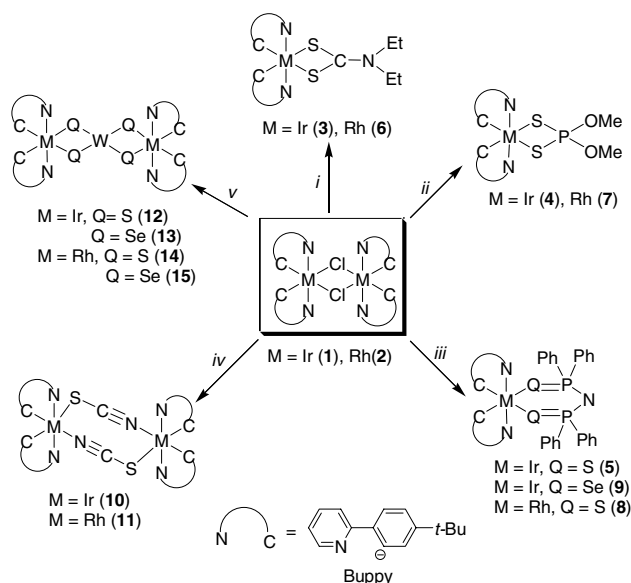
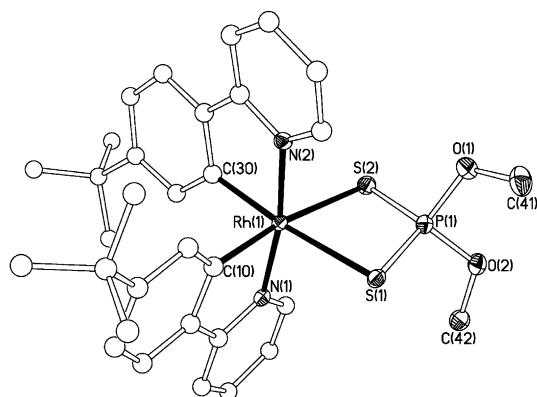
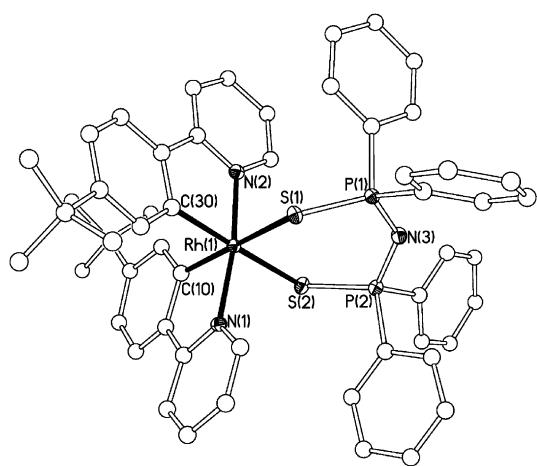


Fig. 2. Perspective view of $[\text{Ir}(\text{Buppy})_2\{\text{S}_2\text{P}(\text{OMe})_2\}]$ (**4**).



Scheme 1.

Fig. 3. Perspective view of $[\{\text{Rh}(\text{Buppy})_2\}_2\{\text{S}_2\text{P}(\text{OMe})_2\}]$ (**7**).Fig. 4. Perspective view of $[\{\text{Rh}(\text{Buppy})_2\}_2\{\text{N}(\text{SPh})_2\}]$ (**8**).

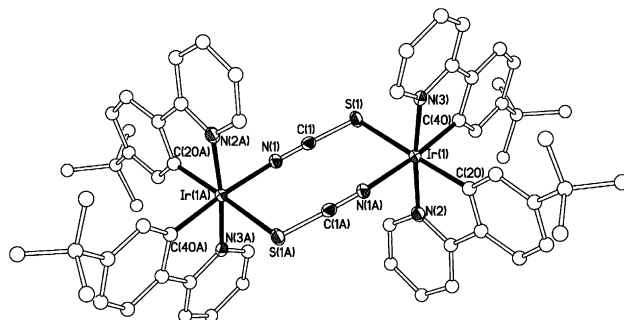
distances for **7** (2.548(2) Å) and **8** (2.487(2) Å) are longer than those in $[\text{Rh}(\text{Et}_2\text{NCS}_2)_3]$ (2.364(3) Å) [36] due to *trans* influence of the phenyl groups.

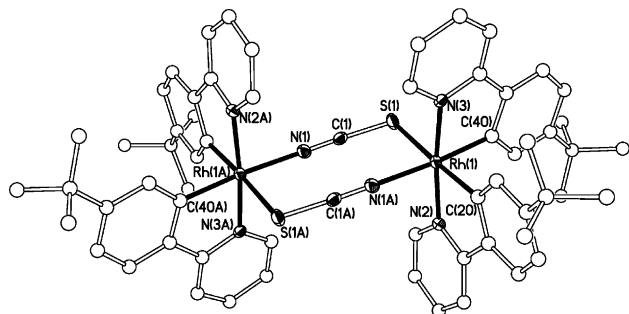
Table 3

Selected bond lengths (Å) and angles (°) for $[\text{Ir}(\text{Buppy})_2(\text{Et}_2\text{NCS}_2)]$ (**3**), $[\text{Ir}(\text{Buppy})_2\{\text{S}_2\text{P}(\text{OMe})_2\}]$ (**4**), $[\text{Rh}(\text{Buppy})_2\{\text{S}_2\text{P}(\text{OMe})_2\}] \cdot 4\text{CH}_2\text{Cl}_2$ (**7** · 4CH₂Cl₂), and $[\text{Rh}(\text{Buppy})_2\{\text{N}(\text{SPh})_2\}]$ (**8**)

	3 (M = Ir)	4 (M = Ir)	7 · 4CH ₂ Cl ₂ (M = Rh)	8 (M = Rh)
<i>Bond lengths</i>				
M–S	2.471(1)	2.528(3)	2.5284(4)	2.4761(5)
	2.484(1)	2.535(3)	2.5674(5)	2.4986(6)
M–N	2.050(3)	2.054(8)	2.044(2)	2.050(2)
	2.053(3)	2.054(8)	2.047(2)	2.058(2)
M–C	2.010(4)	2.018(9)	1.995(2)	2.002(2)
	2.013(4)	2.030(9)	1.996(2)	2.003(2)
<i>Bond angles</i>				
S(1)–M–S(2)	71.20(4)	79.45(9)	79.40(1)	100.81(2)
N(1)–M–N(2)	170.1(1)	170.8(3)	170.94(6)	171.79(7)
C–M–C'	91.1(1)	89.1(3)	89.49(7)	90.70(8)
C–M–N	80.2(1)	80.0(4)	81.05(7)	80.73(8)
	80.1(1)	80.8(3)	81.16(6)	80.93(8)
C–M–N'	92.1(1)	92.9(3)	92.26(6)	92.15(8)
	93.8(1)	93.2(3)	92.62(6)	94.86(8)

As previously reported, **1** reacted with Ag(OTf) to give the aquo compound $[\text{Ir}(\text{Buppy})_2(\text{H}_2\text{O})_2][\text{OTf}]$ and AgCl [37]. Interaction of $[\text{Ir}(\text{Buppy})_2(\text{H}_2\text{O})_2][\text{OTf}]$ with KSCN in MeOH gave dimeric $[\{\text{Ir}(\text{Buppy})_2\}_2(\mu\text{-SCN})_2]$ (**10**) that has been characterized by X-ray crystallography. The rhodium analogue $[\{\text{Rh}(\text{Buppy})_2\}_2(\mu\text{-SCN})_2]$ (**11**) was prepared similarly and structurally characterized. The preparation of $[\text{Ir}(\text{ppy})(\text{SCN})_2]^-$ from $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ and SCN^- has been reported recently [12]. Figs. 5 and 6 show the molecular structures of **10** and **11**, respectively; selected bond lengths and angles are listed in Table 4. In both structures, the asymmetric unit consists of half of the molecule and is related by an inversion center. The M–C and M–N(Buppy) distances in both complexes are normal. The M–S distance for the Rh compound **11** (2.529(2) Å) is slightly longer than that in the Ir compound **10** (2.496(1) Å). In both **10** and **11**, the bridging SCN^- ligands bind to the two metal centers in a $\mu\text{-S,N}$ fashion. The M–S–C≡N units are approximately linear (the C–N–M angle of 165.1(3) and 164.1(4)° for **10** and **11**, respectively) and the S–M–N#(CS) angles ($-x + 1, -y + 1, -z + 1$) are close to 90°.

Fig. 5. Perspective view of $[\{\text{Ir}(\text{Buppy})_2\}_2(\mu\text{-SCN})_2]$ (**10**).

Fig. 6. Perspective view of $[\{\text{Rh}(\text{Buppy})_2\}_2(\mu\text{-SCN})_2]$ (**11**).Table 4
Selected bond lengths (Å) and angles (°) for $[\{\text{M}(\text{Buppy})_2\}_2(\mu\text{-SCN})_2] \cdot (\text{M} = \text{Ir or Rh})$

	10 (M = Ir)	11 (M = Rh)
<i>Bond lengths</i>		
M(1)–S(1)	2.4957(8)	2.5289(15)
M(1)–N(1) ^a	2.105(3)	2.125(4)
M(1)–N(2)	2.052(3)	2.047(4)
M(1)–N(3)	2.033(3)	2.029(4)
M(1)–C(20)	2.018(3)	2.002(5)
M(1)–C(40)	2.004(3)	1.988(5)
<i>Bond angles</i>		
N(3)–M(1)–N(2)	172.6(1)	172.2(2)
N(2)–M(1)–S(1)	96.71(8)	96.9(1)
N(3)–M(1)–S(1)	90.19(8)	90.3(1)
C(20)–M(1)–S(1)	174.69(9)	174.5(1)
C(40)–M(1)–S(1)	85.91(9)	86.2(2)
C(20)–M(1)–N(2)	80.6(2)	80.8(2)
C(40)–M(1)–N(2)	97.5(1)	96.4(2)
C(20)–M(1)–N(3)	92.3(1)	91.8(2)
C(40)–M(1)–N(3)	80.3(1)	81.1(2)
C(40)–M(1)–C(20)	89.9(1)	89.1(2)

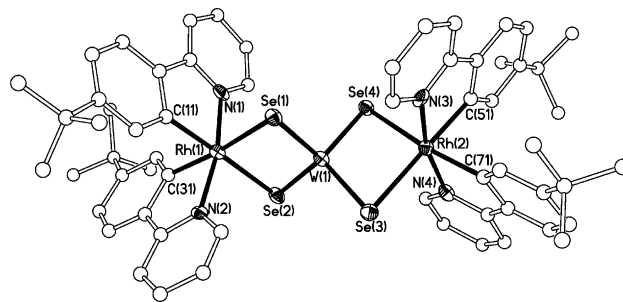
^a Symmetry operation: $-x + 1, -y + 1, -z + 1$.

Thus, the eight-membered $\text{M}_2(\text{SCN})_2$ core in these complexes can be roughly described as a rectangle.

3.2. Heterobimetallic complexes containing $[\text{WQ}_4]^{2-}$ ($\text{Q} = \text{S or Se}$)

Treatment of **1** or **2** with 0.5 equiv. of $[\text{Et}_4\text{N}]_2[\text{WS}_4]$ afforded the trinuclear heterobimetallic complexes $[\{\text{M}(\text{Buppy})_2\}_2(\mu\text{-WS}_4)]$ (M = Ir (**12**), Rh (**13**)). Similarly, reaction of **1** or **2** with $[\text{Et}_4\text{N}]_2[\text{WSe}_4]$ afforded $[\{\text{M}(\text{Buppy})_2\}_2(\mu\text{-WSe}_4)]$ (M = Ir (**14**), Rh (**15**)). The FAB mass spectra of complexes **12**–**15** display molecular ion peaks corresponding to M^+ . A preliminary study showed that **12** and **15** exhibit both non-linear absorption and non-linear refraction properties [38].

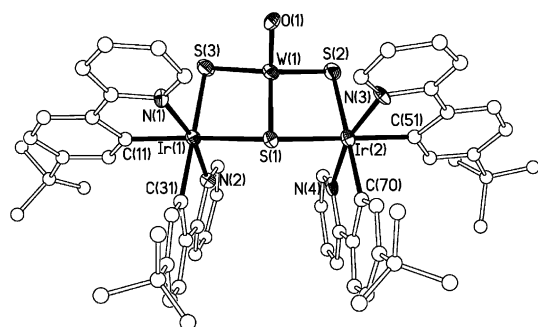
Complex **15** has been characterized by X-ray diffraction. Fig. 7 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 5. To our knowledge, this is the first structurally characterized

Fig. 7. Perspective view of $[\{\text{Rh}(\text{Buppy})_2\}_2(\mu\text{-WSe}_4)]$ (**15**).Table 5
Selected bond lengths (Å) and angles (°) for $[\{\text{Rh}(\text{Buppy})_2\}_2(\mu\text{-WSe}_4)]$ (**15**)

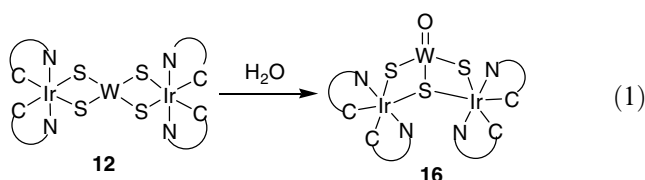
<i>Bond lengths</i>			
W(1)–Se(1)	2.335(1)	W(1)–Se(2)	2.322(1)
W(1)–Se(3)	2.328(1)	W(1)–Se(4)	2.331(1)
W(1)–Rh(1)	3.031(1)	W(1)–Rh(2)	3.049(1)
Rh(1)–C(11)	1.98(1)	Rh(1)–C(31)	1.99(1)
Rh(2)–C(51)	2.04(1)	Rh(2)–C(71)	2.03(1)
Rh(1)–N(1)	2.073(9)	Rh(1)–N(2)	2.061(9)
Rh(2)–N(3)	2.04(1)	Rh(2)–N(4)	2.06(1)
Rh(1)–Se(1)	2.545(2)	Rh(1)–Se(2)	2.558(2)
Rh(2)–Se(4)	2.563(1)	Rh(2)–Se(3)	2.583(2)
<i>Bond angles</i>			
Se(2)–W(1)–Se(3)	111.20(5)	Se(2)–W(1)–Se(4)	107.91(5)
Se(3)–W(1)–Se(4)	109.45(4)	Se(2)–W(1)–Se(1)	109.85(5)
Se(3)–W(1)–Se(1)	108.93(5)	Se(4)–W(1)–Se(1)	109.47(4)
N(2)–Rh(1)–N(1)	168.9(4)	N(3)–Rh(2)–N(4)	167.0(4)
Se(1)–Rh(1)–Se(2)	96.67(5)	Se(4)–Rh(2)–Se(3)	95.33(5)
C(11)–Rh(1)–C(31)	84.1(5)	C(71)–Rh(2)–C(51)	85.9(4)
W(1)–Se(1)–Rh(1)	76.64(5)	W(1)–Se(2)–Rh(1)	76.61(5)
W(1)–Se(3)–Rh(2)	76.55(4)	W(1)–Se(4)–Rh(2)	76.90(4)
Rh(1)–W(1)–Rh(2)	169.24(3)		

organorhodium(III) compound containing the $[\text{WSe}_4]^{2-}$ anion. A trinuclear Rh/W/S complex $[\{(\text{COD})\text{Rh}\}_2(\mu\text{-WS}_4)]$ (COD = 1,5-cyclooctadiene) has been synthesized by Rauchfuss and coworkers [39]. The solid-state structure of **15** contains two symmetry-related $\{(\text{Buppy})_2\text{Rh}(\mu\text{-Se})_2\}$ units with the W at the center of inversion. The geometry around Rh is octahedral and that around W is tetrahedral (average Se–W–Se bond angle = 109.47(5)°). The Rh–C and Rh–N distances are similar to those in **8**. The average Rh–Se bond distance of 2.562(2) Å in **15** is longer than that in $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\eta^2\text{-C,Se-C}_4\text{H}_4\text{Se})]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (2.456(3) Å) [40]. Similar to other trinuclear heterosele-nometallic complexes [41,42], the Rh(1)···W(1)···Rh(2) unit in **15** is approximately linear (169.24(3)°).

Attempts to grow X-ray quality crystals for **12** were unsuccessful. However, recrystallization of **12** from CH_2Cl_2 in air over a long period of time (>1 month) afforded yellow crystals that were identified as the

Fig. 8. Perspective view of $[\{\text{Ir}(\text{Buppy})_2\}_2(\mu_3\text{-WOS}_3)]$ (**16**).

$[\text{WOS}_3]^{2-}$ -bridged trinuclear complex $[\{\text{Ir}(\text{Buppy})_2\}_2\{\text{WO}(\mu\text{-S})_2(\mu_3\text{-S})\}]$ (**16**) (Eq. (1))



The IR spectrum of **16** shows a sharp peak at 881 cm^{-1} assignable to the $\text{W}=\text{O}$ stretch. It is believed that the $\text{W}=\text{O}$ group was formed by hydrolysis of a $\text{W}=\text{S}$ group in **12** during recrystallization [43]. The crystal structure of **16** is shown in Fig. 8; selected bond lengths and angles are listed in Table 6. The structure of **16** consists of two $[\text{Ir}(\text{Buppy})_2]^+$ fragments bridged by a $[\text{W}(\text{O})(\mu\text{-S})_2(\mu_3\text{-S})]^{2-}$ ligand. A similar binding mode has been found for related heterometallic $\text{Cu}(\text{Ag}, \text{Au})/\text{Mo}(\text{W})/\text{S}$ clusters containing the $[\text{W}(\text{S})(\mu\text{-S})(\mu_3\text{-S})]^{2-}$ anion [44]. The average $\text{W}\cdots\text{Ir}$ separation is $2.912(2)\text{ \AA}$. The average $\text{Ir}-\text{S}$ distance is $2.467(2)\text{ \AA}$. The geometry around W is tetrahedral with bond angles ranging from $106.6(3)^\circ$ to $112.83(12)^\circ$. The $\text{W}-(\mu_3\text{-S})$ distance ($2.291(3)$

\AA) is slightly longer than the $\text{W}-(\mu\text{-S})$ distance (average $2.242(3)\text{ \AA}$).

3.3. UV-Vis spectra

The UV-Vis spectral data for the $\text{Ir}(\text{III})$ and $\text{Rh}(\text{III})$ cyclometalated complexes in CH_2Cl_2 are summarized in Table 7. For the Ir complexes **3–5** and **10**, the absorptions in the higher energy region (ca. $245\text{--}374\text{ nm}$) are attributed to electronic transitions arising from the Buppy and bidentate sulfur ligands. Similar absorption bands were found for the corresponding free S^\wedgeS ligands and unmetalated Buppy. For comparison, the ligand-centered (LC) bands for $[\text{Ir}(\text{ppy})_2(\text{acac})]$ [**9a**] and $[\text{Ir}(\text{Dtb})_3]$ ($\text{Dtb} = \text{dithiobenzoate}$) [**20a**] were observed at $250\text{--}360$ and $288\text{--}340\text{ nm}$, respectively. Similarly, the absorptions at $245\text{--}290\text{ nm}$ for the $\text{Rh}(\text{III})$ analogues **6–8** and **11** are assigned as LC (Buppy and S^\wedgeS) bands. Previously, the absorptions at 410 and 460 nm for $[\text{Ir}(\text{tpy})_2(\text{acac})]$ ($\text{tpyH} = 2\text{-}(p\text{-tolyl})\text{pyridine}$) have been assigned as the singlet and triplet MLCT [$d\pi(\text{Ir}) \rightarrow \pi^*(\text{ppy})$] transitions, respectively. Thus, the lower energy bands ($\lambda_{\text{max}} > 400\text{ nm}$) for the Ir complexes **3–5** and **10** are attributed to the MLCT [$d\pi(\text{Ir}) \rightarrow \pi^*(\text{Buppy})$] transition that may be mixed with transition(s) arising from the $\text{Ir}(\text{S}^\wedge\text{S})$ moiety. The corresponding absorptions for the Rh complexes **6–8** and **11** were found in shorter wavelengths ($330\text{--}393\text{ nm}$). Additional works are required to unambiguously confirm the origin of electronic transition for these lower energy absorption bands. For the heterometallic $\text{Ir}/\text{W}/\text{S}$ complex **12**, in addition to the LC absorptions, an intense band at 483 nm ($\epsilon = 7.8 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$) was observed. This low energy band may be due to the LMCT

Table 6

Selected bond lengths (\AA) and angles ($^\circ$) for $[\{\text{Ir}(\text{Buppy})_2\}_2\{\text{WO}(\mu\text{-S})_2(\mu_3\text{-S})\}]$ (**16**)

Bond lengths			
$\text{W}(1)-\text{O}(1)$	1.740(7)	$\text{W}(1)-\text{S}(1)$	2.291(3)
$\text{W}(1)-\text{S}(2)$	2.226(3)	$\text{W}(1)-\text{S}(3)$	2.257(3)
$\text{Ir}(1)-\text{S}(1)$	2.461(3)	$\text{Ir}(1)-\text{S}(3)$	2.484(3)
$\text{Ir}(2)-\text{S}(1)$	2.437(3)	$\text{Ir}(2)-\text{S}(2)$	2.486(3)
$\text{Ir}(1)-\text{W}(1)$	2.910(2)	$\text{Ir}(2)-\text{W}(1)$	2.914(2)
$\text{Ir}(1)-\text{C}(11)$	2.06(1)	$\text{Ir}(1)-\text{C}(31)$	2.03(1)
$\text{Ir}(2)-\text{C}(51)$	2.03(1)	$\text{Ir}(2)-\text{C}(70)$	2.05(1)
$\text{Ir}(1)-\text{N}(1)$	2.077(9)	$\text{Ir}(1)-\text{N}(2)$	2.060(9)
$\text{Ir}(2)-\text{N}(3)$	2.101(9)	$\text{Ir}(2)-\text{N}(4)$	2.089(9)
Bond angles			
$\text{O}(1)-\text{W}(1)-\text{S}(2)$	108.5(2)	$\text{O}(1)-\text{W}(1)-\text{S}(3)$	106.6(3)
$\text{S}(2)-\text{W}(1)-\text{S}(3)$	112.8(1)	$\text{O}(1)-\text{W}(1)-\text{S}(1)$	108.6(3)
$\text{S}(2)-\text{W}(1)-\text{S}(1)$	109.6(1)	$\text{S}(3)-\text{W}(1)-\text{S}(1)$	110.6(1)
$\text{W}(1)-\text{S}(1)-\text{Ir}(2)$	76.04(9)	$\text{W}(1)-\text{S}(1)-\text{Ir}(1)$	75.4(1)
$\text{Ir}(2)-\text{S}(1)-\text{Ir}(1)$	129.0(1)	$\text{W}(1)-\text{S}(2)-\text{Ir}(2)$	76.20(9)
$\text{W}(1)-\text{S}(3)-\text{Ir}(1)$	75.6(1)	$\text{S}(1)-\text{Ir}(1)-\text{S}(3)$	98.2(1)
$\text{S}(1)-\text{Ir}(2)-\text{S}(2)$	97.1(1)	$\text{N}(2)-\text{Ir}(1)-\text{N}(1)$	167.0(3)
$\text{N}(4)-\text{Ir}(2)-\text{N}(3)$	165.7(4)	$\text{C}(31)-\text{Ir}(1)-\text{C}(11)$	87.6(4)

Table 7

UV-Vis spectral data for cyclometalated $\text{Ir}(\text{III})$ and $\text{Rh}(\text{III})$ complexes in CH_2Cl_2 at room temperature

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3\text{ M}^{-1}\text{ cm}^{-1}$)
3	245 (40.8), 290 sh (10.4), 365 (6.66), 400 sh (2.69), 455 (0.99)
4	262 (42.1), 290 sh (12.6), 350 (7.58), 400 sh (4.67), 450 (0.98)
5	263 (45.2), 347 sh (4.60), 374 (4.01), 399 sh (3.60), 451 (0.90)
6	245 (59.8), 285 sh (40.0), 393 (14.3)
7	246 (60.0), 276 sh (45.9), 330 (4.70)
8	245 (61.2), 290 sh (39.8), 377 (16.0)
9	256 (60.1), 289 sh (36.0), 357 sh (5.30), 380 (4.80), 403 (3.90)
10	246 (60.6), 276 sh (45.9), 363 (30.7)sh, 393 (7.50), 427 sh (4.60), 475 (1.00)
11	247 (58.4), 266 sh (27.7), 307 sh (25.8), 381 (8.0)
12	247 (55.4), 281 sh (684.3), 359 sh (2.90), 483 (7.80)
13	255 (61.6), 378 sh (29.0), 461 sh (5.62), 544 (9.65)
14	246 (60.9), 310 sh (32.1), 435 (6.92)
15	250 (61.8), 355 (27.8)sh, 438 (7.39) sh, 510 (6.10)
16	257 (64.1), 351 (7.27) sh, 481 (3.32)

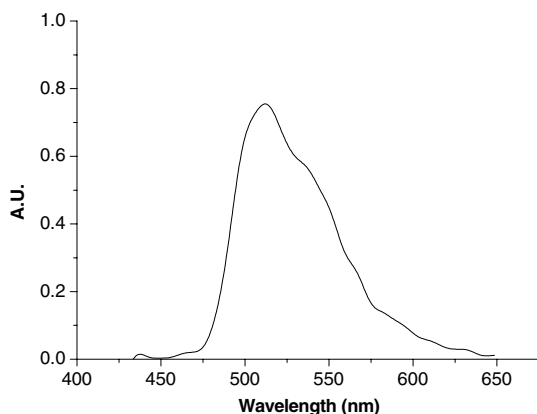


Fig. 9. Emission spectrum for **3** in CH_2Cl_2 at room temperature (excitation wavelength = 455 nm).

$[\text{p}\pi(\text{S}) \rightarrow \text{d}\pi(\text{W})]$ together with MLCT $[\text{d}\pi(\text{Ir}) \rightarrow \pi^*(\text{Buppy})]$ transitions. It has been reported that the LMCT $[\text{p}\pi(\text{S}) \rightarrow \text{d}\pi(\text{W})]$ bands for $[\text{WS}_4]^{2-}$ ($\lambda_{\text{max}} = 392, 277$ and 216 nm) [45] are red-shifted upon coordination of transition metal ions [22,23]. Further support for the LMCT $[\text{p}\pi(\text{S}) \rightarrow \text{d}\pi(\text{W})]$ contribution to the 483-nm band comes from the observations that this band is red-shifted to 544 nm upon substitution of $[\text{WSe}_4]^{2-}$ for $[\text{WS}_4]^{2-}$ (complex **13**) and blue-shifted to 435 nm upon substitution of Rh for Ir (complex **14**). However, this spectral assignment is only tentative. Additional experimental works are required to confirm the exact origin of electronic transition for these absorption bands.

A preliminary study showed that the Ir(III) bis-ppy complexes **3–5** and **10** are luminescent in fluid solutions. For example, complex **3** exhibited an emission centered at ca. 500 nm (excited wavelength = 455 nm) in CH_2Cl_2 at room temperature (Fig. 9). Previously, the emission for $[\text{Ir}(\text{ppy})_2(\text{acac})]$ at 516 nm has been assigned as the MLCT $[\text{d}\pi(\text{Ir}) \rightarrow \pi^*(\text{ppy})]$ excited state [9a]. Thus, it seems that an MLCT $[\text{d}\pi(\text{Ir}) \rightarrow \pi^*(\text{Buppy})]$ excited state may also be responsible for the emission of **3**. Trinuclear Ir/W/S(Se) complexes **12** and **13** are non-emissive probably due to quenching of the excited state by the $[\text{WQ}_4]^{2-}$ moiety.

4. Conclusions

We have demonstrated that $[\text{M}(\text{Buppy})_2\text{Cl}]_2$ ($\text{M} = \text{Ir}$ and Rh) reacted with a variety of sulfur and selenium ligands to give stable mononuclear complexes. These complexes have been characterized by spectroscopic methods and X-ray crystallography. The first trinuclear Ir(III) and Rh(III) cyclometalated complexes containing $[\text{WQ}_4]^{2-}$ ($\text{Q} = \text{S}$ or Se) have been synthesized and structurally characterized. Efforts are being made to design and synthesize higher nuclearity iridium cyclometalated complexes using appropriate bridging sulfur donor ligands.

5. Supporting information available

Crystallographic data for complexes **3**, **4**, **7** · $4\text{CH}_2\text{Cl}_2$, **8**, **10** · C_6H_{14} , **11** · C_6H_{14} · $2\text{H}_2\text{O}$, **15** · $2\text{C}_6\text{H}_{14}$, and **16** · $4\text{CH}_2\text{Cl}_2$ · $0.5\text{H}_2\text{O}$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 231906, 231905, 231908, 231907, 231903, 231904, and 231902, respectively, in CIF format. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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