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Synthesis and Structure of Heterodinuclear Rhodium and Iridium Borylene Complexes

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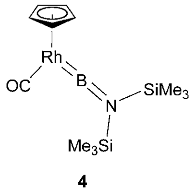
Abstract: Herein we report on the synthesis and structural characterization of a representative range of novel heterodinuclear bridging rhodium and iridium borylene complexes. The iridium borylene complexes feature an unusual coordination mode of the borylene ligand. Furthermore, the first instance of a heterodinuclear-bridged borylene compound containing a chromium atom in the three-membered ring is reported.

Keywords: boron · borylene complexes · bridging ligands · iridium · rhodium

Introduction

Since the advent of the first bridged[1] and terminal[2] borylene complexes, they have attracted growing attention.[3] A number of theoretical[4] studies disclosed the close electronic relationship between borylene and the ubiquitous carbonyl complexes, thus accounting for the importance of the former for organometallic chemistry. Recent experimental work has significantly extended the scope of metal-bound borylene ligands with respect to different coordination modes, including for example, heterodinuclear[5] and semibridged complexes,[6] thus emphasizing their relationship with CO. However, certain bonding patterns, in particular the pronounced propensity of M=B−R moieties to bind metal bases[7] appear to be restricted to borylene complexes and find no parallels in carbonyl chemistry. In addition to the fundamental interest that the metal–borylene linkage has received, recent efforts have indicated a certain applicability of these species in organic and organometallic synthesis. Apart from a first report on the use of borylene complexes as catalysts for a specific organic transformation,[8] borylene transfer to organic substrates[9] and borylene-based metathesis reactions[10] were reported. Whereas cationic borylene complexes of iron, manganese,[11] and platinum[12] can be obtained by halide abstraction from suitable precursors, the synthesis of corresponding neutral species has to rely on salt elimination reactions. The latter method has been successfully applied to dinuclear borylene complexes, particularly of iron,[13] and to corresponding terminal species of the Group VI metals.[2a,14] Although salt elimination can be regarded as the most facile method for the build up of transition-metal–element bonds, in the case of terminal borylene complexes it appears to be restricted to the aforementioned compounds of the type $[(OC)_5M{=}B{-}R]$ (M = Cr, Mo, W; R = $N(SiMe_3)_2$, $Si(SiMe_3)_3$, $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe]$). To provide a more general access to borylene complexes of different metals, we have started to investigate the propensity of complexes $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (**1**, M = Cr; **2**, M = Mo; **3**, M = W) to transfer the $B{=}N(SiMe_3)_2$ moiety upon photolysis[15] or under thermal conditions,[16] thus yielding a variety of mono-, di-, and oligonuclear borylene complexes.

These studies revealed that the photochemically induced transfer of $B{=}N(SiMe_3)_2$ from the tungsten complex



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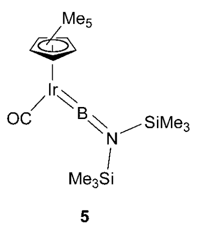

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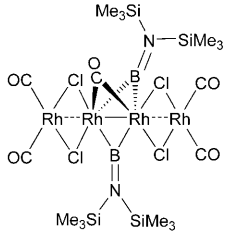

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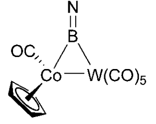

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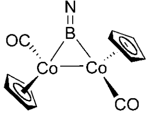

7

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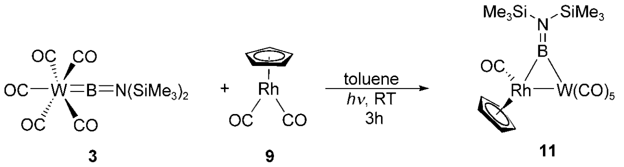
$[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**3**) to $[(\eta^5\text{-}C_5H_5)Co(CO)_2]$ proceeds via the heterodinuclear species $[(\eta^5\text{-}C_5H_5)(OC)Co\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**6**), thus providing evidence for a stepwise course of the borylene transmetalation.[15b] In contrast, the more reactive molybdenum complex $[(OC)_5Mo{=}B{=}N(SiMe_3)_2]$ (**2**), provided direct access to the rhodium and iridium borylene species $[(\eta^5\text{-}C_5H_5)(OC)Rh{=}B{=}N(SiMe_3)_2]$ (**4**) and $[(\eta^5\text{-}C_5Me_5)(OC)Ir{=}B{=}N(SiMe_3)_2]$ (**5**) in the absence of UV light and without evidence for a corresponding heterodinuclear intermediate.[16b]

Herein we provide full experimental details on the synthesis of novel heterodinuclear borylene complexes obtained from the reaction of **1** and **3** with $[(\eta^5\text{-}C_5R_5)M(CO)_2]$ (**9**, M = Rh, R = H; **10**, M = Ir; R = Me).

Results and Discussion

Photolysis of equimolar amounts of $[(OC)_5W{=}BN(SiMe_3)_2]$ (**3**) and $[(\eta^5\text{-}C_5H_5)Rh(CO)_2]$ (**9**) in toluene for 3 h results in the formation of the heterodinuclear borylene-bridged complex $[(\eta^5\text{-}C_5H_5)(OC)Rh\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**11**) (Scheme 1). After recrystallization from hexane, **11** was isolated as air- and moisture-sensitive red crystals in 63% yield.



Scheme 1. Synthesis of the heterodinuclear borylene complex $[(\eta^5\text{-}C_5H_5)(OC)Rh\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**11**) upon photolysis of $[(OC)_5W{=}BN(SiMe_3)_2]$ (**3**) and $[(\eta^5\text{-}C_5H_5)Rh(CO)_2]$ (**9**).

The ^1H NMR spectrum of **11** shows one singlet for the trimethylsilyl group at $\delta = 0.23$ ppm, which is slightly deshielded with respect to that of the borylene precursor **3** ($\delta = 0.12$ ppm).[2a] The new compound displays a broad singlet in the $^{11}B\{^1H\}$ NMR spectrum ($\delta = 95$ ppm) which is slightly downfield-shifted with respect to that of the starting material **3** ($\delta = 87$ ppm),[2a] thus indicating the presence of a bridging borylene ligand.[17]

The exact constitution of **11** was determined by performing a single-crystal X-ray diffraction study (Figure 1). Crystals of **11** were obtained by cooling a concentrated hexane solution to −35 °C; the complex crystallizes in the monoclinic space group $P2_1/n$.

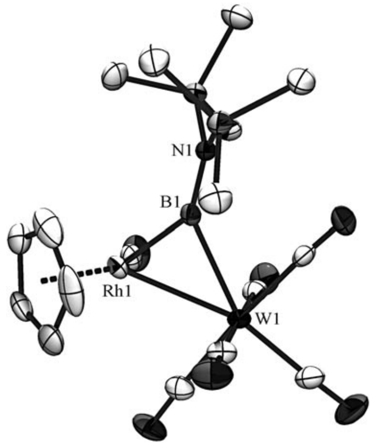
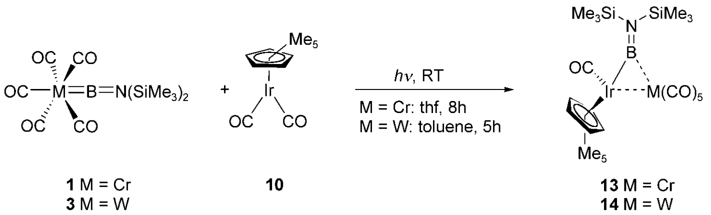


Figure 1. Molecular structure of **11** in the solid state. Bond lengths [Å] and angles [°]: B1−Rh1 2.004(4), B1−N1 1.390(5), B1−W1 2.423(4), Rh1−W1 2.892(4); W1-B1-N1-Si1 77.70(5), N1-B1-Rh1 139.40(3), N1-B1-W1 139.60(3), B1-Rh1-W1 55.83(13), B1-W1-Rh1 43.20(9). Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

In the solid state the $\{W(CO)_5\}$ and the $\{(\eta^5\text{-}C_5H_5)Rh(CO)\}$ fragments are linked by a bridging borylene ligand $BN(SiMe_3)_2$. The W1−B1 distance (2.423(4) Å) is considerably elongated in comparison to that of the corresponding terminal borylene complex **3** (2.151(7) Å),[2a] in agreement with the increased coordination number of the boron center. The B1−Rh1 distance (2.004(4) Å) is similar to corresponding distances found in the bridged bisborylene complex $[Rh_4\{\mu\text{-}BN(SiMe_3)_2\}_2(\mu\text{-}Cl)_4(\mu\text{-}CO)(CO)_4]$ (**8**), which features two three-coordinate boron atoms linked to two rhodium centers (2.004(3), 2.076(3), 2.051(3) Å).[16a] The Si1-B1-N1-Si2 plane is twisted by 78° with respect to the Rh1-B1-W1 plane. This effect is probably due to the presence of the bulky Me_3Si groups, as observed in the bridged borylene complexes $[(\eta^5\text{-}C_5H_5)(OC)Co\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**6**) (79°)[15b] and $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}]$ (**12**) (53°). The increased B1−N1 bond length of 1.412(4) Å in **12** suggests a less effective π interaction between the nitrogen and the boron atom.[13b] However, the B1−N1 bond (1.390(5) Å) of **11** is only slightly longer than that observed in the corresponding terminal borylene complex **3** (1.338(3) Å),[2a] thus indicating significant double-bond character of the boron–nitrogen linkage.

When the iridium dicarbonyl complex $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ (**10**) was photolyzed in the presence of $[(OC)_5M{=}BN(SiMe_3)_2]$ (**1**: thf; **3**: toluene) at ambient temperature, multinuclear NMR spectroscopy revealed gradual consumption of the starting materials within 8 h (**1**)/5 h (**3**) and the formation of new boron-containing complexes.

The ^1H NMR spectra display one new singlet for the trimethylsilyl group around $\delta = 0.24$ ppm, which is slightly deshielded in comparison to that of the borylene precursors **1** and **3** ($\delta = 0.12$–0.14 ppm).[2a] The new compounds both feature a broad upfield-shifted singlet in the $^{11}B\{^1H\}$ NMR spectra ($\delta = 73$ and 70 ppm), thus clearly suggesting the formation of terminal borylene species.[17] This behavior of **10** was observed before upon reaction with $[(OC)_5Mo{=}B{=}N(SiMe_3)_2]$ (**2**) and ascribed to its electron-rich and sterically demanding nature, which should protect the borylene fragment from scavenging a second metal center.[16b] However, single-crystal X-ray crystallography on those products revealed an unexpected course of this reaction according to Scheme 2 and thus, formation of the heterodinuclear species



Scheme 2. Synthesis of the heterodinuclear borylene complex $[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}M(CO)_5]$ (**13**, M = Cr; **14**, M = W) upon photolysis of $[(OC)_5M{=}BN(SiMe_3)_2]$ (**1**, M = Cr; **3**, M = W) and $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ (**10**).

$[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}Cr(CO)_5]$ (**13**) and $[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**14**).

Crystals of **13** and **14** were obtained by cooling a concentrated hexane solution to −35 °C; the complexes crystallize in the orthorhombic space groups $Pna2_1$ (**13**) and $P2_12_12_1$ (**14**) (Figure 2).

The B1−N1 separations (**13**: 1.381(9) Å; **14**: 1.381(6) Å) and the dihedral angles between the bonding planes of the boron and nitrogen centers (**13**: 70.9°; **14**: 71.4°) indicate a geometry of the *exo*-amino group similar to that observed for **11**. The pertinent structural data for the central Ir−B−M (M = Cr, W) triangles, however, differ significantly from those of the rhodium species **11** or any other structurally authenticated heterodinuclear borylene complex. In both cases, the short Ir−B distances (**13**: 1.931(8) Å; **14**: 1.935(5) Å) and the large Ir-B-N angles (**13**: 157.8(6)°**;** **14**: 157.5(4)°) are comparable to those of the terminal Ir−borylene species $[(\eta^5\text{-}C_5Me_5)(OC)Ir{=}BN(SiMe_3)_2]$ (**5**) (1.892(3) Å; 175.9(3)°)[16b] rather than a bridged complex (for example, **11**: 139.4(3)°). On the other hand, the Ir−M distances (**13**: 2.918(1) Å; **14**: 2.986(3) Å) are considerably longer than expected in comparison to the heterodinuclear bridged cobalt and rhodium borylene complexes (Co−W: 2.816(4) (**6**);[15b] Rh−W: 2.892 (4) Å (**11**)). Likewise, the B−M separations (**13**: 2.816(8) Å; **14**: 2.848(4) Å) are significantly elongated and much larger than the sum of the covalence radii of the respective atoms (**13**: 2.08 Å; **14**: 2.20 Å). These findings reflect a highly distorted coordination mode for the bridging borylene ligand $B{=}N(SiMe_3)_2$, which appears to be much more localized at the Ir center, despite the presence of a bulky (η^5-C_5Me_5) moiety. A rationale for the significantly different geometries of the rhodium and iridium complexes described here, might arise from earlier DFT studies on terminal borylene complexes, which revealed a stronger metal–boron interaction for 5d metals in comparison to their lighter homologues.[14d]

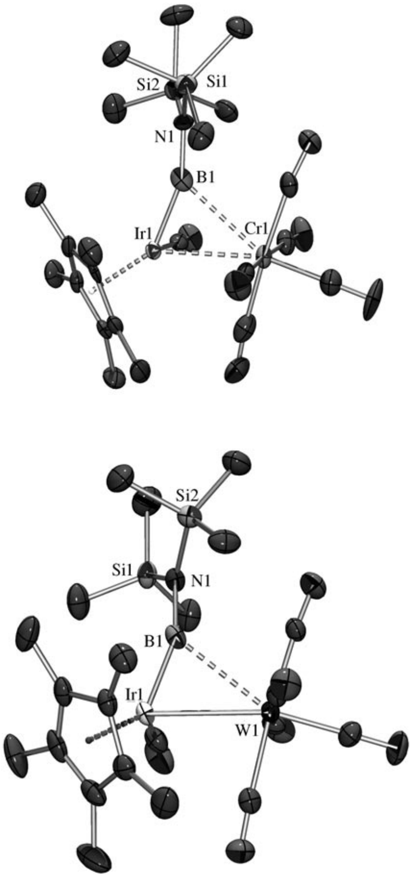


Figure 2. Molecular structures of **13** and **14** in the solid state. Bond lengths [Å] and angles [°]: **13**: B1−Ir1 1.931(8), B1−N1 1.381(9), B1−Cr1 2.816(8), Ir1−Cr1 2.918(1); N1-B1-Ir1 157.8(6), B1-Ir1-Cr1 67.50(2). **14**: B1−Ir1 1.935(5), B1−N1 1.381(6), B1−W1 2.848 (4), Ir1−W1 2.986(3); N1-B1-Ir1 157.5(4), B1-Ir1-W1 66.89(14). Thermal ellipsoids are set at 50 % probability. Hydrogen atoms are omitted for clarity.

Conclusion

In conclusion, we have described the synthesis and full characterization of novel heterodinuclear borylene complexes of rhodium and iridium. Spectroscopic and structural data revealed that the borylene ligand in the dinuclear complex $[(\eta^5\text{-}C_5H_5)(OC)Rh\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**11**) adopts a symmetrically bridging position between rhodium and tungsten. In the case of the corresponding iridium complexes $[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}Cr(CO)_5]$ (**13**) and $[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (**14**), however, the $B{=}N(SiMe_3)_2$ group is much more localized at the electron-rich Ir center, as reflected in solution by ^{11}B NMR shifts, which are reminiscent of those of terminal borylene complexes, and in the crystal by short Ir−B separations and an almost linear arrangement of the Ir-B-N moieties. These findings lend support to the description of these Ir species as a terminal borylene complex $[(\eta^5\text{-}C_5Me_5)(OC)Ir{=}B{=}N\text{-}(SiMe_3)_2\}]$ (**5**) being side-on coordinated to a $\{M(CO)_5\}$ fragment (M = Cr, W) via the Ir−B multiple bond.

Experimental Section

General: All manipulations were conducted either under an atmosphere of dry argon inside a glove-box or employing standard Schlenk techniques. Solvents were dried by standard procedures and stored under argon over molecular sieves. NMR: Bruker Avance 500 at 500 MHz (^{1}H, internal standard TMS), 125.77 MHz (^{13}C{^{1}H}, APT, internal standard TMS), and 160.46 MHz (^{11}B, $BF_3{\cdot}OEt_2$ in C_6D_6 as external standard).

$[(\eta^5\text{-}C_5H_5)(OC)Rh\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (11): A yellow solution of $[(OC)_5W{=}BN(SiMe_3)_2]$ (**3**) (0.25 g, 0.50 mmol) and $[(\eta^5\text{-}C_5H_5)Rh(CO)_2]$ (**9**) (0.13 g, 0.50 mmol) in toluene (10 mL) was photolyzed at ambient temperature for 3 h. The solvent of the dark orange solution was removed in vacuo, and the resulting red solid was dissolved in hexane (2 mL). After filtration, the solution was cooled to −35 °C, which yielded red crystals of **11** (0.15 g, 63 %). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 5.05$ (s, 5H, C_5H_5), 0.23 ppm (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C, TMS): $\delta = 198.53$ (d, $^1J_{Rh,C} = 91.8$ Hz, CO), 191.61 (s, CO), 92.26 (d, C_5H_5), 4.31 ppm (s, $SiMe_3$); $^{11}B\{^1H\}$ NMR (64 MHz, C_6D_6, 25 °C): $\delta = 95$ ppm (br s, $\omega_{1/2} = 333$ Hz); IR (toluene): $\tilde{\nu} = 2061$, 1984, 1933 cm^{-1}, ν(CO); elemental analysis calcd (%) for $C_{17}H_{23}NBRhO_6Si_2W$: C 29.55, H 3.35, N 2.03; found: C 29.51, H 3.36, N 1.95.

$[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}Cr(CO)_5]$ (13): An orange solution of $[(OC)_5Cr{=}BN(SiMe_3)_2]$ (**1**) (0.18 g, 0.50 mmol) and $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ (**10**) (0.20 g, 0.50 mmol) in THF (10 mL) was photolyzed at ambient temperature for 8 h. All volatiles were removed in vacuo. All impurities were removed by sublimation. The resulting yellow solid was dissolved in hexane (2 mL). After filtration the solution was cooled to −35 °C, which yielded orange crystals of **13** (0.18 g, 52 %). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.77$ (s, 15H, C_5Me_5), 0.23 ppm (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6 25 °C, TMS): $\delta = 216.45$ (s, CO), 210.49 (s, CO), 99.80 (s, C_5Me_5), 10.06 (s, C_5Me_5) 3.67 ppm (s, $SiMe_3$); $^{11}B\{^1H\}$ NMR (64 MHz, C_6D_6, 25 °C): $\delta = 70$ ppm (bs, $\omega_{1/2} = 238$ Hz); IR (toluene): $\tilde{\nu} = 2036$, 1982, 1909, 1889 cm^{-1}, ν(CO); elemental analysis calcd (%) for $C_{22}H_{33}NBIrO_6Si_2Cr$: C 36.78, H 4.63, N 1.95; found: C 36.85, H 4.63, N 2.05.

$[(\eta^5\text{-}C_5Me_5)(OC)Ir\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (14): A pale brown solution of **3** (0.25 g, 0.50 mmol) and **10** (0.20 g, 0.50 mmol) in toluene (10 mL) was photolyzed at ambient temperature for 5 h. The solvent was removed in vacuo. All impurities were removed by sublimation. The resulting yellow solid was dissolved in hexane (2 mL). After filtration, the solution was cooled to −70 °C, which provided dark orange crystals of **14** (0.13 g, 31 %). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.80$ (s, 15H, C_5Me_5), 0.26 ppm (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C, TMS): $\delta = 199.79$ (s, CO), 195.09 (s, CO), 190.15 (s, CO), 98.31 (s, C_5Me_5),8.98 (s, C_5Me_5) 2.59 ppm (s, $SiMe_3$); $^{11}B\{^1H\}$ NMR (64 MHz, C_6D_6, 25 °C): $\delta = 73$ ppm (bs, $\omega_{1/2} = 829$ Hz); IR (toluene): $\tilde{\nu} = 2049$, 1971, 1911, 1890 cm^{-1}, ν(CO); elemental analysis calcd (%) for $C_{22}H_{33}NBIrO_6Si_2W$: C 31.05, H 3.91, N 1.64; found: C 30.99, H 3.85, N 1.61.

The crystal data of **11**, **13**, and **14** were collected on a Bruker D8 APEX diffractometer with a CCD area detector and graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Cryst. Sect. A* **2008**, *64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

Crystal data for **11**: $C_{17}H_{23}BNO_6RhSi_2W$, $M_r = 691.11$, red block, $0.16 \times 0.25 \times 0.28$ mm^3, monoclinic space group $P2_1/n$, $a = 8.7328(7)$, $b = 18.2946(13)$, $c = 15.0617(12)$ Å, $\beta = 94.949(2)°$, $V = 2397.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.915$ g cm^{-3}, $\mu = 5.613$ mm^{-1}, $F(000) = 1328$, $T = 173(2)$ K, $R_1 = 0.0273$, $wR^2 = 0.0700$, 4629 independent reflections [$2\theta \leq 52.02°$] and 262 parameters.

Crystal data for **13**: $C_{22}H_{33}BCrIrNO_6Si_2$, $M_r = 718.68$, yellow block, $0.24 \times 0.12 \times 0.09$ mm^3, Orthorhombic space group $Pna2_1$, $a = 19.4542(14)$, $b = 9.4739(7)$, $c = 15.4475(11)$ Å, $V = 2847.1(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.677$ g cm^{-3}, $\mu = 5.169$ mm^{-1}, $F(000) = 1416$, $T = 173(2)$ K, $R_1 = 0.0355$, $wR^2 = 0.0703$, 5841 independent reflections [$2\theta \leq 52.86°$] and 312 parameters.

Crystal data for **14**: $C_{22}H_{33}BIrNO_6Si_2W$, $M_r = 850.53$, yellow block, $0.17 \times 0.11 \times 0.07$ mm^3, Orthorhombic space group $P2_12_12_1$, $a = 9.6402(10)$, $b = 16.9494(18)$, $c = 17.7700(19)$ Å, $V = 2903.5(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.946$ g cm^{-3}, $\mu = 8.654$ mm^{-1}, $F(000) = 1616$, $T = 173(2)$ K, $R_1 = 0.0177$, $wR^2 = 0.0404$, 5722 independent reflections [$2\theta \leq 52.12°$] and 312 parameters.

CCDC-697398, CCDC-697399, and CCDC-697400 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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