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Cationic rhodium(I) and iridium(I) α-diimine complexes

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ABSTRACT

Condensation of glyoxal with fluoroarylanilines [Ar^FNH_2; Ar^F = 4-C_6H_4F; 2,4-$C_6H_3F_2$; 2,4,6-$C_6H_2F_3$] generates new fluorine-substituted aryl α-diimines, $Ar^FNCH{=}CHNAr^F$; Ar^F = 4-C_6H_4F and 2,4,6-$C_6H_2F_3$ have been structurally characterised. Displacement of acetonitrile from $[M(COD)(MeCN)_2][BF_4]$ (M = Rh, Ir, COD = 1,5-cyclooctadiene) with fluorine- and non-fluorine-substituted aryl α-diimines yields cationic rhodium(I) and iridium(I) complexes, that can be carbonylated to $[M(CO)_2(\alpha\text{-diimine})][BF_4]$.

1. Introduction

The renewed attention that late transition metal 1,4-diazabutadiene (α-diimine) complexes have received recently, particularly in regard to their value in olefin polymerisation chemistry [1,2], has led us to investigate exploiting the power of the α-diimine ligand set to stabilise late transition metal fluoride complexes of rhodium and iridium [3,4]. Previously, a few square planar cationic rhodium [5–7] α-diimine systems had been described that appeared potentially amenable to oxidative fluorination chemistry, and here we describe the synthesis of a series of new cationic rhodium(I) and iridium(I) complexes with COD (COD = 1,5-cyclooctadiene) and CO co-ligands. We also have a long-standing interest in the coordination properties of fluorine-containing ligands and have investigated a broad range of F-substituted ligands, including triarylphosphines [8,9], triarylphosphites [10], phenylimides [11], β-diketonates [12], phenylphosphonates [13], dithiophosphates [14] and xanthates [15]. Only four fluoroaryl α-diimine ligands have been reported previously [16,17]. $Ar^FNC(Me)C(Me)NAr^F$ (Ar^F = 4-C_6H_4F, 3,5-$C_6H_3F_2$, C_6F_5) are formed via aminoalane reactions with 2,3-butanedione [16], and $Ar^FNCHCHNAr^F$ (Ar^F = 2,6-dimethyl-4-fluorophenyl) has been prepared as an intermediate in a study on the influence of electronic properties of NHC ligands on the catalytic activity of Grubbs II metathesis catalysts [17]. As part of this study, we also describe the synthesis and characterisation of a set of related fluoroaryl α-diimine ligands, $Ar^FNCHCHNAr^F$ (Ar^F = 4-C_6H_4F, 2,4-$C_6H_3F_2$, 2,4,6-$C_6H_2F_3$), and their cationic rhodium(I) complexes.

2. Results and discussion

The non-fluorinated glyoxal α-diimines (**L1**–**L4**) (Scheme 1) used in this study were readily prepared by literature routes [18–20]. Surprisingly, the first glyoxal fluoroaryl α-diimines have only very recently been reported in the literature [17]. Cowley and co-workers [16,21] have speculated that these derivatives may be difficult to prepare via the conventional condensation route as a consequence of the electronegative fluorine atoms. As an alternative, a structurally characterised series of fluoroarylimidoalane derivatives were prepared as potential activated intermediates in the generation of fluoroaryl α-diimines and their use in the preparation of fluoroaryl α-diimines based on the 2,3-butanedione backbone was reported. In this work, as suggested by Cowley, the reaction of fluorinated anilines with glyoxal is slow but, by increasing the reaction temperatures and reaction times, the new fluoroaryl α-diimines ($Ar^FNCH{=}CHNAr^F$; Ar^F = 4-C_6H_4F (**L5**), 2,4-$C_6H_3F_2$ (**L6**), 2,4,6-$C_6H_2F_3$ (**L7**)) could be isolated directly in reasonable yields without the need to exploit the greater reactivity of the imidoalane derivatives. These new imines were characterised by multinuclear NMR spectroscopy, IR spectroscopy, mass spectrometry, elemental analyses and in addition, for **L5** and **L7**, by single crystal X-ray diffraction.

Crystals of **L5** and **L7** suitable for the X-ray determination were grown by slow evaporation of THF solutions. A view of **L7** is shown in Fig. 1 as a representative example; lists of bond lengths and angles for **L5** and **L7** can be found in the Supplementary material. The

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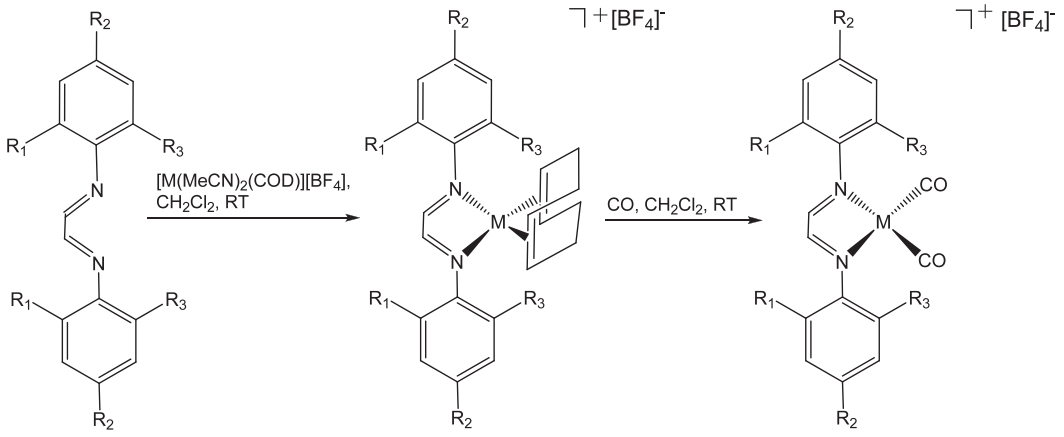

$R_1 = R_2 = R_3 = Me$ (**L1**);
$R_1 = R_3 = {}^{i}Pr$, $R_2 = H$ (**L2**);
$R_1 = R_3 = Me$, $R_2 = H$ (**L3**);
$R_1 = R_3 =$ adamantyl, $R_2 = H$ (**L4**);
$R_1 = R_3 = H$, $R_2 = F$ (**L5**);
$R_1 = R_2 = F$, $R_3 = H$ (**L6**);
$R_1 = R_2 = R_3 = F$ (**L7**)

$R_1 = R_2 = R_3 = Me$, M = Rh (**1**);
$R_1 = R_3 = {}^{i}Pr$, $R_2 = H$, M = Rh (**2**);
$R_1 = R_3 = Me$, $R_2 = H$, M = Rh (**3**);
$R_1 = R_3 = H$, $R_2 = F$, M = Rh (**4**);
$R_1 = R_2 = F$, $R_3 = H$, M = Rh (**5**)
$R_1 = R_2 = R_3 = Me$, M = Ir (**6**);
$R_1 = R_3 = {}^{i}Pr$, $R_2 = H$, M = Ir (**7**);
$R_1 = R_3 =$ adamantyl, $R_2 = H$, M = Ir (**8**)

$R_1 = R_2 = R_3 = Me$, M = Rh (**9**);
$R_1 = R_3 = {}^{i}Pr$, $R_2 = H$, M = Rh (**10**);
$R_1 = R_3 = Me$, $R_2 = H$, M = Rh (**11**);
$R_1 = R_3 = H$, $R_2 = F$, M = Rh (**12**);
$R_1 = R_2 = R_3 = Me$, M = Ir (**13**)
$R_1 = R_3 = {}^{i}Pr$, $R_2 = H$, M = Ir (**14**);
$R_1 = R_3 =$ adamantyl, $R_2 = H$, M = Ir (**15**)

Scheme 1. Synthetic route to cationic and rhodium complexes **1**–**15**.

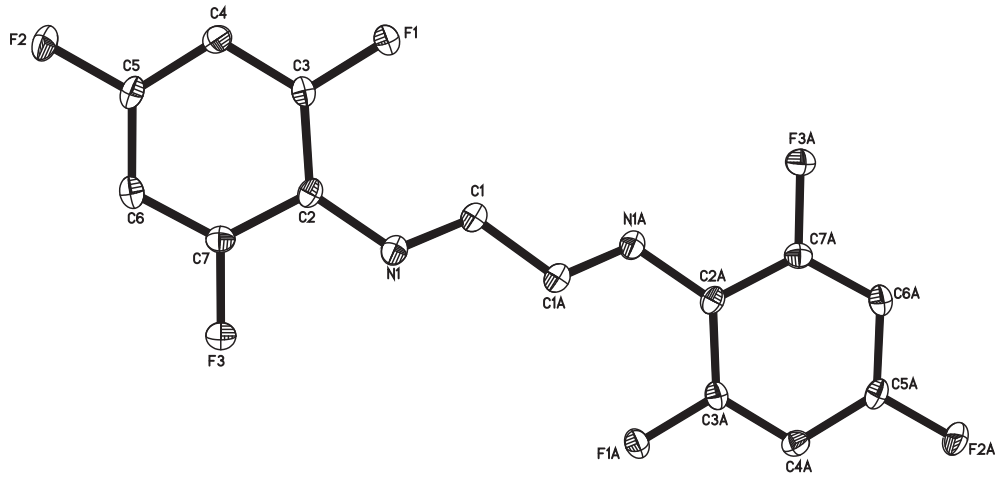

Fig. 1. Molecular structure of **L7** with 30% displacement ellipsoids.

molecule lies on a crystallographic centre of inversion and hence the two imine groups are *s-trans*, as has been observed in other systems [16,22,23]. The crystallographic data suggests that the environment around the imine bonds in these fluoroaryl α-diimines and the related mesityl [24] and pentafluorophenyl [16] analogues appears relatively insensitive to the substituents on the aryl rings, with modest shortening in the aryl-N bond with increasing numbers of fluorine substituents. In contrast, the values of ν_{CN}, δ(NCH) and δ(NC*H*) exhibit definite trends. As the number of electron-withdrawing fluorine atoms on the aryl rings increases, the values of ν_{CN} [1605 cm^{-1} (**L5**), 1603 cm^{-1} (**L6**), 1589 cm^{-1} (**L7**)] decrease and δ(NCH) [δ 159.3 (**L5**), δ 161.4 (**L6**)] and δ(NC*H*) [δ 8.35 (**L5**), δ 8.49 (**L6**), δ 8.52 (**L7**)] shift to lower field, indicating a change in the electronic environment and a weakening of the imine bond.

The displacement of acetonitrile from $[M(COD)(MeCN)_2]^+[BF_4]^-$ (M = Rh, Ir) with α-diimines was facile, affording a series of new rhodium(I) and iridium(I) cationic complexes $[M(COD)(ArNCHCHNAr)]^+[BF_4]^-$ {M = Rh, Ar = 2,4,6-$Me_3C_6H_2$ (**1**), 2,6-$^{i}Pr_2C_6H_3$ (**2**), 2,6-$Me_2C_6H_3$ (**3**), 4-C_6H_4F (**4**), 2,4-$F_2C_6H_3$ (**5**), M = Ir, Ar = 2,4,6-$Me_3C_6H_2$ (**6**), 2,6-$^{i}Pr_2C_6H_3$ (**7**)} and [Ir(COD)(AdamantylNCHCHNAdamantyl)]$^+[BF_4]^-$ (**8**) in good yields (Scheme 1). Carbonylation of complexes (**1**, **2**, **3**, **4**, **6**–**8**) at ambient temperatures generated the new carbonyl complexes $[M(CO)_2(ArNCHCHNAr)]^+[BF_4]^-$ {M = Rh, Ar = 2,4,6-$Me_3C_6H_2$ (**9**), 2,6-$^{i}Pr_2C_6H_3$ (**10**), 2,6-$Me_2C_6H_3$ (**11**), 4-C_6H_4F (**12**); M = Ir, Ar = 2,4,6-$Me_3C_6H_2$ (**13**), 2,6-$^{i}Pr_2C_6H_3$ (**14**)} and $[Ir(CO)_2(AdamantylNCHCHNAdamantyl)]^+[BF_4]^-$ (**15**) in quantitative yield (Scheme 1). All complexes were characterised by multinuclear NMR spectroscopies, mass spectrometry, IR spectroscopy and, for selected examples, elemental analyses (see Table 1 and Section 4).

For all the COD complexes (**1**–**8**), as expected ν_{CN} decreases on coordination due to a mild degree of backbonding from the metal into the π* orbitals of the imine [25]. Indeed, a theoretical study [26] on metal to ligand electron transfer in bis(imino)pyridine complexes of the first row transition metals (Mn to Zn) has

Table 1
Selected spectroscopic data for rhodium and iridium aryl α-diimine complexes.

	ν(CN) (cm^{-1})	ν(CO) (cm^{-1})	δ(NC*H*) (ppm)
[Rh(COD)(**L1**)]$^+$[BF$_4$]$^-$ (**1**)	1592	–	8.15
[Rh(COD)(**L2**)]$^+$[BF$_4$]$^-$ (**2**)	1608	–	8.35
[Rh(COD)(**L3**)]$^+$[BF$_4$]$^-$ (**3**)	1591	–	8.23
[Rh(COD)(**L5**)]$^+$[BF$_4$]$^-$ (**4**)	1592	–	8.14
[Rh(COD)(**L6**)]$^+$[BF$_4$]$^-$ (**5**)	1597	–	8.54
[Ir(COD)(**L1**)]$^+$[BF$_4$]$^-$ (**6**)	1614	–	8.76
[Ir(COD)(**L2**)]$^+$[BF$_4$]$^-$ (**7**)	1611	–	9.03
[Ir(COD)(**L4**)]$^+$[BF$_4$]$^-$ (**8**)	1634	–	8.84
[Rh(CO)$_2$(**L1**)]$^+$[BF$_4$]$^-$ (**9**)	1623	2109, 2071	8.31
[Rh(CO)$_2$(**L2**)]$^+$[BF$_4$]$^-$ (**10**)	1620	2102, 2041	8.43
[Rh(CO)$_2$(**L3**)]$^+$[BF$_4$]$^-$ (**11**)	1622	2107, 2067	8.42
[Rh(CO)$_2$(**L5**)]$^+$[BF$_4$]$^-$ (**12**)	1594	2103, 2053	8.35
[Ir(CO)$_2$(**L1**)]$^+$[BF$_4$]$^-$ (**13**)	1619	2095, 2025	8.68
[Ir(CO)$_2$(**L2**)]$^+$[BF$_4$]$^-$ (**14**)	1618	2089, 2023	8.97
[Ir(CO)$_2$(**L4**)]$^+$[BF$_4$]$^-$ (**15**)	1629	2076, 2004	8.82

indicated that such synergic bonding may be of more importance in imine coordination than previously thought. The same trends are observed for the metal complexes with both the fluorinated and non-fluorinated α-diimines (**4**, **5**). In contrast, the greater competition for backbonding in the carbonyl complexes (**9**–**15**) leaves ν_{CN} virtually unaltered from those for the free ligands. There are no discernible trends in the NMR parameters, δ(NC*H*) and δ(NC*H*), on coordination.

Complexes **14** and **15** were also the subject of single crystal X-ray diffraction studies; suitable crystals for the studies could be grown by slow evaporation from dichloromethane solutions. Perspective views of the complexes are shown in Figs. 2 and 3; selected bond lengths and angles collected in Table 2. As expected the cationic unit in both iridium(I) complexes display square planar geometries with the carbonyl ligands configured mutually *cis*. While a number of iridium(III) complexes containing α-diimine ligands have been previously reported [27,28], the only crystallographically characterised example of an iridium(I) species to date is neutral [IrCl(CN^{t}Bu)(2,6-Me$_2$C$_6$H$_3$NCMeCMeN-2,6-Me$_2$C$_6$H$_3$)] [29]. In comparison with [IrCl(CN^{t}Bu)(2,6-Me$_2$C$_6$H$_3$NCMeCMeN-2,6-Me$_2$C$_6$H$_3$)], the Ir–N bond lengths in **14** are similar [2.080(2) and 2.074(2) Å], while a distinct variation is apparent in the former complex [2.053(2) and 1.966(2) Å] reflecting the differing nature of the *trans* ligands. On the other hand, for the bisadamantylimine complex **15** there is asymmetry in the metal carbonyl bond lengths [1.836(9) and 1.866(10) Å], arising from relatively short interactions with the tetrafluoroborate anion (O(2)···F(2) 3.213 Å, O(1)···F(3) 3.406 Å); in **14** the cation and anion are discrete. Furthermore, the iridium–nitrogen(imine) bond lengths in **15** are longer [2.111(6) and 2.117(7) Å] than those for **14** reflecting the poorer donor properties for the bisadamantylimine ligand.

3. Conclusions

Three new fluoroaryl α-diimines have been synthesised by condensation of glyoxal with fluorinated anilines at elevated temperatures. X-ray structural characterisations reveal that these adopt an *E* geometry at the imino unit. The new fluoroaryl α-diimines, and related non-fluorinated ligands, coordinate to rhodium(I) and iridium(I) centres to generate stable α-diimine-COD and α-diimine-CO cationic complexes that are valuable derivatives for further synthetic chemistry.

4. Experimental

4.1. General experimental procedures

Proton, ^{13}C and ^{19}F NMR spectroscopic studies were carried out on a Bruker DPX300 spectrometer at 300.14, 75.47 and 282.41 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^{1}H and ^{13}C NMR spectra were referenced to external SiMe$_4$ and ^{19}F NMR spectra to external CFCl$_3$. Elemental analyses were performed either by the Elemental Analysis Service at the London Metropolitan University. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. IR spectra were recorded as solid samples on a Perkin Elmer Spectrum One FT-IR spectrometer. 1,4-Bis(2,4,6-trimethylphenyl)-1,4-diaza-1,3-butadiene (**L1**), 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**L2**), 1,4-bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene (**L3**)

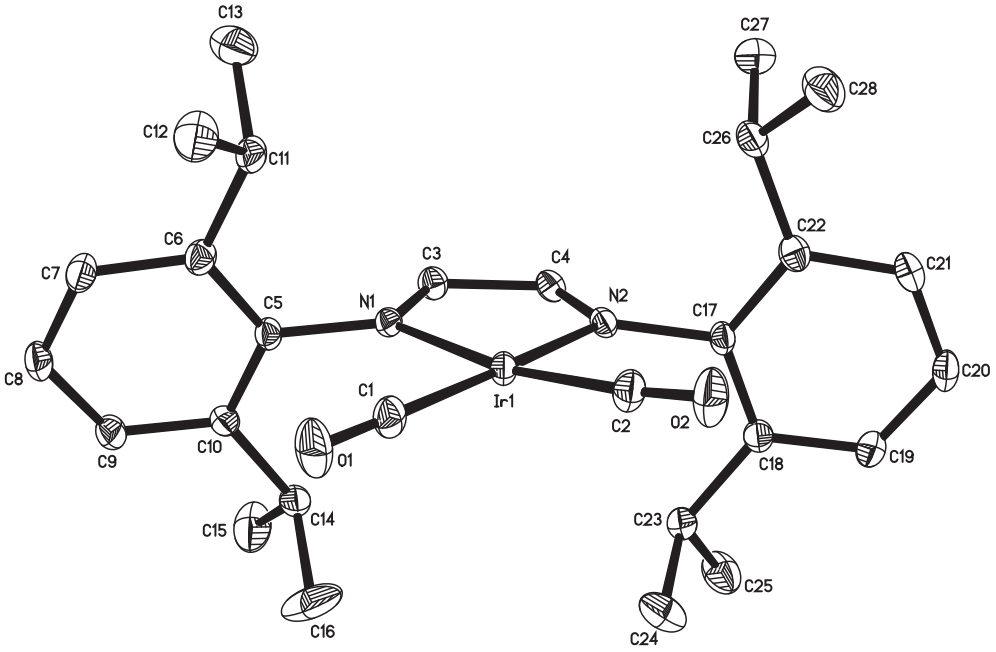

Fig. 2. Molecular structure of the cationic unit in **14** with 30% displacement ellipsoids. H atoms and BF$_4^-$ anion have been omitted for clarity.

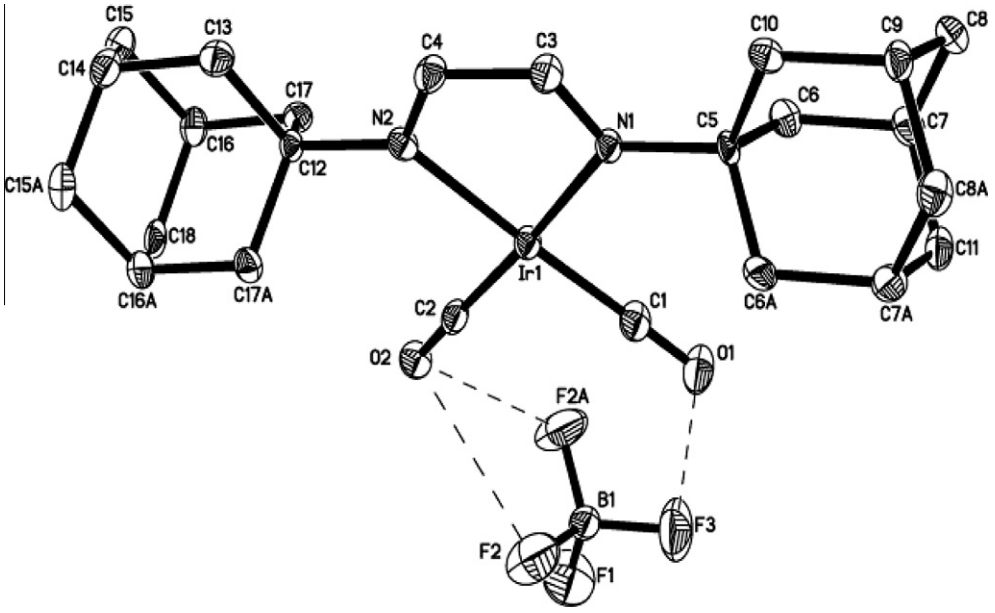

Fig. 3. Molecular structure of **15** with 30% displacement ellipsoids; dotted lines show O···F interactions. H atoms and lattice CH_2Cl_2 have been omitted for clarity.

Table 2
Selected bond length (Å) and bond angle (°) data for **14** and **15**.

$[Ir(CO)_2(RNCHCHNR)]^+[BF_4]^-$	R = 2,6-$C_6H_3{}^iPr_2$ (**14**)	R = adamantyl (**15**)
Bond lengths		
Ir(1)–C(1)	1.866(3)	1.836(9)
Ir(1)–C(2)	1.861(3)	1.866(10)
Ir(1)–N(1)	2.080(2)	2.111(6)
Ir(1)–N(2)	2.074(2)	2.117(7)
N(1)–C(3)	1.270(2)	1.277(10)
N(2)–C(4)	1.279(3)	1.264(10)
N(1)–C(5)	1.452(3)	1.488(9)
N(2)–C(17/C12)	1.458(3)	1.502(10)
C(1)–O(1)	1.134(3)	1.141(10)
C(1)–O(2)	1.136(3)	1.124(10)
Av B–F	1.388	1.354
Bond angles		
C(1)–Ir(1)–C(2)	90.11(12)	84.5(4)
N(1)–Ir(1)–N(2)	77.60(9)	78.0(3)
N(1)–C(3)–C(4)	116.5(3)	117.6(7)
N(2)–C(4)–C(3)	116.0(3)	118.7(8)

and 1,4-bisadamantyl-1,4-diaza-1,3-butadiene (***L4***) were prepared by the literature routes [18–20].

4.2. Synthesis of 1,4-bis(4-fluorophenyl)-1,4-diaza-1,3-butadiene (*L5*)

A solution of glyoxal (19.620 g of a 40% aqueous solution, 135 mmol) in *n*-propanol (50 cm^3) was added slowly to a stirred solution of *para*-fluoroaniline (30.000 g, 270 mmol) in *n*-propanol (50 cm^3) at room temperature. Once addition was complete, the yellow solution was heated to 60 °C for 3 h. The volume of solvent was reduced *in vacuo* to ca. 15 cm^3, and the resulting yellow precipitate was collected by filtration and washed with ice-cold methanol, giving the product as a pale yellow powder in 52% yield. M.p. 128–129 °C. *Anal.* Calc. for $C_{14}H_{10}F_2N_2$: C, 68.83; H, 4.13; N, 11.47. Found: C, 68.81; H, 4.06; N, 11.49%. ν_{max}/cm^{-1} 1605s (CN), 1557w, 1496s, 1031s, 1221s, 1156s, 826s. ^1H NMR ($CDCl_3$): 8.35 (s, 2H, NC*H*CH), 7.31 (dd, 4H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HF}$ = 4.0 Hz, 3-C*H*), 7.15 (d, 4H, $^3J_{HH}$ = 8.5 Hz, 2-C*H*). $^{19}F\{^1H\}$ ($CDCl_3$): −113.7 (s, 4-C*F*). ^{13}C NMR ($CDCl_3$): 162.4 (d, $^1J_{CF}$ = 248 Hz, 4-*C*), 159.3 (s, HCN), 146.0 (s, 1-*C*), 123.0 (d, $^3J_{CF}$ = 9 Hz, 2-*C*), 116.3 (d, $^2J_{CF}$ = 23 Hz, 3-*C*). *m*/*z* (FAB) 245 ($[MH]^+$). Acc. Mass: $C_{14}H_{11}F_2N_2$ ($[MH]^+$), requires 245.08903, found 245.08900.

4.3. Synthesis of 1,4-bis(2,4-difluorophenyl)-1,4-diaza-1,3-butadiene (*L6*)

The title compound was isolated in a similar manner. M.p. 147–149 °C. ν_{max}/cm^{-1} 3378br, 1603s (CN), 1505vs, 1429s, 1262s, 1141s, 957s, 848s, 800s, 722s (solid state). ^1H NMR ($CDCl_3$): 8.49 (s, 2H, NC*H*CH), 7.29 (m, 2H, 3-C*H*), 6.95 (m, 4H, 5-/6-C*H*). $^{19}F\{^1H\}$ ($CDCl_3$): −109.5 (s, 2F, 2-C*F*), −119.0 (s, 2F, 4-C*F*). ^{13}C NMR ($CDCl_3$): 162.2 (dd, $^1J_{CF}$ = 251 Hz, $^3J_{CF}$ = 11 Hz, 4-*C*), 161.4 (s, HCN), 156.1 (dd, $^1J_{CF}$ = 256 Hz, $^3J_{CF}$ = 12 Hz, 2-*C*), 134.2 (d, $^2J_{CF}$ = 10 Hz, 1-*C*), 122.4 (d, $^3J_{CF}$ = 9 Hz, 6-*C*), 111.9 (d, $^2J_{CF}$ = 22 Hz, 5-*C*), 105.2 (t, $^2J_{CF}$ = 25 Hz, 3-*C*). *m*/*z* (+FAB) 281 ($[MH]^+$). Acc. Mass: $C_{14}H_9F_4N_2$ ($[MH]^+$), requires 281.07028, found 281.07019.

4.4. Synthesis of 1,4-bis(2,4,6-trifluorophenyl)-1,4-diaza-1,3-butadiene (*L7*)

The title compound was isolated in a similar manner. M.p. 163–165 °C. *Anal.* Calc. for $C_{14}H_6F_6N_2$: C, 53.16; H, 1.91; N, 8.86. Found: C, 53.23; H, 1.85; N, 8.75%. ν_{max}/cm^{-1} 3104br, 1589s (CN), 1508s, 1485s, 1446s, 1116s, 1038s, 996s, 845s, 786s, 724s, 654br. ^1H NMR ($CDCl_3$): 8.52 (s, 2H, NC*H*CH), 6.73 (t, 2H, $^3J_{HF}$ = 8.4 Hz, 3-C*H*). $^{19}F\{^1H\}$ NMR ($CDCl_3$): −108.8 (s, 4F, 2-C*F*), −118.9 (s, 2F, 4-C*F*). *m*/*z* (FAB) 317 ($[MH]^+$). Acc. Mass: $C_{14}H_7F_6N_2$ ($[MH]^+$), requires 317.05134, found 317.05140.

4.5. Synthesis of [Rh(COD)(*L1*)][BF_4] (*1*)

A solution of **L1** (154 mg, 0.526 mmol) in dichloromethane (5 cm^3) was added dropwise at room temperature to a stirred solution of $[Rh(COD)(MeCN)_2]^+[BF_4]^-$ (200 mg, 0.526 mmol) in dichloromethane (5 cm^3). Stirring was continued for 6 h, after which the deep green solution was added to diethyl ether (200 cm^3). The resulting deep green solid was recrystallised from dichloromethane/hexane, giving the product as an air-sensitive green solid in 92% yield. *Anal.* Calc. for $C_{28}H_{36}BF_4N_2Rh$: C, 56.93; H, 6.15; N, 4.75. Found: C, 56.95; H, 5.97; N, 4.87%. ν_{max}/cm^{-1} 2911br, 1592br (CN),

1477s, 1206s, 1029br ($[BF_4]^-$), 842s. ^{1}H NMR ($CDCl_3$): 8.15 (br s, 2H, NC*H*C*H*N), 6.85 (s, 4H, Ar-C*H*), 3.75 (br s, 4H, COD-C*H*), 2.38–2.22 (m, 16H, *ortho*-Ar-CH_3 and COD-CH_2), 2.21 (s, 6H, *para*-Ar-CH_3), 1.88 (m, 4H, COD-CH_2). ^{19}F{^{1}H} NMR ($CDCl_3$): −152.0 (s, $[BF_4]^-$). *m*/*z* (FAB) 503 ($[M-BF_4]^+$), 395 ($[M-BF_4$-COD$]^+$).

4.6. Synthesis of [Rh(COD)(**L2**)][BF_4] (**2**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{34}H_{48}BF_4N_2Rh$: C, 60.51; H, 7.17; N, 4.15. Found: C, 60.57; H, 7.04; N, 4.07%. ν_{max}/cm^{-1} 2964s, 1608br (CN), 1552w, 1461s, 1368s, 1056vs ($[BF_4]^-$), 806s. ^{1}H NMR ($CDCl_3$): 8.35 (br s, 2H, NC*H*C*H*N), 7.25 (t, 2H, $^3J_{HH}$ = 6.8 Hz, *para*-Ar-C*H*), 7.18 (d, 4H, $^3J_{HH}$ = 6.9 Hz, *meta*-Ar-C*H*), 3.84 (br s, 4H, COD-C*H*), 3.22 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, CH_3CH), 2.29 (m, 4H, COD-CH_2), 1.89 (m, 4H, COD-CH_2), 1.40 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3CH), 1.16 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3CH). ^{19}F{^{1}H} NMR ($CDCl_3$): −151.8 (s, $[BF_4]^-$). *m*/*z* (FAB) 587 ($[M-BF_4]^+$), 479 ($[M-BF_4-COD]^+$).

4.7. Synthesis of [Rh(COD)(**L3**)][BF_4] (**3**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{26}H_{32}BF_4N_2Rh$: C, 55.50; H, 5.74; N, 4.98. Found: C, 55.64; H, 5.93; N, 4.96%. ν_{max}/cm^{-1} 1591s (CN), 1471s, 1431s, 1199s, 1045br ($[BF_4]^-$). ^{1}H NMR ($CDCl_3$): 8.23 (br s, 2H, NC*H*C*H*N), 7.06 (m, 6H, ArH), 3.76 (s, 4H, COD-C*H*), 2.35 (m, 16H, Ar-CH_3 and COD-CH_2), 1.89 (m, 4H, COD-CH_2). ^{19}F{^{1}H} NMR ($CDCl_3$): −152.0 (s, $[BF_4]^-$). *m*/*z* (FAB) 475 ($[M-BF_4]^+$).

4.8. Synthesis of [Rh(COD)(**L5**)][BF_4] (**4**)

The title compound was isolated in a similar manner. ν_{max}/cm^{-1} 2922w, 1592s (CN), 1492s, 1231br, 1030s ($[BF_4]^-$), 840s. ^{1}H NMR ($CDCl_3$): 8.14 (br s, 2H, NC*H*C*H*N), 7.22 (m, 4H, *meta*-Ar-C*H*), 7.10 (d, 4H, $^3J_{HH}$ = 8.1 Hz, *ortho*-Ar-C*H*), 4.05 (br s, 4H, COD-C*H*), 2.37 (m, 4H, COD-CH_2), 1.85 (m, 4H, COD-CH_2). ^{19}F{^{1}H} NMR ($CDCl_3$): −111.8 (s, 2F, 4-C*F*), −149.8 (s, 4F, $[BF_4]^-$). *m*/*z* (FAB) 455 ($[M-BF_4]^+$), 347 ($[M-BF_4-COD]^+$).

4.9. Synthesis of [Rh(COD)(**L6**)][BF_4] (**5**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{22}H_{20}BF_8N_2Rh$: C, 45.67; H, 3.49; N, 4.84. Found: C, 45.74; H, 3.51; N, 4.80%. ν_{max}/cm^{-1} 1597s (CN), 1500s, 1240br, 1159s, 1032s ($[BF_4]^-$). ^{1}H NMR (d^6-DMSO): 8.54 (s, 2H, NC*H*C*H*N), 7.63 (m, 2H, ArH), 7.42 (m, 2H, ArH), 7.18 (m, 2H, ArH), 4.00 (br s, 4H, COD-C*H*), 2.42 (m, 4H, COD-CH_2), 1.71 (m, 4H, COD-CH_2). ^{19}F{^{1}H} NMR (d^6-DMSO): −110.1 (s, 2F, 2-C*F*), −119.0 (s, 2F, 4-C*F*), −148.2 (s, 4F, $[BF_4]^-$). *m*/*z* (FAB) 491 ($[M-BF_4]^+$), 383 ($[M-BF_4-COD]^+$).

4.10. Synthesis of [Ir(COD)(**L1**)][BF_4] (**6**)

The title compound was isolated in a similar manner. NMR spectra were recorded at −60 °C. *Anal.* Calc. for $C_{28}H_{36}BF_4IrN_2$: C, 49.45; H, 5.34; N, 4.12. Found: C, 49.59; H, 5.27; N, 4.10%. ν_{max}/cm^{-1} 2924w, 1614br (CN), 1480br, 1385s, 1215s, 1028s ($[BF_4]^-$) (solid state). ^{1}H NMR ($CDCl_3$): 8.76 (s, 2H, NC*H*C*H*N), 6.87 (s, 4H, *meta*-C*H*), 3.92 (br s, 4H, COD-C*H*), 2.24 (s, 12H, *ortho*-CH_3), 2.09 (s, 6H, *para*-CH_3), 2.15–1.60 (m, 8H, COD-CH_2). ^{19}F{^{1}H} NMR ($CDCl_3$); −152.1 (s, $[BF_4]^-$). *m*/*z* (FAB) 593 ($[M-BF_4]^+$).

4.11. Synthesis of [Ir(COD)(**L2**)][BF_4] (**7**)

The title compound was isolated in a similar manner. NMR spectra were recorded at −60 °C. *Anal.* Calc. for $C_{34}H_{48}BF_4IrN_2.CH_2Cl_2$: C, 49.50; H, 5.94; N, 3.30. Found: C, 49.95; H, 5.84; N, 3.32%. ν_{max}/cm^{-1} 2958s, 1611br (CN), 1457s, 1435w, 1365s, 1030s ($[BF_4]^-$) (solid state). ^{1}H NMR ($CDCl_3$): 9.03 (s, 2H, NC*H*C*H*N), 7.29 (t, 2H, $^3J_{HH}$ = 8.8 Hz, *para*-C*H*), 7.20 (d, 4H, $^3J_{HH}$ = 8.9 Hz, *meta*-C*H*), 4.08 (br s, 4H, COD-C*H*), 3.12 (sep, 4H, $^3J_{HH}$ = 6.9 Hz, CH_3CH), 2.10–1.55 (m, 8H, COD-CH_2), 1.35 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH_3CH), 1.17 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH_3CH). ^{19}F{^{1}H} NMR ($CDCl_3$): −152.2 (s, $[BF_4]^-$). *m*/*z* (FAB) 677 ($[M-BF_4]^+$).

4.12. Synthesis of [Ir(COD)(**L4**)][BF_4] (**8**)

The title compound was isolated in a similar manner. NMR spectra were recorded at −60 °C. *Anal.* Calc. for $C_{30}H_{44}BF_4IrN_2$: C, 50.59; H, 6.23; N, 3.94. Found: C, 50.68; H, 6.05; N, 4.02%. ν_{max}/cm^{-1} 2908s, 2857s, 1634br (CN), 1452m, 1365m, 1306m, 1054vs ($[BF_4]^-$) (solid state). ^{1}H NMR ($CDCl_3$): 8.84 (s, 2H, NC*H*C*H*N), 3.89 (br s, 4H, COD-C*H*), 2.30–1.50 (m, 38H, Ada-CH_2/C*H* and COD-CH_2). ^{19}F{^{1}H} NMR ($CDCl_3$): −150.6 (s, $[BF_4]^-$). *m*/*z* (FAB) 625 ($[M-BF_4]^+$), 517 ($[M-BF_4-COD]^+$).

4.13. Synthesis of [Rh(CO)$_2$(**L1**)][BF_4] (**9**)

Carbon monoxide was bubbled through a stirred solution of **1** (200 mg, 0.339 mmol) in dichloromethane (5 cm^3) at room temperature for 30 min, after which the red solution was poured into diethyl ether (200 cm^3). The precipitate was collected and recrystallised from dichloromethane/hexane, giving the product as air-sensitive deep red needles in quantitative yield. *Anal.* Calc. for $C_{22}H_{24}BF_4N_2O_2Rh$: C, 49.06; H, 4.50; N, 5.20. Found: C, 49.04; H, 4.56; N, 5.26%. ν_{max}/cm^{-1} 2109s (CO), 2071s (CO), 1623s (CN), 1606s (CN), 1480br, 1212s, 1052vs ($[BF_4]^-$). ^{1}H NMR ($CDCl_3$): 8.31 (br s, 2H, NC*H*C*H*N), 6.94 (m, 4H, *meta*-Ar-C*H*), 2.32 (s, 12H, *ortho*-CH_3), 2.25 (s, 6H, para-CH_3). ^{19}F NMR ($CDCl_3$): −151.2 (s, $[BF_4]^-$). *m*/*z* (+FAB) 451 ($[M-BF_4]^+$), 423 ($[M-BF_4-CO]^+$), 395 ($[M-BF_4-2CO]^+$).

4.14. Synthesis of [Rh(CO)$_2$(**L2**)][BF_4] (**10**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{28}H_{36}BF_4N_2O_2Rh$: C, 54.00; H, 5.83; N, 4.50. Found: C, 54.20; H, 5.68; N, 4.42%. ν_{max}/cm^{-1} 2965br, 2102s (CO), 2041s (CO), 1620w (CN), 1589w (CN), 1462s, 1360s, 1033vs ($[BF_4]^-$), 796s, 751s. ^{1}H NMR ($CDCl_3$): 8.43 (br s, 2H, NC*H*C*H*N), 7.36 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *para*-Ar-C*H*), 7.3 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *meta*-Ar-C*H*), 3.20 (sep, 4H, $^3J_{HH}$ = 6.7 Hz, CH_3CH), 1.35 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3CH), 1.21 (d, 12H, $^3J_{HH}$ = 6.5 Hz, CH_3CH). ^{19}F{^{1}H} NMR ($CDCl_3$): −151.1 (s, $[BF_4]^-$). *m*/*z* (FAB) 535 ($[M-BF_4]^+$), 507 ($[M-BF_4-CO]^+$), 479 ($[M-BF_4-2CO]^+$).

4.15. Synthesis of [Rh(CO)$_2$(**L3**)][BF_4] (**11**)

The title compound was isolated in a similar manner. ν_{max}/cm^{-1} 2107s (CO), 2067s (CO), 1622m (CN), 1472s, 1201s, 1023vs ($[BF_4]^-$), 779s. ^{1}H NMR ($CDCl_3$): 8.42 (br s, 2H, NC*H*C*H*N), 7.05 (m, 6H, *meta*-Ar-C*H*), 2.38 (s, 12H, CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$): −150.7 (s, $[BF_4]^-$). *m*/*z* (+FAB) 423 ($[M-BF_4]^+$), 395 ($[M-BF_4-CO]^+$), 367 ($[M-BF_4-2CO]^+$).

4.16. Synthesis of [Rh(CO)$_2$(**L5**)][BF_4] (**12**)

The title compound was isolated in a similar manner. ν_{max}/cm^{-1} 2103s (CO), 2053s (CO), 1594s (CN), 1498s, 1239s, 1035vs ($[BF_4]^-$), 843s. ^{1}H NMR ($CDCl_3$): 8.35 (br s, 2H, NC*H*C*H*N), 7.52 (m, 4H, *meta*-Ar-C*H*), 7.17 (d, 4H, $^3J_{HH}$ = 8.1 Hz, *ortho*-Ar-C*H*). ^{19}F{^{1}H} NMR ($CDCl_3$): −108.0 (s, 2F, 4-C*F*), −149.1 (s, 4F, $[BF_4]^-$). *m*/*z* (+FAB) 403 ($[M-BF_4]^+$), 375 ($[M-BF_4-CO]^+$), 347 ($[M-BF_4-2CO]^+$).

Table 3
Crystal data and structure refinement of compounds **L5**, **L7**, **14** and **15**.

	L5	**L7**	**14**	**15**
Formula	$C_{14}H_{10}F_2N_2$	$C_{14}H_6F_6N_2$	$C_{28}H_{36}BF_4IrN_2O_2$	$C_{25}H_{34}BCl_2F_4IrN_2O_2$
Formula weight	244.24	316.21	711.60	744.45
T (K)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$Pnma$
Unit cell dimensions				
a (Å)	3.9447(19)	3.8927(5)	10.7944(15)	23.76(3)
b (Å)	6.687(3)	5.8614(7)	13.8734(19)	6.671(9)
c (Å)	11.583(6)	25.979(3)	19.928(3)	17.18(2)
α (°)	102.716(7)	90	90	90
β (°)	94.496(8)	91.767(2)	102.544(2)	90
γ (°)	106.790(7)	90	90	90
U (Å^3)	282.0(2)	592.48(13)	2913.1(7)	2723(6)
Z	1	2	4	4
D_{calc} (mg m^{-3})	1. 438	1.772	1.623	1.816
μ (Mo Kα) (mm^{-1})	0.110	0.173	4.636	5.154
F(000)	126	316	1408	1464
Dimensions (mm)	0.29 × 0.10 × 0.05	0.38 × 0.12 × 0.09	0.35 × 0.16 × 0.12	0.26 × 0.05 × 0.03
Data collection range (°)	1.82–25.00	1.57–25.00	1.60–26.00	1.46–26.00
Data collection range	$-4 \leqslant h \leqslant 4$, $-7 \leqslant k \leqslant 7$, $-13 \leqslant l \leqslant 13$	$-4 \leqslant h \leqslant 4$, $-6 \leqslant k \leqslant 6$, $-30 \leqslant l \leqslant 30$	$-13 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 16$, $-24 \leqslant l \leqslant 24$	$-29 \leqslant h \leqslant 28$, $-8 \leqslant k \leqslant 8$, $-21 \leqslant l \leqslant 21$
Reflections	1999	4090	22 562	19 575
Unique reflections	978	1048	5719	2920
R_{int}	0.0475	0.0234	0.0304	0.0935
Completeness of data (%)	98.9	99.8	99.9	100.0
Absorption correction	empirical	empirical	empirical	integration
Maximum/minimum transmission factors	0.96/0.82	0.96/9.75	0.928/0.585	0.8252/0.4306
Data/restraints/parameters	978/0/82	1048/0/100	5719/0/351	2920/0/202
Goodness of fit on F^2	0.968	1.040	0.970	1.043
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0499, wR_2 = 0.1258	R_1 = 0.0330, wR_2 = 0.0806	R_1 = 0.0218, wR_2 = 0.0497	R_1 = 0.0395, wR_2 = 0.0928
R indices all data	R_1 = 0.0660, wR_2 = 0.1333	R_1 = 0.0394, wR_2 = 0.0839	R_1 = 0.0251, wR_2 = 0.0506	R_1 = 0.0545, wR_2 = 0.0978
Largest difference peak and hole (e Å^{-3})	0.253/−0.293	0.215/−0.192	1.586/−0.8533	1.774/−1.363

4.17. Synthesis of [Ir(CO)$_2$(**L1**)][BF$_4$] (**13**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{22}H_{24}BF_4IrN_2O_2$: C, 42.08; H, 3.86; N, 4.46. Found: C, 42.17; H, 3.96; N, 4.47%. ν_{max}/cm^{-1} 2095s (CO), 2025s (CO), 1619br (CN), 1605br (CN), 1558w, 1501w, 1445w, 1212w, 1058s ([BF$_4$]$^-$). ^{1}H NMR (CDCl$_3$): 8.68 (s, 2H, NC*H*C*H*N), 6.88 (s, 4H, *meta*-Ar-C*H*), 2.31 (s, 12H, *ortho*-Ar-C*H*$_3$), 2.25 (s, 6H, *para*-Ar-C*H*$_3$). ^{19}F{^{1}H} NMR (CDCl$_3$): −150.5 (s, [BF$_4$]$^-$). *m*/*z* (FAB) 541 ([M−BF$_4$]$^+$), 513 ([M−BF$_4$−CO]$^+$).

4.18. Synthesis of [Ir(CO)$_2$(**L2**)][BF$_4$] (**14**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{28}H_{36}BF_4IrN_2O_2$: C, 47.22; H, 5.10; N, 3.94. Found: C, 47.27; H, 4.94; N, 3.83. ν_{max}/cm^{-1} 2089s (CO), 2023s (CO), 1618br (CN), 1605br (CN), 1555w, 1500w, 1462br, 1361w, 1058s ([BF$_4$]$^-$). ^{1}H NMR (CDCl$_3$): 8.97 (br s, 2H, NC*H*C*H*N), 7.35 (t, 2H, $^3J_{HH}$ = 7.2 Hz, *para*-Ar-C*H*), 7.25 (d, 4H, $^3J_{HH}$ = 7.3 Hz, *meta*-Ar-C*H*), 3.19 (sep, 4H, $^3J_{HH}$ = 6.7 Hz, CH$_3$C*H*), 1.34 (d, 12H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$CH), 1.22 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$CH). ^{19}F{^{1}H} NMR (CDCl$_3$): −151.2 (s, [BF$_4$]$^-$). *m*/*z* (FAB) 625 ([M−BF$_4$]$^+$), 597 ([M−CO]$^+$).

4.19. Synthesis of [Ir(CO)$_2$(**L4**)][BF$_4$] (**15**)

The title compound was isolated in a similar manner. *Anal.* Calc. for $C_{24}H_{32}BF_4IrN_2O_2$: C, 40.04; H, 3.36; N, 4.67. Found: C, 40.99; H, 3.53; N, 4.63%. ν_{max}/cm^{-1} 2912br, 2076s (CO), 2004s (CO), 1629br (CN), 1453w, 1344w, 1034s ([BF$_4$]$^-$), 728s. ^{1}H NMR (CDCl$_3$): 8.82 (s, 2H, NC*H*C*H*N), 2.25–1.65 (m, 30H, Ada-C*H*$_2$/C*H*). ^{19}F{^{1}H} NMR (CDCl$_3$): −149.6 (s, [BF$_4$]$^-$). *m*/*z* (FAB) 573 ([M−BF$_4$]$^+$), 545 ([M−BF$_4$−CO]$^+$), 517 ([M−BF$_4$−2CO]$^+$).

4.20. X-ray crystallography

Data for **L5**, **L7**, **14** and **15** were collected on a Bruker APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation. Full details of the data collection and refinement are given in Table 3. The data were corrected for Lorentz and polarisation effects and empirical corrections applied. Structure solution by direct methods and structure refinement on F^2 employed SHELXTL version 6.10 [30]. The C–H hydrogen atoms were included in calculated positions (C–H = 0.95–1.00 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic coordinates, bond lengths and angles for **L5**, **L7**, **14** and **15** are available in the Supplementary crystallographic data; selected bond lengths and angles for **14** and **15** are listed in Table 2.

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Appendix A. Supplementary material

CCDC 724968–724972 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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