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Neutral and Cationic Fluorinated N-Heterocyclic Carbene Complexes of Rhodium and Iridium

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Transmetalation of the structurally characterized silver N-heterocyclic carbene (NHC) salt $[Ag(IpFMe)_2]^+$ (**1**, IpFMe = 1-pentafluorobenzyl-3-methylimidazol-2-ylidene) to $[Rh(COD)Cl]_2$ affords Rh(IpFMe)(COD)Cl (**2**). The analogous neutral iridium complex, Ir(IpFMe)(COD)Br (**5**), may be formed upon elimination of MeOH from $[Ir(COD)(OMe)]_2$ in the reaction with 1-pentafluorobenzyl-3-methylimidazolium bromide. Thermolysis of $[Ag(IpFMe)_2]^+$ with either **5** or $[Ir(COD)Cl]_2$ yields the cationic bis-NHC complex $[Ir(IpFMe)_2(COD)](AgX_2)$ (**6**, X = Cl, Br), which exists as a mixture of conformers in solution. Addition of CO or AgOTf to **2** gives $Rh(IpFMe)(CO)_2Cl$ (**3**) and Rh(IpFMe)(COD)(OTf) (**4**), respectively. The molecular structures of compounds **1**−**6** have been determined by X-ray crystallography.

Introduction

It is now over a decade since the first report of fluorous ponytails on tertiary phosphine ligands.[1] In the intervening time, considerable advances have been made[2] in employing fluorous biphasic catalysts in a range of reactions including hydroformylation,[3] oxidation,[4] and C−C bond formation.[5] Given the interest in this area, it is somewhat surprising that there have been very few reports of fluorinated N-heterocyclic carbene (NHC) ligands.[6] Since their reinvigoration at the start of the 1990s, NHCs have been the subject of considerable attention, as M−NHC complexes often show significantly enhanced stability, reactivity, and selectivity compared to their $M-PR_3$ counterparts in a host of catalytic reactions including alkene metathesis and Heck coupling.[7] Given that the attachment of fluorinated groups may significantly change ligand properties, we were interested in investigating fluorinated NHCs to assess (a) whether they lead to the generation of metal complexes with very different reactivities and catalytic capabilities from their hydrocarbon analogues and (b) whether they are at all susceptible to intramolecular C−F bond activation. The related process of C−H activation has now been seen in a number of N-aryl and N-alkyl NHC-containing metal complexes[8] and often proves to be reversible in the presence of H_2 or alcohol, effectively providing a hemilabile NHC linkage.

We report herein our results on the reactivity of the well-known group 9 metal precursors $[M(COD)Cl]_2$ (M = Rh, Ir; COD = η^4-1,5-cyclooctadiene) with the fluorinated N-heterocyclic carbene 1-pentafluorobenzyl-3-methylimidazol-2-ylidene (abbreviated IpFMe), which has recently been isolated as the silver salt **1** by McGrandle and Saunders.[9] These authors briefly described transmetalation reactions of **1** to give half-sandwich complexes of Rh and Ir. We have undertaken a study of the reaction of **1** with $[M(COD)Cl]_2$, which gives the neutral complex Rh(IpFMe)(COD)Cl (**2**) and cationic bis-IpFMe species $[Ir(IpFMe)_2(COD)]^+$ (**6**).

Results and Discussion

Elucidation of the Molecular Structure of 1. Only partial characterization of the silver salt of 1-pentafluorobenzyl-3-methylimidazol-2-ylidene (**1**) was previously reported, so it was unclear as to the exact formulation of the salt.[9] We have been

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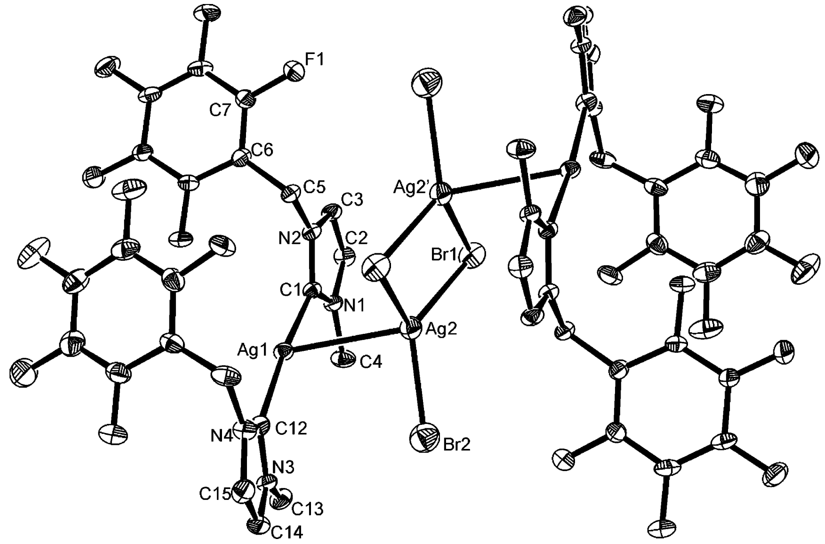
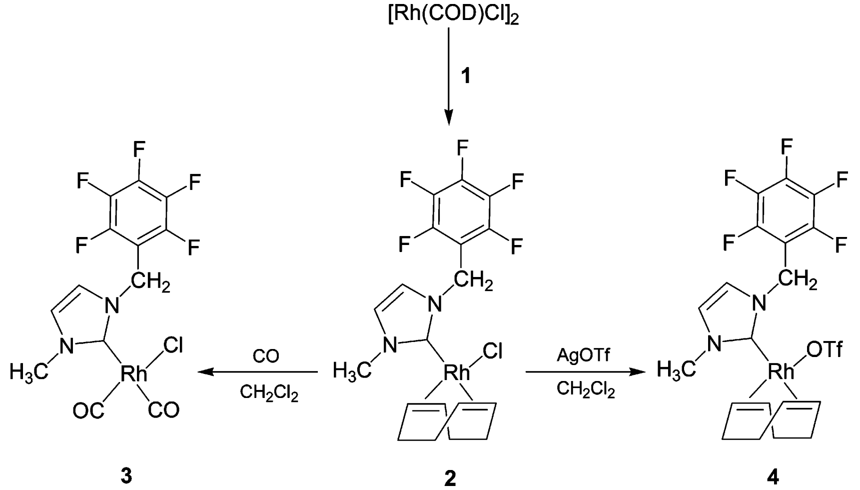


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Primed labeled atoms relate to those in the asymmetric unit by the $-x$, $-y+2$, $-z$ symmetry operation. Selected distances (Å) and angles (deg): Ag(1)−C(1) 2.084(10), Ag(1)−C(12) 2.094(10), Ag(1)−Ag(2) 2.9611(12), Ag(2)−Br(1) 2.6491(18), Ag(2)−Br(2) 2.5217(19), Ag(2)−Ag(2)′ 3.1851(18), C(1)−Ag(1)−C(12) 171.5(4).

Scheme 1. Synthesis of Rh(IpFMe)(COD)Cl (2), Rh(IpFMe)$(CO)_2$Cl (3), and Rh(IpFMe)(COD)(OTf) (4)



able to unequivocally establish the structure of **1** by X-ray crystallography, as shown in Figure 1, which reveals the presence of a tetranuclear complex of molecular formula $[Ag(IpFMe)_2]_2[Ag_2Br_4]$ with the anionic $[Ag_2Br_4]^{2-}$ fragment holding together the two cationic $Ag(NHC)_2$ species via Ag−Ag interactions. The $C_{NHC}-Ag-C_{NHC}$ bond angle is close to linear (171.5(4)°). Associated $Ag-C_{NHC}$ bond distances of 2.084(10) and 2.094(10) Å are similar to literature precedent for metrics observed in analogous silver NHC species.[10] A recent review of silver NHC complexes by Garrison and Youngs[11] provides a useful guide to the strength of the Ag···Ag interaction seen in **1**; the silver cation−silver anion distance of 2.9611(12) Å points to a strong argentophilic interaction.

Synthesis and Solution Reactivity of Rh(IpFMe)(COD)-Cl (2). Silver NHCs have been used with great success in transmetalation reactions for the synthesis of a wide range of metal carbene complexes since the first report by Wang and Lin in 1998.[12] As expected, reaction of **1** with $[Rh(COD)Cl]_2$ in a 1:1 ratio in CH_2Cl_2 generated the expected air-stable, four-coordinate complex Rh(IpFMe)(COD)Cl (**2**) (Scheme 1). This was isolated as a yellow microcrystalline solid in 95% yield and fully characterized by a combination of multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography (vide infra). In line with other reports on N-benzyl-derived NHC complexes,[13,14] a sharp AB pattern was observed for the diastereotopic $N-CH_2$ protons in the room-temperature ^1H NMR spectrum, symptomatic of a lack of rotation about the Rh−carbene bond. The ^{19}F NMR spectrum showed three multiplet signals for the C_6F_5 group integrating in the ratio 2:1:2, indicating that the fluoroaryl part of the ligand freely rotates. Confirmation of NHC binding to ^{103}Rh was evident from the $^{13}C\{^1H\}$ NMR spectrum, which displayed a low-field doublet (δ 184.4, $^1J_{CRh} = 51.8$ Hz) arising from the imidazol-2-ylidene carbon.

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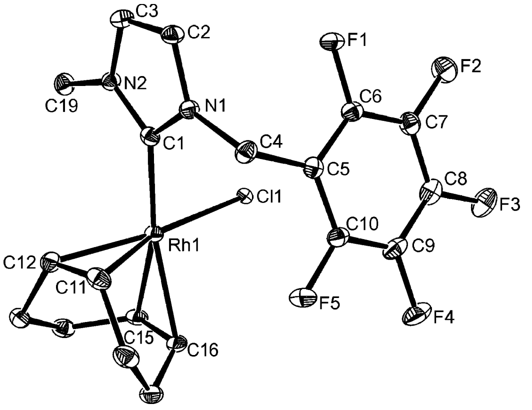


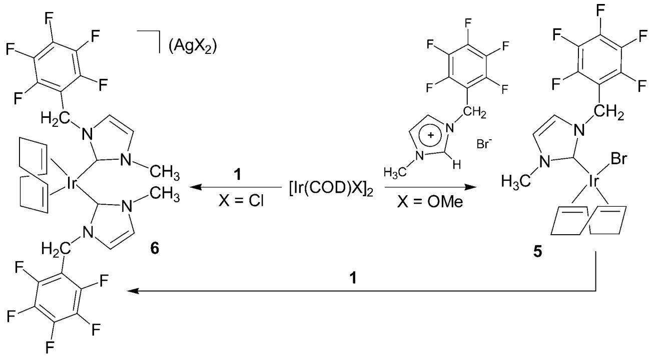
Figure 2. Molecular structure of **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Rh(1)−C(1) 2.022(4), Rh(1)−Cl(1) 2.4338(8), Rh(1)−C(11) 2.105(4), Rh(1)−C(12) 2.110(4), Rh(1)−C(15) 2.194(4), Rh(1)−C(16) 2.213(4), C(1)−Rh(1)−Cl(1) 89.46(15).

The electronic characteristics of the IpFMe ligand were probed by substitution of the COD ligand from **2** with CO to afford Rh(IpFMe)$(CO)_2$Cl (**3**). Stirring a CH_2Cl_2 solution of **2** under CO for 1 h resulted in the appearance of two ν_{CO} bands for the dicarbonyl complex **3** in the IR spectrum at 2003 and 2084 cm^{-1}. As expected, these frequencies are higher than those reported for a range of complexes with N-hydrocarbyl substituents, Rh(IMe)$(CO)_2$Cl (2076, 2006 cm^{-1}; IMe = 1,3-dimethylimidazol-2-ylidene),[15] Rh(tmiy)$(CO)_2$Cl (2076, 1995 cm^{-1}: tmiy = 1,3-bis(*p*-tolylmethyl)imidazol-2-ylidene),[14] or Rh(ImPy)$(CO)_2$Cl (2079, 2000 cm^{-1}; ImPy = imidazol[1,5-*a*]pyridine-3-ylidene),[16] confirming the poorer electron-donating ability of IpFMe. Characterization of **3** as a dicarbonyl complex was further provided by $^{13}C\{^1H\}$ NMR spectroscopy through the appearance of two doublet carbonyl resonances (confirmed by ^{13}CO labeling) at δ 186.0 ($^1J_{CRh} = 54.2$ Hz) and 182.6 ($^1J_{CRh} = 73.5$ Hz).

The chloride ligand in **2** proved susceptible to abstraction, as evidenced by the reaction with AgOTf, which gave the Rh(I) triflate complex Rh(IpFMe)(COD)(OTf) (**4**) in 85% yield (Scheme 1). The ^{19}F chemical shift of the triflate can be used to differentiate between bound and free anionic OTf,[17] and in the case of **4** the appearance of a singlet in the ^{19}F spectrum at δ −78.8 confirmed the coordination of the ligand to the Rh center. As a consequence, **2** was also reacted with $AgBF_4$ and $NaBAr^F_4$ ($BAr_4^F = B(3,5\text{-}C_6H_3(CF_3)_2)_4$) with the expectation that use of a noncoordinating anion would afford $[Rh(IpFMe)(COD)]^+$,[18] which might then undergo intramolecular C−F activation of the pentafluorobenzyl ring. However, in all cases upon reaction with either $[BF_4]^-$ or $[BAr^F_4]^-$ for short (15 min) or long (16 h) periods of time at either low (−78 °C) or ambient temperature, a mixture of inseparable products was formed.

Structural Characterization of 2−4. The molecular structures of **2**−**4** are shown in Figures 2, 3, and 4. As expected, all three structures have the anticipated square-planar arrangements at the metal centers, with the NCN plane of the carbene approximately perpendicular to the coordination plane at rhodium in each case. In the COD complexes **2** and **4**, the Rh−C_{NHC} and Rh−C_{COD} distances are unremarkable,[19] with the shorter mean M−COD and longer COD C═C distances found *trans* to IpFMe consistent with the larger *trans* influence of NHC compared to either halide or triflate.[14,20] There is a noticeable lengthening of the Rh−C_{NHC} distance in the structure of **3** (2.064(2) Å) due to the position of the IpFMe ligand *trans* to CO. Similarly, the two Rh−CO distances in **3** are significantly different (1.902(3), 1.842(3) Å), with the longer bond found *trans* to the NHC ligand. This CO *trans*-NHC distance is in line with other, albeit cationic, NHC-stabilized Rh−CO complexes.[21]

Scheme 2. Formation of Ir(IpFMe)(COD)Br (5) and $[Ir(IpFMe)_2(COD)]^+$ (6)



Iridium Complexes Bearing the IpFMe Ligand. The iridium analogue of **2**, Ir(IpFMe)(COD)Br (**5**), was readily prepared by stirring a dichloromethane solution of $[Ir(COD)(OMe)]_2$ with 1-pentafluorobenzyl-3-methylimidazolium bromide at room temperature (Scheme 2). The clearest indication for formation of **5** was provided by the $^{13}C\{^1H\}$ NMR spectrum, which displayed a characteristic M−C_{NHC} low-field singlet at 182.1 ppm. The X-ray crystal structure of **5** is shown in Figure 5 and reveals an Ir−C_{NHC} distance of 2.035(4) Å, consistent with similar structures in the literature.[14]

Upon heating **5** with additional silver salt **1** (0.5 equiv), a mixture of **5** and unreacted **1** was formed, along with the cationic bis-carbene complex $[Ir(IpFMe)_2(COD)][AgBr_2]$ (**6**).[22] Complex **6** could be formed as the sole product, albeit with both $[AgBr_2]^-$ and $[AgBrCl]^-$ present as anions (X-ray crystallography and FAB-MS show a 60% chloride:40% bromide ratio), upon

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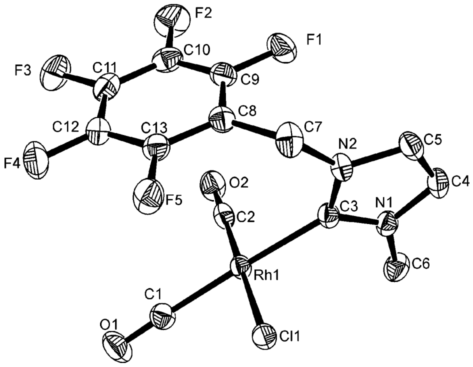

Figure 3. Molecular structure of **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Rh(1)−C(1) 1.902(3), Rh(1)−C(2) 1.842(3), Rh(1)−C(3) 2.064(2), Rh(1)−Cl(1) 2.3859(6), C(1)−Rh(1)−C(2) 91.37(11), C(1)−Rh(1)−C(3) 176.74(10), C(2)−Rh(1)−C(3) 91.89(10).

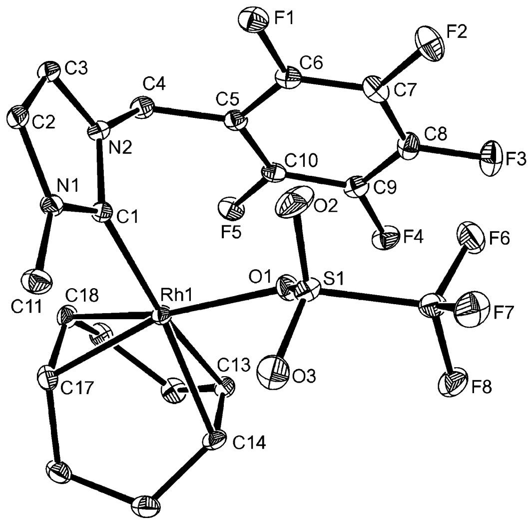

Figure 4. Molecular structure of **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Rh(1)−C(1) 2.034(2), Rh(1)−O(1) 2.1804(12), Rh(1)−C(13) 2.1991(17), Rh(1)−C(14) 2.1835(18), Rh(1)−C(17) 2.1021(17), Rh(1)−C(18) 2.1004(18), C(1)−Rh(1)−O(1) 92.876(6).

reacting **1** with $[Ir(COD)Cl]_2$ (3:1 molar ratio NHC:Ir) at 70 °C (Scheme 2). Red-orange crystals of $[Ir(IpFMe)_2(COD)][AgBr_2]$ were subsequently isolated, which proved suitable for X-ray crystallography (Figure 6). The metal center in **6** is located on a crystallographic 2-fold axis, which accounts for the C_2 symmetric arrangement of the IpFMe ligands in the cation.[23] The Ir−C_{NHC} distance (2.053(3) Å) and C_{NHC}−Ir−C_{NHC} angle (94.23(18)°) compare favorably with other reported cationic bis-NHC iridium species.[24]

In solution, both ^1H and ^{19}F NMR spectroscopy indicate that $[Ir(IpFMe)_2(COD)][AgBr_2]$ exists as a mixture of conformers, **6A** and **6B**.[25] Although extensive overlap of NHC and COD signals occurred in the proton spectrum in CD_2Cl_2 recorded at ambient temperature, two closely interpenetrating AB methylene resonances were apparent centered at δ 5.48 and 5.57 (Figure 7). In the ^{19}F NMR spectrum, two sets of partially overlapping multiplets are seen for the *meta*- and *para*-fluorine resonances (Figure 7). Only in the case of the *ortho*-signals are the resonances for the two conformers resolved, allowing a relative ratio of 1:0.42 to be determined.[26] This ratio remained unchanged upon cooling the system to 223 K. When the solvent was changed from CD_2Cl_2 to the more coordinating pyridine-d_5, the ratio of conformers at room temperature was only slightly different (1:0.47) and also remained constant between 248 and 208 K.

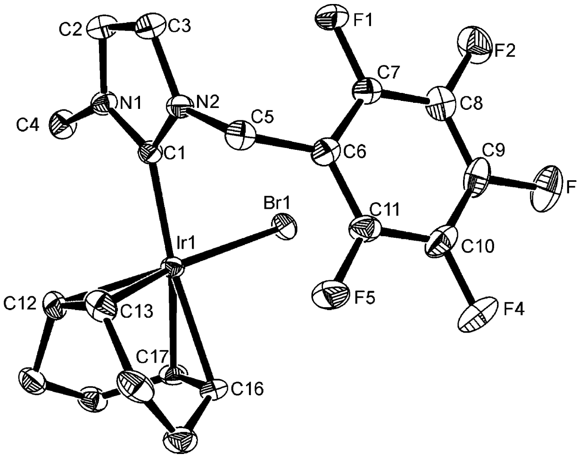

Figure 5. Molecular structure of **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−C(1) 2.035(4), Ir(1)−Br(1) 2.5096(4), Ir(1)−C(12) 2.117(4), Ir(1)−C(13) 2.106(4), Ir(1)−C(16) 2.196(4), Ir(1)−C(17) 2.176(4), C(1)−Ir(1)−Br(1) 90.29(10).

Efforts to shed more light on the structures of the two conformers **6A** and **6B** have proved to be unsuccessful. Thus both ^1H NOESY and $^1H-^{19}F$ 1D-HOE experiments reveal significant N*Me*/*CH*$_2C_6F_5$ and N*Me*/*o*-C_6F_5 interactions, suggesting that the two $-CH_2C_6F_5$ groups have an *anti* arrangement in both conformers.

Conclusions

Transfer of the fluorinated N-heterocyclic carbene ligand 1-pentafluorobenzyl-3-methylimidazol-2-ylidene (IpFMe) from silver has been used to form four-coordinate, square-planar complexes of rhodium and iridium. While rhodium shows little tendency to incorporate a second NHC ligand, the opposite is true with iridium, and formation of the cationic bis-IpFMe complex $[Ir(IpFMe)_2(COD)]^+$ (**6**) is very facile. As expected, the presence of the N-pentafluorobenzyl substituent reduces the electron-donating power of the NHC ligand judging by the values of ν_{CO} for the rhodium dicarbonyl complex **3**.[27]

Given the catalytic activity associated with the group 9 metal complexes M(NHC)(COD)X and $[M(NHC)_2(COD)]^+$,[19b,e,20,28] it now remains to be established whether the incorporation of fluorinated substituents will induce significantly different catalytic reactivity. Similarly, while we have so far been unable to find any willingness for the IpFMe ligand to undergo intramolecular activation of the C_6F_5 ring, this may be due to

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(23) Disorder bedeviled the structure, in particular, the perfluorinated phenyl ring, which was modeled over two positions in a 60:40 ratio.

(24) Mas-Marzá, E.; Peris, E.; Castro-Rodríguez, I.; Meyer, K. *Organometallics* **2005**, *24*, 3158.

(25) Conformers have not been observed for the isoelectronic d^8 species *cis*-Pd(1-benzyl-3- methylimidazol-2-ylidene)$_2Cl_2$. Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617*−*618*, 546.

(26) This same ratio of conformers was observed upon dissolution of crystalline samples of **6** containing either a mixture of $[AgBrCl]^-/[AgBr_2]^-$ anions or just $[AgBr_2]^-$.

(27) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

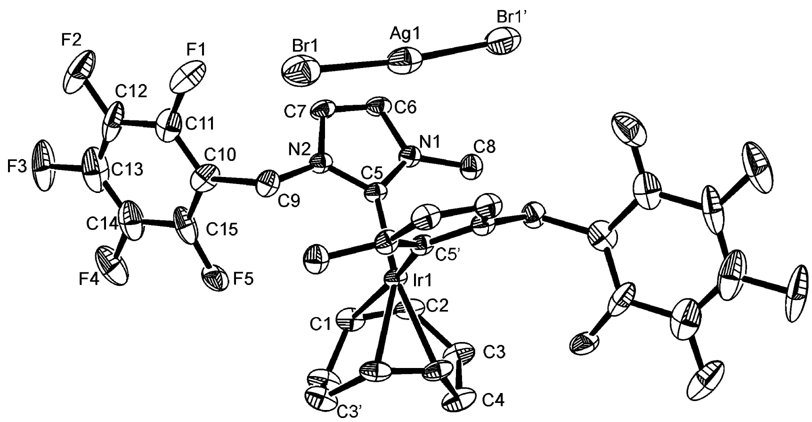

Figure 6. Molecular structure of **6**. Thermal ellipsoids are shown at the 30% probability level. Primed labeled atoms relate to those in the asymmetric unit by the $-x, y, -z+1/2$ symmetry operation. Hydrogen and disordered atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−C(5) 2.053(3), Ir(1)−C(1) 2.200(4), Ir(1)−C(2) 2.179(4), C(5)−Ir(1)−C(5)′ 94.23(18).

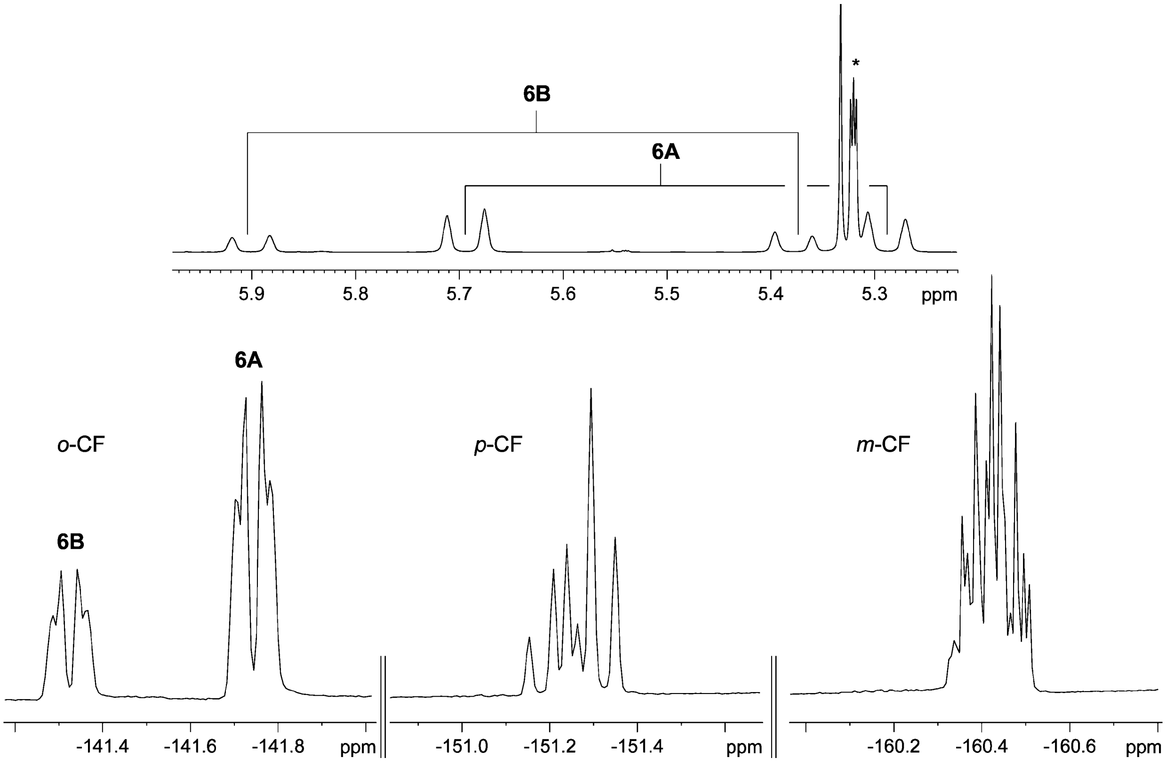

Figure 7. ^1H (top) and ^{19}F (bottom) NMR spectra in CD_2Cl_2 (298 K) showing the existence of the two conformers, **6A** and **6B**, in solution (solvent resonance indicated by *).

inappropriate metal:ancillary ligand combinations or, simply, the inability of the pentafluorobenzyl group to orient itself correctly for activation. To this end, further studies are ongoing.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under argon. Solvents were purified using an MBraun SPS solvent system (CH_2Cl_2), distilled from sodium under nitrogen (hexane) or distilled under a nitrogen atmosphere from Mg/I_2 (ethanol). Literature routes were used to prepare **1**,[9] $[Rh(COD)Cl]_2$,[29] and $[Ir(COD)X]_2$ (X = Cl,[30] OMe[31]). NMR spectra were recorded in dry CD_2Cl_2 or C_5D_5N on Bruker Avance 300 and 400 MHz NMR spectrometers and referenced to solvent resonances as follows: CD_2Cl_2, δ 5.32 (^1H), 53.73 ($^{13}C\{^1H\}$); C_5D_5N, δ 8.72 (^1H), 149.50 ($^{13}C\{^1H\}$). All NMR data are quoted at 298 K, unless otherwise stated. ^{19}F NMR chemical shifts were referenced to $CFCl_3$ at δ 0.0. ^1H COSY, $^1H-^{13}C\{^1H\}$ HMQC, and HMBC experiments were performed using standard Bruker

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[28] (a) Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. *J. Org. Chem.* **2006**, *71*, 91. (b) Bortenschlager, M.; Schütz, J.; von Preysing, D.; Nuyken, O.; Herrmann, W. A.; Weberskirch, R. *J. Organomet. Chem.* **2005**, *690*, 6233. (c) Andavan, G. T. S.; Bauer, E. B.; Letko, C. S.; Hollis, T. K.; Tham, F. S. *J. Organomet. Chem.* **2005**, *690*, 5938. (d) Özdemir, I.; Demir, S.; Çetinkaya, B.; Çetinkaya, E. *J. Organomet. Chem.* **2005**, *690*, 5849. (e) Mas-Marzá, E.; Poyatos, M.; Sanaú, M.; Peris, E. *Inorg. Chem.* **2004**, *43*, 2213. (f) Zarka, M. T.; Bortenschlager, M.; Wurst, K.; Nuyken, O.; Weberskirch, R. *Organometallics* **2004**, *23*, 4817. (g) Poyatos, M.; Uriz, P.; Mata, J. A.; Claver, C.; Fernandez, E.; Peris, E. *Organometallics* **2003**, *22*, 440. (h) Poyatos, M.; Mas-Marzá, E.; Mata, J. A.; Sanaú, M.; Peris, E. *Eur. J. Inorg. Chem.* **2003**, 1215. (i) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617−618*, 70. (j) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913. (k) Çetinkaya, B.; Özdemir, I.; Dixneuf, P. H. *J. Organomet. Chem.* **1997**, *534*, 153. (l) Enders, D.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3571. (m) Herrmann, W. A.; Goossen, L. J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2805.

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pulse sequences. The IR spectrum of **3** was recorded in CH_2Cl_2 solution on a Nicolet Protégé 460 FTIR spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK.

Rh(IpFMe)(COD)Cl (2). A suspension of $[Rh(COD)Cl]_2$ (0.054 g, 0.11 mmol) and **1** (0.1 g, 0.12 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature for 1 h (as usual for syntheses involving silver salts, the reaction was performed with the exclusion of light). The reaction mixture was filtered by cannula and the filtrate concentrated in vacuo to yield Rh(IpFMe)(COD)Cl (**2**) (0.053 g, 95%) as a yellow solid. Crystals suitable for X-ray crystallography were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.90 (s, 1H, NCH=CHN), 6.88 (s, 1H, NCH=CHN), 5.68 (AB, $\Delta\nu$ = 36.9 Hz, $^2J_{HH}$ = 14.8 Hz, 2H, CH_2), 4.92 (br s, 2H, CH_{COD}), 4.08 (s, 3H, CH_3), 3.37 (m, 1H, CH_{COD}), 3.28 (m, 1H, CH_{COD}), 2.54−2.26 (m, 4H, $(CH_2)_{COD}$), 2.00 (m, 2H, $(CH_2)_{COD}$), 1.87 (m, 2H, $(CH_2)_{COD}$). ^{13}C{^{1}H} NMR: δ 184.4 (d, $^1J_{CRh}$ = 51.8 Hz, Rh−C), 147.7 (m, C_{ipso}), 144.4 (m, CF), 139.7 (m, CF), 136.4 (m, CF), 122.4 (s, NCH), 121.5 (s, NCH), 99.3 (d, $^1J_{CRh}$ = 6.8 Hz, CH_{COD}), 99.0 (d, $^1J_{CRh}$ = 6.8 Hz, CH_{COD}), 69.3 (d, $^1J_{CRh}$ = 14.7 Hz, CH_{COD}), 67.1 (d, $^1J_{CRh}$ = 14.7 Hz, CH_{COD}), 42.4 (s, CH_2), 38.2 (s, CH_3), 33.9 (s, $(CH_2)_{COD}$), 32.4 (s, $(CH_2)_{COD}$), 29.3 (s, $(CH_2)_{COD}$), 28.3 (s, $(CH_2)_{COD}$). ^{19}F NMR: δ −140.5 (m, 2F, *o*-CF), −154.2 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-CF), −162.4 (m, 2F, *m*-CF). Anal. Found: C, 44.44; H, 3.60; N, 5.44. $C_{19}H_{19}F_5N_2ClRh$ (508.70) Calc: C, 44.86; H, 3.76; N, 5.51.

Rh(IpFMe)(CO)$_2$Cl (3). Rh(IpFMe)(COD)Cl (0.19 g, 0.37 mmol) was added to an ampule and dissolved in CH_2Cl_2 (10 mL). The solution was freeze−pump−thaw degassed (×3), placed under 1 atm CO, and stirred for 5 min. A second freeze−pump−thaw degassing cycle (×3) was performed before addition of a fresh atmosphere of CO. The reaction mixture was then stirred for 1 h at room temperature before removal of the solvent. The resultant yellow residue was washed with hexane (2 × 5 mL) and dried in vacuo to yield a yellow solid (0.123 g, 72%). Crystals of **3** suitable for X-ray crystallography were obtained upon layering a CH_2Cl_2 solution with hexane. ^{1}H NMR (CD_2Cl_2, 400 MHz, 253 K): δ 7.01 (m, 2H, NCH=CHN), 5.53 (AB, $\Delta\nu$ = 217.3 Hz, $^2J_{HH}$ = 14.6 Hz, 2H, CH_2), 3.86 (s, 3H, CH_3). ^{13}C{^{1}H} NMR: δ 186.0 (d, $^1J_{CRh}$ = 54.2 Hz, Rh−CO), 182.6 (br d, $^1J_{CRh}$ = 73.5 Hz, Rh−CO), 176.3 (d, $^1J_{CRh}$ = 43.2 Hz, Rh−C), 147.2 (m, C_{ipso}), 144.6 (m, CF), 143.4 (m, CF), 140.9 (m, CF) 139.4 (m, CF), 136.8 (m, CF), 123.5 (s, NCH), 122.0 (s, NCH), 42.8 (s, CH_2), 38.9 (s, CH_3). ^{19}F NMR: δ −140.4 (m, 2F, *o*-CF), −153.1 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-CF), −161.7 (m, 2F, *m*-CF). IR (CH_2Cl_2, cm^{-1}): 2003 ν_{CO}, 2084 ν_{CO}. Anal. Found: C, 33.60; H, 1.35; N, 5.86. $C_{13}H_7F_5NO_2ClRh$ (456.55) Calc: C, 34.20; H, 1.55; N, 6.14. Despite repeated attempts, elemental analysis gave a low %C value.

Rh(IpFMe)(COD)(OTf) (4). A CH_2Cl_2 suspension of **2** (0.125 g, 0.247 mmol) and AgOTf (0.063 g, 0.245 mmol) was stirred at room temperature for 30 min (with light excluded) and then filtered by cannula. Removal of the solvent afforded **4** as a yellow-cream solid (0.130 g, 85%). Crystals suitable for X-ray crystallography were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.97 (br s, 1H, NCH=CHN), 6.94 (br s, 1H, NCH=CHN), 5.66 (AB, $\Delta\nu$ = 47.7 Hz, $^2J_{HH}$ = 15.0 Hz, 2H, CH_2), 4.88 (m, 2H, CH_{COD}), 4.09 (s, 3H, CH_3), 3.46 (m, 1H, CH_{COD}), 3.37 (m, 1H, CH_{COD}), 2.59−2.32 (m, 4H, $(CH_2)_{COD}$), 2.03 (m, 2H, $(CH_2)_{COD}$), 1.87 (m, 2H, $(CH_2)_{COD}$). ^{13}C{^{1}H} NMR: δ 179.8 (d, $^1J_{CRh}$ = 50.9 Hz, Rh−C), 147.7 (m, C_{ipso}), 144.4 (m, CF), 143.8 (m, CF), 140.3 (m, CF), 139.7 (m, CF), 136.6 (m, CF), 123.1 (s, NCH), 122.4 (s, NCH), 120.1 (q, $^1J_{CF}$ = 319.4 Hz, CF_3), 101.1 (d, $^1J_{CRh}$ = 6.8 Hz, CH_{COD}), 100.4 (d, $^1J_{CRh}$ = 6.8 Hz, CH_{COD}), 78.9 (d, $^1J_{CRh}$ = 14.4 Hz, CH_{COD}), 67.1 (d, $^1J_{CRh}$ = 14.4 Hz, CH_{COD}), 42.2 (s, CH_2), 38.2 (s, CH_3), 33.8 (s, $(CH_2)_{COD}$), 32.4 (s, $(CH_2)_{COD}$), 28.8 (s, $(CH_2)_{COD}$), 27.9 (s, $(CH_2)_{COD}$). ^{19}F NMR: δ −78.8 (s, 3F, OTf), −140.9 (m, 2F, *o*-CF), −153.7 (t, $^3J_{FF}$ = 23.0 Hz, 1F, *p*-CF), −162.1 (m, 2F, *m*-CF). Anal. Found: C, 38.66; H, 3.07; N, 4.45. $C_{20}H_{19}F_8N_2O_3SRh$ (622.26) Calc: C, 38.60; H, 3.08; N, 4.50.

Ir(IpFMe)(COD)Br (5). 1-Pentafluorobenzyl-3-methylimidazolium bromide (0.67 g, 1.95 mmol) and $[Ir(COD)(OMe)]_2$ (0.43 g, 0.89 mmol) were dissolved in CH_2Cl_2 (15 mL), and the mixture was stirred at room temperature for 1 h, resulting in a slight darkening of the yellow solution. The reaction mixture was filtered via cannula through a plug of silica (which was subsequently washed with 2 × 10 mL of CH_2Cl_2) and the resulting filtrate concentrated under vacuum to yield **5** as a yellow solid (0.473 g, 47%). X-ray quality crystals were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.90 (br m, 1H, NCH=CHN), 6.88 (br s, 1H, NCH=CHN) 5.54 (AB, $\Delta\nu$ = 22.9 Hz $^2J_{HH}$ = 14.8 Hz, 2H, CH_2), 4.62 (m, 1H, CH_{COD}), 4.54 (m, 1H, CH_{COD}) 3.91 (s, 3H, CH_3), 3.05 (m, 1H, CH_{COD}), 2.87 (m, 1H, CH_{COD}), 2.28 (m, 2H, $(CH_2)_{COD}$), 2.12 (m, 2H, $(CH_2)_{COD}$), 1.85 (m, 2H, $(CH_2)_{COD}$) 1.61 (m, 2H, $(CH_2)_{COD}$). ^{13}C{^{1}H}: δ 182.1 (s, Ir−C), 147.4 (m, C_{ipso}), 144.9 (m, CF), 143.3 (m, CF), 140.7 (m, CF) 139.4 (m, CF), 136.9 (m, CF), 122.2 (s, NCH), 121.3 (s, NCH), 85.5 (s, CH_{COD}), 84.5 (s, CH_{COD}), 53.6 (s, CH_{COD}), 51.4 (s, CH_{COD}), 42.4 (s, CH_2), 38.0 (s, CH_3), 34.5 (s, $(CH_2)_{COD}$), 32.6 (s, $(CH_2)_{COD}$), 30.6 (s, $(CH_2)_{COD}$), 29.0 (s, $(CH_2)_{COD}$). ^{19}F NMR: δ −140.4 (m, 2F, *o*-CF), −154.2 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-CF), −162.4 (m, 2F, *m*-CF). Anal. Found: C, 35.44; H, 3.00; N, 4.32. $C_{19}H_{19}F_5N_2BrIr$ (642.47) Calc: C, 35.52; H, 2.98; N, 4.36.

[Ir(IpFMe)$_2$(COD)](AgBr$_2$) (6). A suspension of **1** (0.561 g, 0.68 mmol) and **5** (0.147 g 0.23 mmol) in CH_2Cl_2 (25 mL) was heated in an ampule fitted with a J. Youngs PTFE tap at 70 °C for 5 h (with light excluded). After being cooled to room temperature the mixture was filtered by cannula and the filtrate concentrated in vacuo to yield an orange-red solid. Dissolution in CH_2Cl_2 and layering with hexane afforded a mixture of colorless crystals of **1** and orange crystals of **6**. The mixture was washed with CH_2Cl_2 (3 × 5 mL) to remove the colorless crystals of **1**. The remaining solid was dried to yield a crystalline orange solid (0.136 g, 55%). Crystals of **6** suitable for X-ray crystallography were obtained by layering a CH_2Cl_2 solution with Et_2O. Conformer **6A**: ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.14 (m, 2H, NCH=CHN) 5.48 (AB, $\Delta\nu$ = 163.4 Hz $^2J_{HH}$ = 14.5 Hz, 4H, CH_2), 4.30 (m, CH_{COD}, 2H), 4.14 (s, 6H, CH_3), 3.78 (m, CH_{COD}, 2H), 2.45−2.29 (m, $(CH_2)_{COD}$, 4H), 2.16−1.94 (m, $(CH_2)_{COD}$, 4H. ^{13}C{^{1}H} NMR: δ 178.2 0 (s, Ir−C), 147.2 (m, C_{ipso}), 144.7 (m, CF), 143.7 (m, CF), 141.1 (m, CF), 139.5 (m, CF), 137.0 (m, CF), 124.3 (s, NCH), 120.6 (br s, NCH), 79.9 (m, CH_{COD}), 78.9 (m, CH_{COD}), 77.4 (m, CH_{COD}), 77.3 (m, CH_{COD}), 42.5 (m, CH_2), 39.1 (s, CH_3), 32.9 (s, $(CH_2)_{COD}$), 31.7 (s, $(CH_2)_{COD}$), 31.6 (s, $(CH_2)_{COD}$), 30.2 (s, $(CH_2)_{COD}$). ^{19}F NMR: δ −141.7 (m, 4F, *o*-CF), −151.3 (m, 2F, *p*-CF), −160.4 (m, 4F, *m*-CF). Conformer **6B**: ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.12 (m, 2H, NCH=CHN) 5.57 (AB, $\Delta\nu$ = 210.6 Hz $^2J_{HH}$ = 14.5 Hz, 4H, CH_2), 4.30 (m, CH_{COD}, 2H), 4.05 (s, 6H, CH_3), 3.78 (m, CH_{COD}, 2H), 2.45−2.29 (m, $(CH_2)_{COD}$, 4H), 2.16−1.94 (m, $(CH_2)_{COD}$, 4H). ^{13}C{^{1}H} NMR: δ 178.50 (s, Ir−C), 147.2 (m, C_{ipso}), 144.7 (m, CF), 143.7 (m, CF), 141.1 (m, CF), 139.5 (m, CF), 137.0 (m, CF), 124.3 (s, NCH), 120.6 (br s, NCH), 79.9 (m, CH_{COD}), 78.9 (m, CH_{COD}), 77.4 (m, CH_{COD}), 77.3 (m, CH_{COD}), 42.9 (m, CH_2), 39.2 (s, CH_3), 32.9 (s, $(CH_2)_{COD}$), 31.7 (s, $(CH_2)_{COD}$), 31.6 (s, $(CH_2)_{COD}$), 30.2 (s, $(CH_2)_{COD}$). ^{19}F NMR: δ −141.3 (m, 4F, *o*-CF), −151.3 (m, 2F, *p*-CF), −160.4 (m, 4F, *m*-CF). Anal. Found: C, 33.52; H, 2.40; N, 5.11. $C_{30}H_{26}F_{10}N_4Br_2AgIr$ (1092.71) Calc: C, 32.98; H, 2.40; N, 5.13. HRMS (EI) found (calcd for ^{193}Ir): 825.1588 (825.1622).

X-ray Crystallography. Single crystals of compounds **1**−**6** were analyzed at 150(2) K using graphite-monochromated Mo(Kα) radiation and a Nonius Kappa CCD diffractometer. Details of the data collections, solutions, and refinements are given in Table 1. The structures were uniformly solved using SHELXS-97[32] and

Table 1. Crystal Data and Structure Refinement for Compounds 1−6

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{44}H_{28}Ag_4Br_4F_{20}N_8$	$C_{19}H_{17}ClF_5N_2Rh$	$C_{13}H_7ClF_5N_2O_2Rh$	$C_{20}H_{19}F_8N_2O_3RhS$	$C_{19}H_{19}BrF_5IrN_2$	$C_{30.80}H_{27.60}AgBr_2Cl_{1.60}F_{10}IrN_4$
fw	1799.86	506.71	456.57	622.34	642.47	1160.38
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$Pbca$	$P2_1/n$	$P\bar{1}$	$C2/c$
a/Å	11.2700(1)	7.8590(1)	7.7990(1)	9.9760(1)	8.0270(1)	23.3480(3)
b/Å	8.5420(1)	9.2050(2)	12.4040(1)	8.6440(1)	9.0590(1)	11.2850(1)
c/Å	26.6020(3)	13.8360(3)	31.3860(3)	25.4620(3)	13.9810(2)	13.3300(2)
β/deg	90.671	76.938	90	97.060(1)	77.091(1)	96.708(1)
U/Å^3	2560.75(5)	948.01(3)	3036.24(5)	2179.01(4)	963.01(2)	3488.17(8)
Z	2	2	8	4	2	4
D_c/g cm^{-3}	2.334	1.775	1.998	1.897	2.216	2.210
μ/mm^{-1}	4.745	1.096	1.366	0.975	9.061	6.870
F(000)	1712	504	1776	1240	608	2206
cryst size/mm	0.20 × 0.20 × 0.05	0.25 × 0.20 × 0.10	0.40 × 0.40 × 0.30	0.50 × 0.40 × 0.40	0.20 × 0.20 × 0.15	0.13 × 0.13 × 0.05
θ range for data collection	3.54 to 30.06	3.80 to 27.98	3.53 to 29.97	4.11 to 27.48	3.70 to 27.50	3.59 to 30.23
index ranges	$-15 \leq h \leq 15$	$-10 \leq h \leq 10$	$-10 \leq h \leq 10$	$-12 \leq h \leq 12$	$-10 \leq h \leq 10$	$-32 \leq h \leq 32$
	$-12 \leq k \leq 12$	$-12 \leq k \leq 12$	$-17 \leq k \leq 17$	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$	$-15 \leq k \leq 15$
	$-37 \leq l \leq 37$	$-18 \leq l \leq 18$	$-44 \leq l \leq 44$	$-33 \leq l \leq 33$	$-18 \leq l \leq 18$	$-18 \leq l \leq 18$
no. of reflns collected	46 391	19 132	40 492	28 553	13 822	28 963
no. of ind reflns, R(int)	7459, 0.0707	4520, 0.0489	4387, 0.0553	4951, 0.0347	4368, 0.0374	5115, 0.0538
no. of reflns obsd (>2σ)	6588	3661	3412	4429	4339	4692
data completeness	0.995	0.988	0.993	0.994	0.986	0.986
abs corr	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan
max., min. transmn factors	0.76, 0.59	0.90, 0.82	0.67, 0.56	0.77, 0.77	0.28, 0.16	0.52, 0.41
no. of data/restraints/params	7459/0/365	4520/4/271	4387/0/218	4951/4/334	4368/4/265	5115/3/303
goodness-of-fit on F^2	1.029	1.037	1.057	1.034	1.124	1.092
R1, wR2 [$I > 2\sigma(I)$]	0.0926, 0.2775	0.0421, 0.1076	0.0320, 0.0851	0.0217, 0.0517	0.0316, 0.0810	0.0339, 0.0844
R1, wR2 (all data)	0.1055, 0.2968	0.0583, 0.1150	0.0482, 0.0917	0.0270, 0.0538	0.0317, 0.0811	0.0398, 0.0875
largest diff peak and hole/e Å^{-3}	3.921, −5.103	1.519, −0.939	1.207, −1.110	0.431, −0.464	2.746, −2.853	1.913, −2.575

refined using full-matrix least squares in SHELXL-97.[32] Convergence was uneventful, with the exception of the following noteworthy points. The asymmetric unit in **1** consisted of half a dimer molecule proximate to a crystallographic inversion center. In **6** the asymmetric unit also consisted of half of a cation and half an anion, with the central metal in each located on a crystallographic 2-fold rotation axis. A 60:40 disorder of carbons 9−15 and the fluorine atoms was also successfully modeled in **5**. Hydrogen atoms in the 1,5-COD moieties in structures **2**, **4**, **5**, and **6** were located and refined at a fixed distance from the relevant parent carbon. Analysis of the gross structure in **4** suggests the possible existence of C−H···O interactions involving the triflate oxygen atoms.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 603275 (compound **1**), 273558 (**2**), 603276 (**3**), 273559 (**4**), 603278 (**5**), and 603277 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

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