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C–H Activation with Iridium(III) and Rhodium(III) Alkyl Complexes Containing a 2,2′-Bipyridyl Ligand

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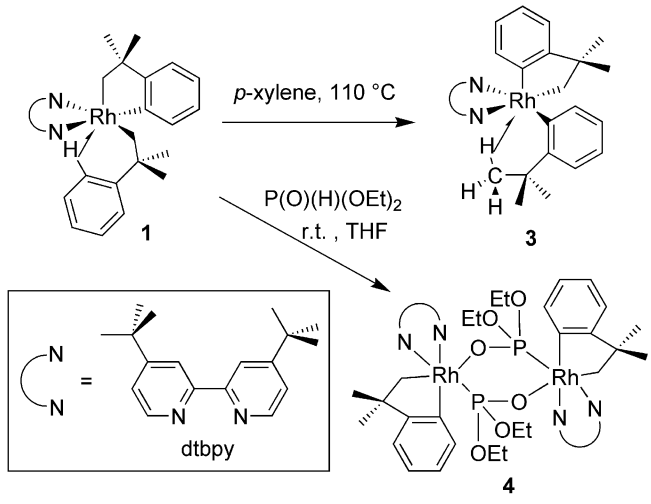
Heating [Rh(dtbpy)(κ$_2$-*C*,*C*′-$CH_2CMe_2C_6H_4$)(CH_2CMe_2Ph)] (**1**; dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) in *p*-xylene at 110 °C resulted in the formation of the 2-*tert*-butylphenyl complex [Rh(dtbpy)(κ$_2$-*C*,*C*′-$CH_2CMe_2C_6H_4$)(C_6H_4tBu-2)] (**3**). Treatment of complex **1** with diethyl phosphite gave the phosphito-bridged dimer [Rh(dtbpy)(κ$_2$-*C*,*C*′-$CH_2CMe_2C_6H_4$){P(O)$(OEt)_2$}]$_2$ (**4**). Refluxing [Ir(dtbpy)(κ$_2$-*C*,*C*′-$CH_2CMe_2C_6H_4$)(C_6H_4tBu-2)] (**2**) with 2-phenylpyridine (ppyH) and 4-(2-pyridyl)benzaldehyde in toluene followed by column chromatography afforded [Ir(dtbpy)(CH_2CMe_2Ph)Cl(κ$_2$-*N*,*C*-ppy)] (**5**) and the carbonyl complex [Ir(dtbpy)(CH_2CMe_2Ph)(CO)(R)] (**6**) [R = 4-(2-pyridyl)phenyl], respectively. Anion metathesis of [M(dtbpy)(CH_2CMe_2Ph)(H_2O)$(OTs)_2$] with $NaBAr^F_4$ [Ar^F = 3,5-$(CF_3)_2C_6H_3$] afforded cationic [M(dtbpy)(CH_2CMe_2Ph)(H_2O)(μ-OTs)]$_2$[BAr^F_4]$_2$ [M = Rh (**7**), Ir (**8**)] that are capable of catalyzing H/D exchange of tetrahydrofuran by using D_2O as the deuterium source. The crystal structures of complexes **4**–**7** were determined.

Introduction

Organoiridium complexes stabilized by 2,2′-bipyridyl (bpy) are of interest due to their applications as catalysts for borylation of arenes with borane and diborane reagents.[1] It is believed that the mechanism of Ir(bpy)-catalyzed borylation involves oxidative addition of the arene C–H bond with Ir^{III} boryl species.[2] Therefore, to develop new Ir-based catalysts for C–H activation and functionalization, knowledge of the organometallic chemistry of Ir(bpy) alkyl complexes is essential.

Previously, we reported the syntheses of Ir and Rh alkyl complexes stabilized by 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy).[3,4] We found that the alkylation of [Rh(dtbpy)Cl_3(dmf)] (dmf = *N*,*N*-dimethylformamide) with $Me_2CCH_2PhMgCl$ afforded the neophyl complex [Rh(dtbpy)(κ$_2$-*C*,*C*′-$CH_2CMe_2C_6H_4$)(CH_2CMe_2Ph)] (**1**), whereas that with [Ir(dtbpy)Cl_3(dmf)] yielded the 2-*tert*-butylphenyl complex [Ir(dtbpy)(κ$_2$-*C*,*C*′-$CH_2CMe_2C_6H_4$)(C_6H_4tBu-2)] (**2**; structures of complexes **1** and **2** are shown Schemes 1 and 2, respectively). It seems likely that intramolecular C–H activation of an unisolated Ir^{III} neophyl intermediate that is isostructural with complex **1** is involved in the formation of complex **2**. Reaction of complexes **1** and **2** with disulfides in refluxing toluene gave Rh^{III} and Ir^{III} bis(thiolate) complexes.[5] These results suggest that electron-rich M^{III}(dtbpy) (M = Ir, Rh) alkyl complexes exhibit interesting organometallic chemistry and thus are potentially useful in C–H activation. Recently, Periana and coworkers reported that cyclometalated Ir complexes with N^N^C ligands can mediate C–H activation and H/D exchange reactions.[6] This prompted us to explore the reactivity of Ir and Rh dtbpy alkyl complexes in C–H activation.



Scheme 1. Syntheses of complexes **3** and **4**.

Cationic late transition-metal diimine alkyl complexes have attracted much attention due to their catalytic activity in organic transformations. In particular, the C–H activation and functionalization with cationic [Pt(N^N)R(solv)]$^+$ complexes has been studied extensively.[7,8] Bergman and co-workers demonstrated that the activity of [Cp*Ir(PMe_3)Me(OTf)] (Cp* = η^5-C_5Me_5) in C–H acti-

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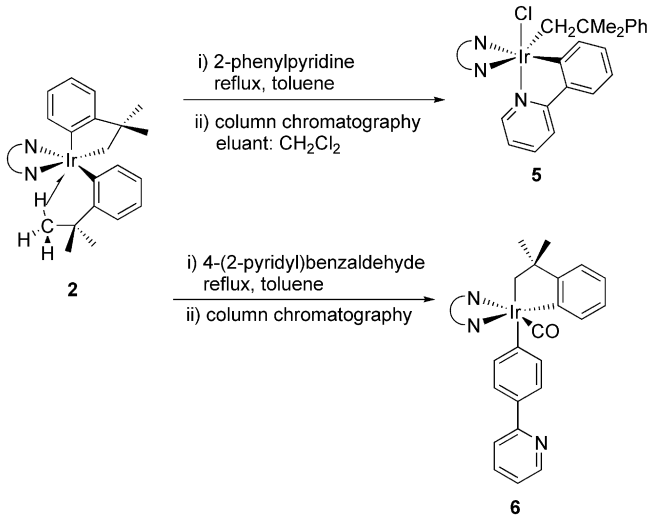


Scheme 2. Syntheses of complexes **5** and **6**.

vation is greatly enhanced by replacing the weakly coordinating triflate (OTf^-) ligand with noncoordinating $BAr^F{}_4$ [Ar^F = 3,5-$(CF_3)_2C_6H_3$], demonstrating the significance of a vacant coordination site in the Ir^{III}-based C–H activation.[9] These findings led us to explore the C–H activation chemistry of cationic Ir and Rh complexes $[M^{III}(dtbpy)R]^+$ (M = Ir, Rh) complexes containing noncoordinating $BAr^F{}_4^-$. In this paper, we report the intramolecular C–H activation of complex **1** to give a 2-*tert*-butylphenyl complex. The cyclometalation of 2-phenylpyridine and decarbonylation of 4-(2-pyridyl)benzaldehyde with complex **2** will be described. The synthesis and characterization of cationic Ir and Rh dtbpy alkyl complexes and their catalytic activity in H/D exchange of tetrahydrofuran will be reported.

Results and Discussion

Intramolecular C–H Activation of Complex 1

Heating complex **1** in *p*-xylene at 110 °C for 48 h resulted in the formation of orange species **3** (Scheme 1). ^1H NMR spectroscopy indicated that the conversion of complex **1** into **3** was a clean process that did not involve any detectable intermediate(s). A preliminary X-ray diffraction study confirmed that complex **3** is a Rh^{III} 2-*tert*-butylphenyl complex that is isostructural with complex **2**, featuring an agostic interaction between Rh and a methyl C–H bond of the 2-*tert*-butylphenyl ligand.[10] The conversion of complex **1** to **3** presumably involves intramolecular C–H activation of the neophyl ligand and subsequent C–H bond elimination. The ^1H NMR spectrum of complex **3** is similar to that of **2**, except that the methylene protons in the metallacycle (H^a) appeared as two doublets of doublets at δ = 2.56 and 2.62 ppm ($^2J_{Rh,H}$ = 9.4 Hz) instead of two doublets. Only a singlet at δ = 0.98 ppm was observed for the *tert*-butyl protons at 25 °C, indicating that the three methyl groups in the 2-*tert*-butylphenyl ligands are scrambling rapidly around Rh on the NMR timescale. A similar result was found for Ir analogue **2**.[4]

Reaction of Complex 1 with Diethyl Phosphite

Reactivity of complex **1** toward main group hydride compounds was examined. No reaction was found when complex **1** was treated with boranes such as pinBH (pin = pinacolate) and Et_3SiH. However, complex **1** reacted readily with diethyl phosphite to give the phosphito-bridged dimer $[Rh(dtbpy)(\kappa_2\text{-}C,C'\text{-}CH_2CMe_2C_6H_4)\{P(O)(OEt)_2\}]_2$ (**4**). The $^{31}P\{^1H\}$ NMR spectrum showed two doublets of doublets at δ = 100.99 and 120.63 ppm due to the bridged phosphite ligands.

The structure of complex **4** (Figure 1) consists of two symmetry-related $\{Rh(dtbpy)(\kappa_2\text{-}C,C'\text{-}CH_2CMe_2C_6H_4)\}^+$ fragments bridged by two μ-phosphito P,O ligands. Dinuclear complexes containing μ-phosphito P,O ligands, for example, $[\{(tBu_4Ph_2O_2)P{=}O\}Rh(CO)(MeCN)]_2$,[11,12] are well documented. The geometry around Rh in complex **4** is pseudo-octahedral with the P=O group opposite to the methylene group of the rhodacycle. The Rh–C(*trans* to N) and Rh–C(*trans* to O) distances are 2.000(2) and 2.047(2) Å, respectively. The Rh–O distance is 2.2142(15) Å, which is longer than that in $[\{(tBu_4Ph_2O_2)P{=}O\}Rh(CO)(MeCN)]_2$ (2.071 Å). The Rh–P distance of 2.2057(6) Å is comparable to that in $[\{(tBu_4Ph_2O_2)P{=}O\}Rh(CO)(MeCN)]_2$ (2.207 Å).[12] The Rh···Rh separation is 3.933 Å, indicating the absence of a direct Rh–Rh bond.

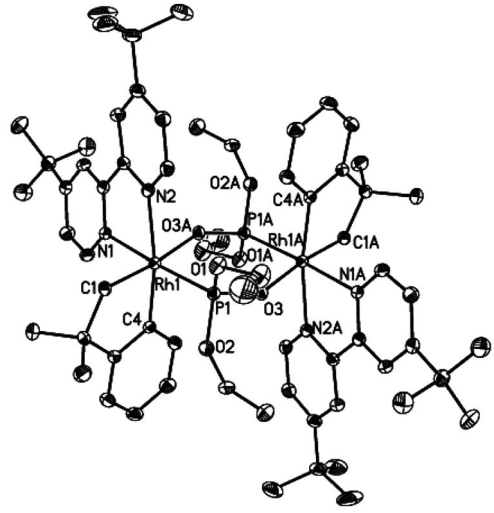


Figure 1. Molecular structure of $[Rh(dtbpy)(\kappa_2\text{-}C,C'\text{-}CH_2CMe_2C_6H_4)\{P(O)(OEt)_2\}]_2$ (**4**). Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Symmetry operator: A = $-x + 1, -y + 1, -z + 1$. Selected bond lengths [Å]: Rh1–C4 2.000(2), Rh1–C1 2.047(2), Rh1–N1 2.1543(18), Rh1–N2 2.171(2), Rh1–P1 2.2057(6), Rh1–O3A 2.2142(15).

Reaction of Complex 2 with 2-Arylpyridines

No reaction was found when complex **2** was heated at reflux in arene solvents such as benzene, toluene, and *p*-

xylene. We next turned our attention to the C–H activation of 2-arylpyridines. Treatment of complex **2** with 2-phenylpyridine (ppyH) in refluxing toluene followed by column chromatography on silica (CH_2Cl_2) afforded [Ir(dtbpy)(CH_2CMe_2Ph)Cl(κ^2-*N*,*C*-ppy)] (**5**; Scheme 2). It seems likely that the reaction between complex **2** and ppyH involved C–H activation of ppyH and the formation of an unisolated Ir^{III} κ_2-*N*,*C*-ppy bis(neophyl) intermediate. Column chromatography on silica resulted in protonolysis of one Ir–neophyl bond of this intermediate. The resulting cationic mononeophyl species reacted with chloride (presumably derived from CH_2Cl_2) to afford chloride product **5**. Complex **5** was not isolated if the initial product was not purified by silica column chromatography.

The molecular structure of complex **5** is shown in Figure 2. The geometry around Ir is pseudo-octahedral with the neophyl and the pyridyl ring of the ppy ligand opposite to dtbpy. The ligand atom (N42) opposite to N22 of dtbpy is assigned as a nitrogen instead of carbon because the Ir–N22 bond [2.061(4) Å] is shorter than the Ir–N11 bond [2.125(4) Å]. By comparison, the Ir–N(dtbpy) distance (*trans* to phenyl) in complex **2** is 2.142(3) Å, whereas the Ir–N(dtbpy) distance (*trans* to Cl) in [Ir(dtbpy)(CH_2CMe_2Ph)Cl_2]$_2$ is 2.029(4) Å.[4] Consistent with this assignment, the Ir–Cl distance in complex **5** is rather long {2.4961(14) Å cf. 2.383 Å for [Ir(dtbpy)(CH_2CMe_2Ph)Cl_2]$_2$} due to the *trans* influence of the opposite phenyl ring.[4] The Ir–C(ppy) [2.011(5) Å] and Ir–N(ppy) [2.038(5) Å] distances are similar to those in [Ir(di-*n*-nonylbpy)(κ_2-*N*,*C*-ppy)$_2$][PF_6] (di-*n*-nonylbpy = 4,4′-di-*n*-nonyl-2,2′-bipyridyl) [av. 2.015(7) and 2.057(6) Å, respectively].[13]

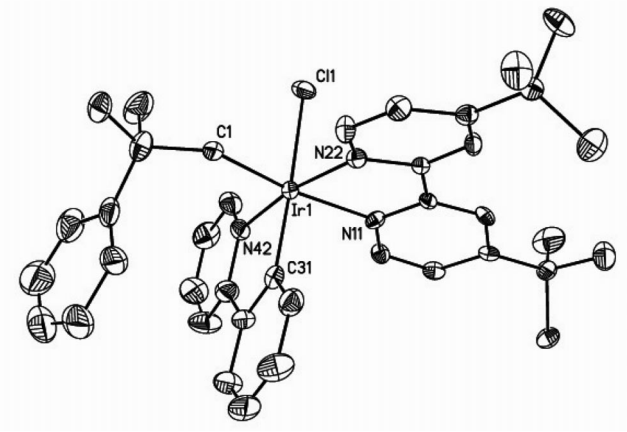


Figure 2. Molecular structure of [Ir(dtbpy)(CH_2CMe_2Ph)Cl(κ_2-*N*,*C*-ppy)] (**5**). Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths [Å]: Ir1–C1 2.086(6), Ir1–C31 2.011(5), Ir1–N42 2.038(5), Ir1–N11 2.125(4), Ir1–N22 2.061(4), Ir1–Cl1 2.4961(14).

To compare the reactivity of phenyl and formyl C–H bonds in the oxidative addition with Ir^{III}, the reaction of complex **2** with 4-(2-pyridyl)benzaldehyde was studied. Treatment of complex **2** with 4-(2-pyridyl)benzaldehyde in refluxing toluene followed by column chromatography led to isolation of the carbonyl complex [Ir(dtbpy)(κ_2-*C*,*C*′-CH_2CMe_2Ph)(CO)(R)] (**6**), where R = 4-(2-pyridyl)phenyl (Scheme 2). Therefore, the decarbonylation of the formyl group with complex **2** is favored over phenyl C–H activation. It may be noted that for the reaction of $IrCl_3$ with 4-(2-pyridyl)benzaldehyde, the cyclometalated product [Ir(κ_2-*N*,*C*-ppy-CHO)$_2$Cl]$_2$ was isolated.[14] The IR spectrum of complex **6** displayed the ν_{CO} band at 1986 cm^{-1}, which is typical for Ir^{III} carbonyl complexes.

The asymmetric unit of complex **6** in the solid state consists of a pair of enantiomers, the structures of which are shown in Figure 3. The geometry around Ir in each enantiomer is pseudo-octahedral with the carbonyl and the phenyl ring of the iridacycle opposite to dtbpy. The three Ir–C bonds adopt a *mer* arrangement possibly because the *trans* arrangement between the *trans*-directing alkyl and π-accepting carbonyl ligands is not favored. By contrast, a *fac* arrangement was found for the three Ir–C bonds in [Ir(dtbpy)(C_8H_9)$_3$(xylNC)] (C_8H_9 = 2,5-dimethylphenyl; xyl = 2,6-dimethylphenyl).[3] As expected, the two *transoid* Ir–C bonds [av. 2.147(7) Å] are longer than the Ir–C(trans to N) bond [av. 2.059(7) Å] due to the *trans* influence of the alkyl/phenyl ligand. The average Ir–CO distances [av. 1.806(8) Å] are shorter than that of [IrMe(CO)(PPh_3)$_2$(mnt)] [1.859(5) Å].[15]

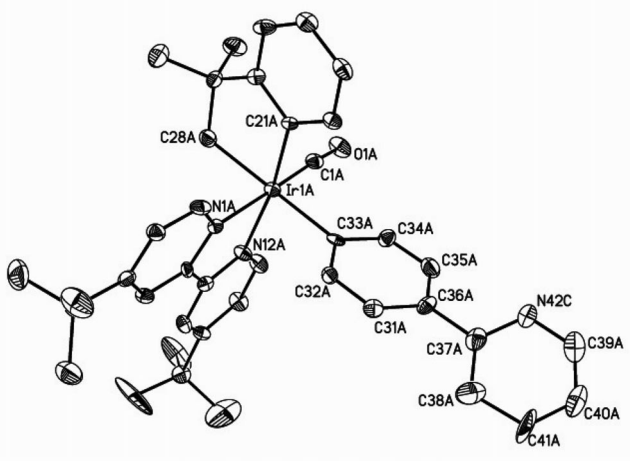
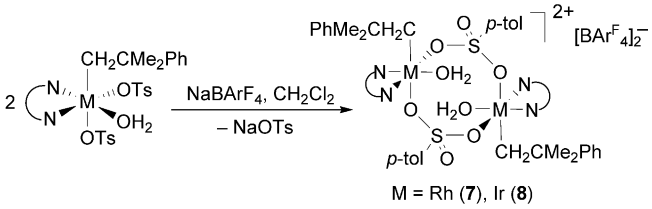


Figure 3. Molecular structures of [Ir(dtbpy)(κ_2-*C*,*C*′-CH_2CMe_2Ph)(CO)(R)] (**6**). Hydrogen atoms, one enantiomer, and cocrystallized solvent are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths [Å]: Ir1A–C1A 1.820(8), Ir1A–C21A 2.056(6), Ir1A–N1A 2.077(5), Ir1A–N12A 2.110(5), Ir1A–C33A 2.151(7), Ir1A–C28A 2.151(6), Ir1B–C(1B) 1.789(8), Ir1B–C21B 2.061(6), Ir1B–N1B 2.122(5), Ir1B–N12B 2.111(5), Ir1B–C33B 2.144(7), Ir1B–C28B 2.143(7).

Cationic Rh and Ir Alkyl Complexes

Protonation of complex **2** with *p*-toluenesulfonic acid afforded the ditosylate complex analyzed as [Ir(dtbpy)(CH_2CMe_2Ph)($OTs)_2$]. A preliminary X-ray diffraction study confirmed that this tosylate compound is a monomeric aqua complex containing one aqua and two η^1-tosylate ligands.[16] Similarly, the Rh analogue [Rh(dtbpy)-

$(CH_2CMe_2Ph)(OTs)_2(H_2O)]$ was prepared by protonation of complex **1** with *p*-toluenesulfonic acid in CH_2Cl_2. In an attempt to increase the reactivity of the Ir and Rh dtbpy alkyl complexes, the tosylate ligands in [M(dtbpy)-$(CH_2CMe_2Ph)(OTs)_2(H_2O)]$ were exchanged with noncoordinating $[BAr^F_4]^-$, where Ar^F = 3,5-$(CF_3)_2C_6H_3$. Treatment of $[M(dtbpy)(CH_2CMe_2Ph)(OTs)_2(H_2O)]$ with NaB-Ar^F_4 in CH_2Cl_2 afforded dimeric $[M(dtbpy)(CH_2CMe_2Ph)$-$(H_2O)(\mu\text{-}OTs)]_2[BAr^F_4]_2$ [M = Rh (**7**), Ir (**8**)] containing two μ-tosylate O,O′ ligands (Scheme 3). Complexes **7** and **8** are highly hygroscopic solids. They exhibit rather broad ^1H NMR signals. The diastereotopic methylene protons of complex **7** appeared as two doublets at δ = 3.40 and 3.44 ppm in the ^1H NMR spectrum, presumably because the Rh–H coupling is too small to be resolved.



Scheme 3. Syntheses of complexes **7** and **8**.

The solid-state structure of complex **7** is shown in Figure 4. The geometry around Rh is pseudo-octahedral with the aqua and the bridged tosylate ligand opposite to dtbpy. The Rh–C distance [2.050(5) Å] is similar to the Rh–C(neophyl) distance in complex **1**.[3] The Rh–OTs bond opposite to carbon [2.379(3) Å] is obviously longer than that opposite to nitrogen [2.108(3) Å] due to the *trans* influence of the neophyl ligand. The long Rh···Rh separation (5.321 Å) indicates the absence of a Rh–Rh bond.

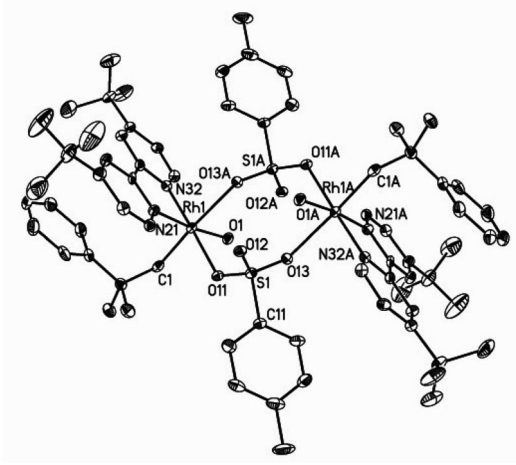
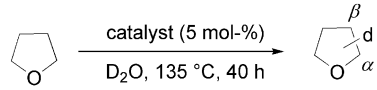


Figure 4. Molecular structure of $[Rh(dtbpy)(CH_2CMe_2Ph)$-$(H_2O)(\mu\text{-}OTs)]_2[BAr^F_4]_2$ (**7**). Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Symmetry operator: A = $-x + 1, -y + 1, -z + 1$. Selected bond lengths [Å]: Rh1–C1 2.050(5), Rh1–N21 2.006(4), Rh1–N32 1.976(4), Rh1–O1 2.080(3), Rh1–O11 2.108(3), Rh1A–O13 2.379(3).

Catalytic H/D Exchange of thf

The catalytic activity of Ir and Rh dtbpy alkyl complexes in H/D exchange of organic substrates was examined. Of particular interest is H/D exchange with the use of D_2O as the deuterium source.[17] The H/D exchange of thf with D_2O in the presence of catalytic amounts of Ir and Rh alkyl complexes was studied by ^1H NMR spectroscopy, and the results are summarized in Table 1. Cationic alkyl complexes **7** and **8** were found to be active catalysts for the H/D exchange of thf. For example, heating thf in D_2O in the presence of complex **8** (5 mol-%) at 135 °C resulted in 59% deuterium incorporation into thf. A slightly lower deuteration level (52%) was found for Rh analogue **7**. For comparison, under the same conditions, a total deuteration level of 61% was obtained with the use of $[Cp^*Ir(PMe_3)Cl_2]$ as the catalyst. When the catalyst loading was reduced to 1 mol-%, the deuteration level was decreased to 38 and 31% for complexes **7** and **8**, respectively. No/little selectivity for either the α- or *β*-position of thf was found for the M(dtbpy)-catalyzed H/D exchange (α/*β* ca. 1). A similar result was found for $[Tp^{Me2}IrH_4]$ [Tp^{Me2} = hydridotris(3,5-dimethylpyrazolyl)borate].[18] This is in contrast with the IrCp* system that exhibits a preference for the α position.[17] Complexes **1** and **2** containing three metal–carbon bonds and $[M(dtbpy)(CH_2CMe_2Ph)(H_2O)(OTs)_2]$ are inactive in the H/D exchange, indicating the presence of a vacant coordination site on the metal center is critical for C–H activation.

Table 1. Catalytic H/D exchange of tetrahydrofuran with D_2O.[a]



Catalyst	% $D_{incorp.}$		
	α	*β*	Total
1	0	0	0
2	0	0	0
$Rh(dtbpy)(CH_2CMe_2Ph)(H_2O)(OTs)_2$	0	0	0
$Ir(dtbpy)(CH_2CMe_2Ph)(H_2O)(OTs)_2$	4	4	4
7	51	53	52
7[b]	30	32	31
8	57	60	59
8[b]	38	37	38

[a] Experimental conditions: thf (0.12 mmol), D_2O (0.5 mL), catalyst (0.006 mmol), 135 °C, 40 h. [b] 1 mol-% of catalyst used.

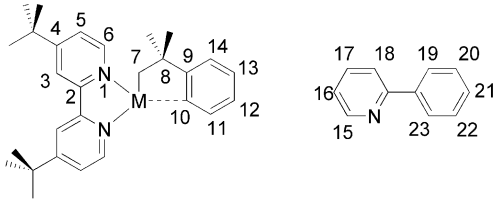
Conclusions

In summary, we found that heating complex **1** in *p*-xylene resulted in intramolecular C–H activation of the neophyl ligand and formation of 2-*tert*-butylphenyl complex **3**. Complex **1** reacted readily with diethyl phosphite to afford a phosphito-bridged dimer. Reaction of complex **2** with 2-phenylpyridine resulted in cyclometalation of 2-phenylpyridine, whereas that with 4-(2-pyridyl)benzaldehyde led to decarbonylation of the formyl group. Cationic Ir and Rh alkyl complexes **7** and **8** containing the noncoordinating

counteranion $BAr^F_4^-$ are capable of catalyzing H/D exchange of thf with the use of D_2O as the deuterium source.

Experimental Section

General Remarks: All manipulations were carried out under an atmosphere of nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded with a Varian Mercury 300 spectrometer operating at 300, 121.5, and 282.3 MHz for ^1H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H and ^{13}C), H_3PO_4 (^{31}P), and $C_6H_5CF_3$ (^{19}F). Infrared spectra were recorded with a Perkin–Elmer 16 PC FTIR spectrophotometer and mass spectra with a Finnigan MAT TSQ-7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK. The compounds [Rh(dtbpy)(κ_2-*C,C'*-$CH_2CMe_2C_6H_4$)(CH_2CMe_2Ph)] (**1**),[3] [Ir(dtbpy)(κ_2-*C,C'*-$CH_2CMe_2C_6H_4$)(C_6H_4tBu-2)] (**2**), [Ir(dtbpy)(CH_2CMe_2Ph)(H_2O)($OTs)_2$],[4] and $NaBAr^F_4$ [Ar^F = 3,5-bis(trifluoromethyl)phenyl][19] were synthesized as described elsewhere. Atom labeling schemes for the metallacycles in cyclometalated complexes and the ppyH and dtbpy ligands are shown below.



[Rh(dtbpy)(κ_2-*C,C'*-$CH_2CMe_2C_6H_4$)(C_6H_4tBu-2)] (3): A solution of complex **1** (50 mg, 0.079 mmol) in *p*-xylene (5 mL) was heated at 110 °C for 48 h. The volatiles were removed in vacuo, and the residue was purified by silica gel column chromatography (ethyl acetate). Recrystallization (Et_2O/hexane) afforded orange crystals. Yield: 40 mg (80%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.98 (s, 9 H, $C_6H_4CMe_3$), 1.26 [s, 6 H, -$C^8(Me)_2$-], 1.38 (s, 9 H, *t*Bu), 1.44 (s, 9 H, *t*Bu), 2.56 (dd, $^2J_{Rh,H}$ = 9.4 Hz, $^2J_{H,H}$ = 2.6 Hz, 1 H, H^7), 2.62 (dd, $^2J_{Rh,H}$ = 9.2 Hz, $^2J_{H,H}$ = 4.3 Hz, 1 H, H^7), 5.80 (d, J = 7.7 Hz, 1 H, H^{14}), 6.39 (dt, J = 7.8, 2.0 Hz, 1 H, H^{13}), 6.64–6.68 (m, 4 H, $C_6H_4CMe_3$, H^{11} and H^{12}), 6.84 (dt, J = 7.4, 3.2 Hz, 1 H, $C_6H_4CMe_3$), 7.07 (dd, J = 7.8 Hz, 1.4 Hz, 1 H, $C_6H_4CMe_3$), 7.36–7.61 (m, 2 H, H^5), 8.05 (s, 1 H, H^3), 8.11 (s, 1 H, H^3), 8.22 (d, J = 5.7 Hz, 1 H, H^6), 9.01 (d, J = 5.8 Hz, 1 H, H^6) ppm. $C_{38}H_{49}N_2Rh{\cdot}0.5Et_2O$ (673.8): C 71.30, H 8.08, N 4.16; found C 71.64, H 8.47, N 4.08.

[Rh(dtbpy)(κ_2-*C,C'*-$CH_2CMe_2C_6H_4$){$P(O)(OEt)_2$}]$_2$ (4): To a solution of complex **1** (50 mg, 0.079 mmol) in thf (5 mL) was added diethyl phosphite (10.9 mg, 0.079 mmol). The mixture was stirred at room temperature for 12 h. The volatiles were removed in vacuo, and the residue was washed with hexane and Et_2O, and then extracted with thf. Recrystallization (thf/hexane) gave yellow crystals, which were suitable for X-ray analysis. Yield: 32 mg (65%). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.29 [s, 12 H, -$C^8(Me)_2$-], 0.85 (s, 18 H, *t*Bu), 1.03 (s, 18 H, *t*Bu), 2.98–3.04 (m, 2 H, H^7), 3.26–3.34 (m, 2 H, H^7), 3.71 (t, J = 7.2 Hz, 4 H, OCH_2CH_3), 3.89 (q, J = 7.4 Hz, 6 H, OCH_2CH_3), 4.25 (t, J = 7.0 Hz, 4 H, OCH_2CH_3), 4.45 (q, J = 7.5 Hz, 6 H, OCH_2CH_3), 6.18 (d, J = 5.9 Hz, 2 H, H^6), 7.05–7.10 (m, 4 H, H^{13} and H^{14}), 7.26–7.30 (m, 4 H, H^{11} and H^{12}), 7.73 (s, 2 H, H^3), 7.86 (s, 2 H, H^3), 8.27–8.30 (m, 2 H, H^5), 8.56–8.59 (m, 2 H, H^5), 10.01 (d, J = 5.9 Hz, 4 H, H^6) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): δ = 100.99 (dd, $^1J_{Rh,P}$ = 205 Hz, $^2J_{Rh,P}$ = 52.0 Hz), 120.63 (dd, $^1J_{Rh,P}$ = 123 Hz, $^2J_{Rh,P}$ = 52.0 Hz) ppm. $C_{64}H_{92}N_4O_6P_2Rh_2$ (1281.2): C 60.00, H 7.24, N 4.37; found C 60.32, H 7.50, N 4.19.

[Ir(dtbpy)(CH_2CMe_2Ph)Cl(κ_2-*N,C*-ppy)] (5): To a solution of complex **2** (100 mg, 0.138 mmol) in toluene (10 mL) was added 2-phenylpyridine (18 μL, 0.138 mmol), and the mixture was heated at reflux for 24 h. The volatiles were removed in vacuo, and the residue was purified by silica gel column chromatography (CH_2Cl_2). Recrystallization (CH_2Cl_2/hexane) afforded brown crystals suitable for X-ray diffraction. Yield: 45 mg (42%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.09 [s, 3 H, -$C^8(Me)_2$-], 1.22 [s, 3 H, -$C^8(Me)_2$-], 1.25 (s, 9 H, *t*Bu), 1.49 (s, 9 H, *t*Bu), 2.37 (d, J = 11.7 Hz, 1 H, H^7), 2.81 (d, J = 11.7 Hz, 1 H, H^7), 6.30 (dd, J = 7.5 Hz, 1.1 Hz, 1 H, H^{18}), 6.65–6.81 (m, 7 H, H^{13}, H^{16}, H^{17}, H^{19}, H^{20}, and H^{21}), 7.02 (d, J = 1.2 Hz, 2 H, H^{14}), 7.05 (dd, J = 6.9, 1.2 Hz, 1 H, H^5), 7.17 (dd, J = 7.6, 1.2 Hz, 1 H, H^{22}), 7.33 (d, J = 7.6 Hz, 1 H, H^{15}), 7.50 (dt, J = 7.6, 1.5 Hz, 1 H, H^{12}), 7.60 (dd, J = 6.2, 2.1 Hz, 1 H, H^5), 7.87 (s, 1 H, H^3), 7.99 (d, J = 2.1 Hz, 1 H, H^3), 9.40 (d, J = 6.2 Hz, 1 H, H^6), 9.67 (dd, J = 5.6, 0.9 Hz, 1 H, H^6) ppm. $C_{39}H_{45}ClIrN_3$ (783.5): C 59.79, H 5.79, N 5.36; found C 59.69, H 5.86, N 5.13.

[Ir(dtbpy)(κ_2-*C,C'*-CH_2CMe_2Ph)(CO)(R)] [R = 4-(2-pyridyl)phenyl] (6): To a solution of complex **2** (100 mg, 0.138 mmol) in toluene (10 mL) was added 4-(2-pyridyl)benzaldehyde (25 mg, 0.138 mmol). The mixture was heated at reflux for 24 h. The volatiles were removed in vacuo, and the residue was purified by silica gel column chromatography (CH_2Cl_2). Recrystallization (CH_2Cl_2/hexane) afforded yellow crystals suitable for X-ray diffraction analysis. Yield: 57 mg (53%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.70 (d, J = 10.5 Hz, 1 H, H^7), 1.16 [s, 3 H, -$C^8(Me)_2$-], 1.20 [s, 3 H, -$C^8(Me)_2$-], 1.40 (s, 9 H, *t*Bu), 1.41 (s, 9 H, *t*Bu), 1.74 (d, J = 10.5 Hz, 1 H, H^7), 6.84–6.95 (m, 2 H, H^{17} and H^{20}), 7.02–7.07 (m, 2 H, H^{13} and H^{14}), 7.28–7.31 (m, 3 H, H^3 and H^{18}), 7.38 (dd, J = 6.0, 1.8 Hz, 1 H, H^{22}), 7.45–7.51 (m, 3 H, H^{12}, H^{19}, and H^{23}), 7.60–7.62 (m, 2 H, H^{11} and H^{16}), 7.91 (d, J = 6.2 Hz, 1 H, H^6), 8.01 (d, J = 1.8 Hz, 1 H, H^5), 8.03 (d, J = 1.8 Hz, 1 H, H^5), 8.54 (td, J = 4.7, 1.2 Hz, 1 H, H^{15}), 8.97 (d, J = 5.9 Hz, 1 H, H^6) ppm. MS (FAB): m/z = 776.5 $[M + 1]^+$, 621.4 $[M - ppy]^+$, 593.1 $[M - ppy - CO]^+$. IR (KBr): 1986 (ν_{CO}) cm^{-1}. $C_{40}H_{44}IrN_3O{\cdot}CH_2Cl_2$ (860.0): C 57.27, H 5.39, N 4.89; found C 57.30, H 5.61, N 4.58.

[Rh(dtbpy)(CH_2CMe_2Ph)(H_2O)($OTs)_2$]: This complex was synthesized by a method similar to that used for Ir(dtbpy)(CH_2CMe_2Ph)(H_2O)($OTs)_2$ by reaction of complex **1** with *p*-toluenesulfonic acid (2 equiv.) in CH_2Cl_2. Recrystallization (CH_2Cl_2/hexane) afforded orange crystals. Yield: 56 mg (47%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.25 [s, 3 H, -$C^8(Me)_2$-], 1.31 [s, 3 H, -$C^8(Me)_2$-], 1.43 (s, 9 H, *t*Bu), 1.48 (s, 9 H, *t*Bu), 1.94 (br. s, 2 H, H_2O), 2.27 (s, 3 H, Me), 2.31 (s, 3 H, Me), 3.60 (d, J = 10.3 Hz, 1 H, H^7), 3.97 (d, J = 10.3 Hz, 1 H, H^7), 6.18 (d, J = 7.9 Hz, 1 H, H^5), 6.44–6.55 (m, 2 H, H^{13}), 6.69 (d, J = 6.5 Hz, 2 H, H^{14}), 6.90 (t, J = 6.9 Hz, 1 H, H^{12}), 7.08 (d, J = 7.3 Hz, 2 H, H^{14} of Ts), 7.16 (d, J = 7.9 Hz, 1 H, H^5), 7.41 (d, J = 4.5 Hz, 2 H, H^{14} of Ts), 7.47 (d, J = 4.5 Hz, 2 H, H^{13} of Ts), 7.70 (br. s, 2 H, H^3), 7.88 (d, J = 7.6 Hz, 2 H, H^{13} of Ts), 8.36 (d, J = 6.2 Hz, 1 H, H^6), 8.59 (d, J = 6.0 Hz, 1 H, H^6) ppm. $C_{42}H_{53}N_2O_7S_2Rh{\cdot}0.5CH_2Cl_2$ (907.4): C 56.26, H 6.00, N 3.09; found C 55.93, H 6.07, N 3.13.

[M(dtbpy)(CH_2CMe_2Ph)(H_2O)(μ-OTs)]$_2$[BAr^F_4]$_2$ [M = Rh (7), Ir (8)]: To a solution of [M(dtbpy)(CH_2CMe_2Ph)(H_2O)($OTs)_2$] (0.058 mmol) in CH_2Cl_2 (8 mL) was added $NaBAr^F_4{\cdot}3H_2O$ (109 mg, 0.116 mmol). The mixture was stirred at room tempera-

Table 2. Crystallographic data and experimental details for complexes **4**–**7**.

Complex	**4**	**5**	[**6**]$_2$·$CHCl_3$·1/2C_6H_{14}	**7**·2$C_4H_{10}O$
Formula	$C_{64}H_{92}N_4O_6P_2Rh_2$	$C_{39}H_{45}ClIrN_3$	$C_{84}H_{188}Cl_3Ir_2N_6O_2$	$C_{142}H_{136}B_2F_{48}N_4O_{10}Rh_2S_2$
Molecular wt. [g mol^{-1}]	1281.18	783.43	1710.4	3262.11
Temperature [K]	173(2)	100(2)	173(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	14.7962(2)	14.5540(10)	12.0181(11)	12.4377(15)
b [Å]	11.95460(10)	16.2247(11)	13.7836(13)	27.256(4)
c [Å]	18.3317(3)	14.9560(10)	25.701(2)	22.429(3)
α [°]	90	90	87.229(2)	90
β [°]	96.309(2)	97.6480(10)	76.717(2)	98.857(3)
γ [°]	90	90	77.595(2)	90
V [Å^3]	3222.92(7)	3500.2(4)	4046.7(7)	7512.7(16)
Z	2	4	2	2
$\rho_{calcd.}$ [g cm^{-3}]	1.32	1.487	1.405	1.442
μ [mm^{-1}]	5.007	3.921	3.432	0.363
F(000)	1344	1576	1722	3320
No. reflections collected	10586	21563	36015	38322
No. independent reflections	5949	5934	13961	13033
R_{int}	0.029	0.0683	0.062	0.0946
R_1 [$I > 2\sigma(I)$]	0.0304	0.0385	0.0467	0.0613
wR_2 (all data)	0.0687	0.0615	0.0828	0.1255
Goodness-of-fit on F^2	1.051	0.999	0.998	1.010

ture for 12 h. The volatiles were removed in vacuo, and the residue was washed with hexane, extracted with Et_2O (10 mL), and further recrystallized (Et_2O/hexane). We have not been able to obtain satisfactory analytical data for the compounds due to their hygroscopic nature. These compounds have, however, been well characterized by spectroscopic methods and X-ray diffraction (compound **7**).

7: Yellow crystals. Yield: 40 mg (43%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 1.04 [s, 6 H, -C^8(Me)$_2$-], 1.08 [s, 6 H, -C^8-(Me)$_2$-], 1.32 (br. s, 36 H, *t*Bu), 1.43 (br. s, 4 H, H_2O), 2.32 (s, 6 H, *p*-Me), 3.40 (d, J = 6.8 Hz, 2 H, H^7), 3.44 (d, J = 6.9 Hz, 2 H, H^7), 6.52 (d, J = 6.7 Hz, 4 H, H^{14}), 6.65 (t, J = 7.5 Hz, 4 H, H^{13}), 6.90 (t, J = 7.2 Hz, 2 H, H^{12}), 7.06–7.19 (m, 6 H, H^5 and OTs), 7.56 (s, 8 H, BAr^F), 7.66 (br. s, 4 H, H^3), 7.74 (s, 24 H, BAr^F), 7.98 (d, J = 6.0 Hz, 4 H, OTs), 8.38 (br. s, 4 H, H^6) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 25 °C): δ = –63.31 (s) ppm.

8: Orange powder. Yield: 32 mg (33%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 0.87 (s, 6 H, *p*-Me), 1.27 [s, 6 H, -C^8(Me)$_2$-], 1.28 [s, 6 H, -C^8(Me)$_2$-], 1.36 (br. s, 36 H, *t*Bu), 1.46 (br. s, 4 H, H_2O), 2.87 (br. s, 4 H, H^7), 6.40 (br. s, 4 H, H^{14}), 6.64 (br. s, 4 H, H^{13}), 6.81 (br. s, 2 H, H^{12}), 6.96–7.17 (m, 6 H, H^5 and OTs), 7.25–7.56 (m, 6 H, H^3 and OTs), 7.57 (s, 8 H, BAr^F), 7.74 (s, 24 H, BAr^F), 8.31 (br. s, 4 H, H^6) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 25 °C): δ = –63.46 (s) ppm.

Catalytic H/D Exchange of Tetrahydrofuran with D_2O: This experiment was performed according to a literature procedure.[17] Typically, catalyst (6 μmol), thf (10 μL), and D_2O (0.5 mL) were charged in a degassed NMR tube, which contained a sealed external standard capillary consisting of an internal standard, hexamethylbenzene (10 mg), dissolved in C_6D_6. The NMR tube was sealed under vacuum. The reaction mixtures were heated at 135 °C for 40 h. The deuteration level (%D) was calculated by dividing the loss of thf signals in the ^{1}H NMR spectrum by the initial standardized integration of thf signals.

X-ray Crystallography: Crystallographic data and experimental details for complexes **4**–**7** are summarized in Table 2. Intensity data were collected with a Bruker SMART APEX 1000 CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data was corrected for absorption by using the program SADABS.[20] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL software package.[21] In complex **5**, the cocrystallized $CHCl_3$ molecule was found to be disordered, and the chlorine atoms Cl2 and Cl3 are split into two sites of 0.6 and 0.4 occupancies. In complex **6**, one ethyl group of the phosphite ligand was found to be disordered; the carbon atom C32 is split into two sites of 0.5 and 0.5 occupancies. The $BAr^F{}_4^-$ anion in **7** was found to be disordered. The fluorine atoms F46, F54, F63, and F72 are split into two sites of 0.6 and 0.4 occupancies; F52, F57, and F73 are split into two sites of 0.5 and 0.5 occupancies; F44 is split into three sites of 0.35, 0.35, and 0.3 occupancies; and F75 is split into three sites of 0.35, 0.15, and 0.5 occupancies.

CCDC-760944 (for **4**), -760945 (for **5**), -760946 (for **6**), and -760947 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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