

Coordination Chemistry

Rhodium(III) Complexes Featuring Coordinated CF₃ AppendagesJack Emerson-King, Ivan Prokes, and Adrian B. Chaplin*^[a]

Abstract: The synthesis and characterisation of a homologous series of rhodium 2,2'-biphenyl complexes featuring intramolecular dative bonding of the nominally inert and weakly coordinating trifluoromethyl group are described. Presence of these interactions is evidenced in the solid state using X-ray diffraction, with Rh–F contacts of 2.36–2.45 Å, and in solution using NMR spectroscopy, through hindered C–CF₃ bond rotation and the presence of time-averaged ¹J_{RhF} and ²J_{PF} coupling.

The coordination chemistry of the transition elements is extensive, but notable for the paucity of well-defined complexes featuring explicit C–F→M bonding interactions.^[1,2] Indeed, the poor ligating characteristics of organofluorine groups, augmented by the inertness of the associated C–F bonds, lend them to notable application as constituents of weakly coordinating anions and solvents.^[3] Of the limited number of structurally characterised examples, the overwhelming majority are based on the electrophilic early transition metals: with A–D particularly notable (Figure 1).^[4,5] Complexes of the platinum group metals are scarce and only E–G feature M–F contacts < 2.5 Å.^[6,7] Building on our recent work, employing the high *trans*-influence 2,2'-biphenyl (biph) ancillary ligand for the systematic study of agostic interactions,^[8] we herein report the synthesis and characterisation of an unprecedented homologous series of late transition metal complexes featuring distinct CF₃→M bonding interactions.

To temper the extremely low nucleophilicity of the CF₃ group, we focused our efforts on probing the intramolecular coordination chemistry of this commonly used appendage and identified PPh₂Ar^F as a prospective ditopic ligand (Figure 1).^[9] Monomeric Rh^{III} complex [Rh(biph)(dtbpm)Cl] (dtbpm = bis(*tert*-butylphosphino)methane) is an established source of the

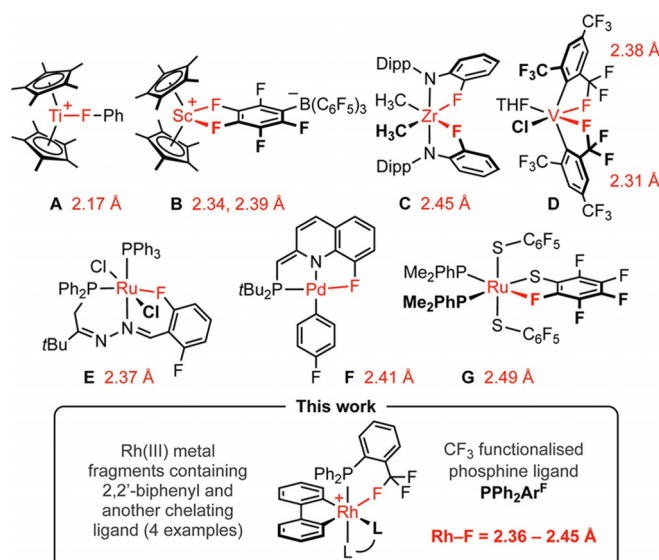


Figure 1. Selected examples of structurally characterised early and platinum group metal complexes featuring explicit C–F→M bonding interactions.

{Rh(biph)Cl} fragment in solution^[8,10] and reaction with excess PPh₂Ar^F in CH₂Cl₂ at RT proceeded, as anticipated, with substitution of the small bite-angle diphosphine alongside precipitation of chloro-bridged dinuclear complex **1** (Figure 2). The structure and purity of this sparingly soluble dimer was corroborated in (dilute) solution by NMR spectroscopy, in the solid state by single-crystal X-ray diffraction, and by combustion analysis. Subsequent substitution reactions enabled synthesis of considerably more soluble mononuclear derivatives **2–5**, which were all isolated in high purity and extensively characterised (Figure 2).

The solid-state structures of **1–4** are all notable for the adoption of distinct CF₃→Rh bonding interactions, characterised by Rh–F contacts of 2.36–2.45 Å, increasing in the order **2** < **4** < **3** < **1**, and significant elongation of the bound C–F bond (ca. 0.04 Å). There are very few crystallographically characterised transition-metal precedents for coordination of the CF₃ appendage and, to the best of our knowledge,^[1,2] only first-row adduct **D** (Figure 1), bearing two rigid 2,4,6-tris(trifluoromethyl)-phenyl ligands, features a shorter contact [V–F = 2.306(2) Å].^[5,11] Coordination of cyclopentadienyl in **5** leads to the nominal monodentate coordination of PPh₂Ar^F, with the CF₃ group projected away from the metal centre [∠Rh–P–C–CCF₃ = 167.7(1)° and Rh...F > 5 Å] demonstrating that this phosphine ligand is sufficiently conformationally flexible as to not enforce the chelation observed in **1–4**.

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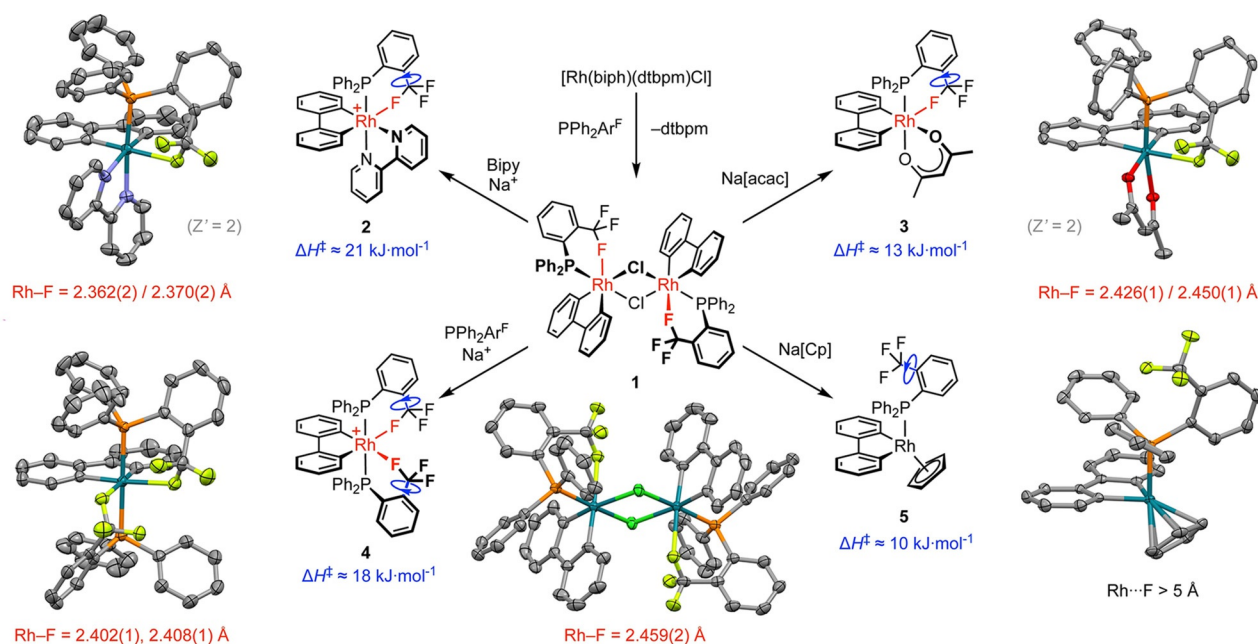


Figure 2. Synthesis, structures and dynamic properties of rhodium(III) complexes of $\text{PPh}_2\text{Ar}^{\text{F}}$; $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$ counter anions omitted for clarity. All reactions were carried out in CH_2Cl_2 at RT; **1** was isolated in 82% yield, and all subsequent substitution reactions proceeded quantitatively by NMR spectroscopy. Solid-state structures drawn with thermal ellipsoids at 50%, and minor disordered components (1 \times Ph group in **1** and **4**) and H atoms are omitted; symmetry equivalent atoms in **1** are generated by using the operation (4/3– x , 5/3– y , 2/3– z), only one of the two unique but structurally similar cations shown for **2** and **3** ($Z' = 2$).^[13]

In CD_2Cl_2 solution at 298 K, coordination of $\text{PPh}_2\text{Ar}^{\text{F}}$ in **1–5** was confirmed by ^{31}P NMR spectroscopy with the associated resonances exhibiting large ^{103}Rh coupling ($^1J_{\text{RhP}} = 124\text{--}170 \text{ Hz}$). Further coupling to magnetically equivalent ^{19}F nuclei ($^2J_{\text{PF}} \approx 5 \text{ Hz}$) is evident from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1–4**, but absent in that of **5**, consistent with the presence of weak and time-averaged $\text{CF}_3 \rightarrow \text{Rh}$ interactions in solution. At ambient temperature, fast rotation of the CF_3 groups on the NMR time scale and coupling to both ^{31}P and ^{103}Rh , with $^1J_{\text{RhF}} \approx ^2J_{\text{PF}}$ are also apparent from the $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **1–4** ($\delta_{\text{CF}_3} -62.8$ to -67.6 ppm ; 376 MHz).^[12] The transient nature of the $\text{CF}_3 \rightarrow \text{Rh}$ interaction in solution inferred from these data is fully in line with expectation and further vindicated through pronounced structural dynamics of asymmetric **1–3** evident by ^1H NMR spectroscopy at 298 K (400 MHz), that results in higher than expected time-averaged symmetry of the biph ancillary ligand and invokes dissociation of the CF_3 group. Equivalent exchange processes are presumably occurring in **4**, although the spectroscopic signatures are asymptomatic due to the inherently higher symmetry of this complex.

Further interrogation of **2–5** in CD_2Cl_2 was possible by variable-temperature NMR spectroscopy (see Figure 3 and Supporting Information), with progressive cooling from 298 to 185 K freezing out the structural dynamics observed for **2** and **3** (^1H NMR, 400 MHz), and inducing the onset of decoalescence of the CF_3 resonances (^{19}F NMR, 376 MHz). Although a full line shape analysis of the latter was not possible, as the slow exchange regime was not reached, the enthalpies of activation for hindered C– CF_3 bond rotation could be estimated from the temperature dependence of the line width (Figures 2 and

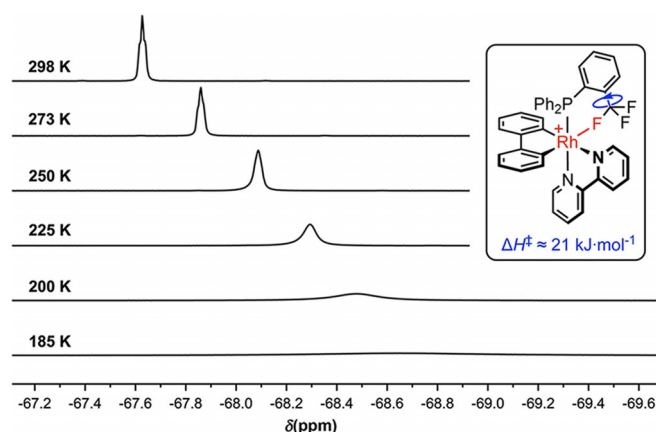


Figure 3. Variable-temperature $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **2** (CD_2Cl_2 , 376 MHz, 298–185 K).

3).^[14,15] The activation barriers increase in the order **3** < **4** < **2**, correlating with the bond lengths observed in the solid state, and are all larger than that measured for **5**. Only minor broadening of the ^1H Ar^{F} signals of **2–5** was observed on cooling, ruling out P– Ar^{F} bond rotation on the NMR time scale.

Through the isolation and structural characterisation of Rh^{III} complexes of $\text{PPh}_2\text{Ar}^{\text{F}}$ **1–4** we have demonstrated the ability of the late-transition-metal complexes to form well-defined, albeit weakly bound, adducts of the widely employed CF_3 functional group. Synthesis of these complexes advances the coordination chemistry of weakly interacting organofluorine compounds, and highlights the use of C– $\text{F} \rightarrow \text{M}$ bonding interac-

tions for the stabilisation of transition metal complexes with a low-coordination number. On the basis of computational predictions,^[16] adducts of this nature have been predicted to be intermediates in the oxidative addition of C(sp³)-F bonds and our future work will be focused on testing this hypothesis experimentally.

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Conflict of interest

The authors declare no conflict of interest.

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