Coordination Chemistry

Rhodium(III) Complexes Featuring Coordinated CF₃ Appendages

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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 J_{Rf} and J_{Hf} 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.[8,9] 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.[6,7] 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 employed addendum and identified PPh₂ArF as a prospective ditopic ligand (Figure 1).[9] Monomeric RhIII complex [Rh(biph)Cl] fragment in solution[8,10] and reaction with excess PPh₂ArF 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 PPh₂ArF, 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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In CD$_2$Cl$_2$ solution at 298 K, coordination of PPh$_2$ArF in 1–5 was confirmed by $^{31}$P NMR spectroscopy with the associated resonances exhibiting large $^{103}$Rh coupling ($J_{RhP}$ = 124–170 Hz). Further coupling to magnetically equivalent $^{19}$F nuclei ($J_{PF}$ ≈ 5 Hz) is evident from the $^{31}$P{1H} NMR spectra of 1–4, but absent in that of 5, consistent with the presence of weak and time-averaged CF$_3$–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 $J_{RhF}$ ≈ $J_{PF}$ are also apparent from the $^{19}$F{1H} NMR spectra of 1–4; the transient nature of the CF$_3$→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 $^1$H 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$_2$Cl$_2$ 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 ($^1$H 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 3).[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 $^1$H Ar$^t$ signals of 2–5 was observed on cooling, ruling out P–Ar$^t$ bond rotation on the NMR time scale.

Through the isolation and structural characterisation of Rh$^{III}$ complexes of PPh$_2$ArF 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–F→M bonding interac-

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**Figure 2.** Synthesis, structures and dynamic properties of rhodium(III) complexes of PPh$_2$ArF ; [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$ counter anions omitted for clarity. All reactions were carried out in CH$_2$Cl$_2$ 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 × 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]

**Figure 3.** Variable-temperature $^1$F{1H} NMR spectra of 2 (CD$_2$Cl$_2$, 376 MHz, 298–185 K).
intermediates in the oxidative addition of C(sp\(^3\))–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.

**Keywords:** coordination chemistry · fluorinated ligands · low-coordinate complexes · phosphane ligands · rhodium


[2] Analysis of the structures deposited in the Cambridge Structure Database (CSD v. 5.39; update Aug 2018) found 110 transition metal complexes with M–F contacts < 3.0 Å. Of these only 12 feature close approaches of Cisp\(^3\)-F bonds.


[13] CSD: CSD No. 1870909, 1870910, 1870911, 1870912, and 1870913 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.


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A late-transition-metal platform for probing the delicate coordination chemistry of the trifluoromethyl functional group.