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Tethering of Pentamethylcyclopentadienyl and *N*-Heterocycle Stabilized Carbene Ligands by Intramolecular 1,4-Addition to a Polyfluorophenyl Substituent

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Supporting Information Placeholder

ABSTRACT: On treatment with silver(I) oxide the complex [Cp*RhCl₂(κC-MeNC₃H₂NCH₂C₆F₅)] undergoes 1,4-addition of rhodium and methylene to the polyfluoroaryl ring, which loses aromaticity, affording [(η⁵,κ²-C₃Me₄CH₂C₆F₅CH₂NC₃H₂NMe)RhCl].

Metal complexes of chelating tethered η⁵-cyclopentadienyl-NHC ligands are desirable as catalysts for a number of reactions because of their greater stability, activity and regio- and stereoselectivity compared to complexes of the untethered ligands.^{1,2} Except for two examples of intermolecular functionalization of metal-bound η⁵-cyclopentadienyl ligands,³ the route to these complexes involves the synthesis of the uncoordinated tethered ligand and subsequent coordination to the metal. Although a number of complexes of similar η⁵-cyclopentadienyl-NHC ligands have been prepared by this route, it is an inconvenient strategy if the synthesis of the desired ligands involves multiple steps, has a low overall yield, and coordination to the metal is compromised by the incompatibility of reagents and functional groups. Linking ligands that are already coordinated to the metal by an intramolecular reaction, as has been demonstrated for a chelating NHC-diphosphine,⁴ is an attractive alternative, because intramolecular reactions are faster and cleaner.

We have previously identified intramolecular dehydrofluorinative carbon-carbon coupling as a rapid, high-yielding route to η⁵,κ^{*P*}-cyclopentadienyl-phosphine complexes of rhodium and^{5,6} iridium.⁷ The cationic complexes [Cp*MCIL(κ^{*P*}-PR₂C₆F₅)]⁺ and [Cp*MCl{κ^{*P*},*L*-(C₆F₅)PR-*L*}]⁺ yielded [(η⁵,κ^{*P*}-C₃Me₄CH₂C₆F₄PR₂)MLCl]⁺ and [(η⁵,κ^{*P*},*L*-C₃Me₄CH₂C₆F₄PR-*L*)MCl]⁺ (*L* = Lewis basic ligand or moiety) respectively on treatment with proton sponge. However, our attempts to synthesize complexes of tethered η⁵,κC-cyclopentadienyl-NHC ligands using this route have been unsuccessful: [Cp*RhCl₂(κC-MeNC₃H₂NCH₂C₆F₅)], **1**, and [Cp*RhCl(CNCMe₃)(κC-MeNC₃H₂NCH₂C₆F₅)]BF₄ were found to undergo no reaction on treatment with proton sponge, even at an elevated temperature for an extended period,⁸ and [Cp*RhCl₂(κC-C₆H₅CH₂NC₃H₂NC₃F₄N-4)] afforded

[Cp*RhCl₂(κC-C₆H₅CH₂NC₃H₂NC₃F₃N-4-(OH)-2)] on treatment with base.⁹ Here we report the formation of a rhodium complex of an η⁵,κC-cyclopentadienyl-NHC ligand by an intramolecular addition reaction.

Our recent observation of carbon-fluorine bond activation on treatment of [Cp*IrCl₂(κC-MeNC₃H₂NCH₂C₆F₅)] with silver(I) oxide, which decomposes to silver on stirring,¹⁰ prompted us to investigate the reaction of the rhodium analogue, **1**. In contrast to the iridium analogue, on addition of silver(I) oxide complex **1** underwent a clean conversion to [(η⁵,κ²-C₃Me₄CH₂C₆F₅CH₂NC₃H₂NMe)RhCl], **2**, over 24 hours. Complex **2** was identified by a single-crystal X-ray diffraction study (Figure 1). 1,4-Addition of the rhodium atom and a methylene carbon atom to the pentafluorophenyl group, and its loss of aromaticity, is clearly evident: the C(16)–C(21) and C(18)–C(19) distances (1.346(9) and 1.312(9) Å) are consistent with double bonds, whereas the C(16)–C(17), C(17)–C(18), C(19)–C(20) and C(20)–C(21) distances (1.472(9), 1.465(8), 1.48(1) and 1.498(8) Å respectively) are consistent with single bonds, and the atoms C(17) and C(20) are in tetrahedral environments (Y–C–X 100.9(4) to 114.6(4)°).

The NMR spectroscopic and mass spectral data are entirely consistent with the structure of **2** (see the Supporting Information). In particular in the ¹H NMR spectrum there are four cyclopentadienyl methyl resonances at δ 0.74, 1.39, 1.80 and 1.86, and two mutually coupled doublet resonances possessing further coupling at δ 1.38 and 1.76. These data are consistent with those of the tethered ligand of [(η⁵,κ^{*P*}-C₃Me₄CH₂C₆F₄PPh₂)RhCl(CNPh)]BF₄⁵ and related complexes.⁶ Further, the ¹⁹F NMR spectrum displays five distinct fluorine resonances of equal integration at δ -145.60, -149.36, -174.06, -176.81 and -185.71, which are consistent with the resonances of other polyfluorocyclohexa-1,4-dienes.¹¹

Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cp*–Rh 1.879(6), Rh–Cl 2.3963(14), Rh–C(11) 2.032(6), Rh–C(17) 2.107(6), Cp*–Rh–Cl 122.6(3), Cp*–Rh–C(11) 126.3(3), Cp*–Rh–C(17) 128.3(3), Cl–Rh–C(11) 95.8(2), Cl–Rh–C(17) 89.9(2), C(11)–Rh–C(17) 82.3(2).

Scheme 1. Proposed mechanism of the reaction between **1** and Silver(I) Oxide

Based on the observations and a previously proposed mechanism for similar reactions,^{5,12} it is suggested that the reaction proceeds by abstraction of chloride to generate a cation, which increases the acidity of the pentamethylcyclopentadienyl hydrogen atoms. Subsequent loss of a proton in the presence of base generates a 16 electron complex which may be considered as a zwitterion,¹² or an η^4 -tetramethylfulvene complex,¹³ possessing a nucleophilic methylene carbon atom and a Lewis acidic metal centre. It is possible that there is η^2 coordination of the pentafluorophenyl ring, which would result in a complex satisfying the 18-electron rule and would bring the pentafluorophenyl ring close to the cyclopentadienyl ring, aiding the subsequent addition. A concerted or stepwise 1,4-addition involving nucleophilic attack by the methylene carbon atom and electrophilic attack by the rhodium atom gives the product (Scheme 1).

No intermediates have been observed, but since this is an intramolecular reaction it is expected to be very rapid once the zwitterion is generated. Formation of the zwitterion is expected to be slow because of the different phases of the reactants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental procedures, characterizing data, spectra and associated figures

Crystallographic data for **2**

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Author Contributions

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Notes

The authors declare no competing financial interests.

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