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

Hayden P. Thomas, † Andrew C. Marr, ‡ Patrick J. Morgan‡ and Graham C. Saunders* †

† School of Science, University of Waikato, Hamilton 3240, New Zealand.
‡ School of Chemistry and Chemical Engineering, Queen’s University Belfast, David Keir Building, Belfast BT9 5AG, United Kingdom.

Supporting Information Placeholder

ABSTRACT: On treatment with silver(I) oxide the complex [Cp*RhCl₂κ-C(MeNC₅H₅)₂C₆H₄NC₆F₄P₂] undergoes 1,4-addition of rhodium and methylene to the polyfluorocyclohexadiene ring, which loses aromaticity, affording [[(κ²C₅Me₅CH₂₂C₆F₄CH₂NC₅H₄[NMe]RhCl]⁺].

Metal complexes of chelating tethered η²-cyclopentadienyl-NHC ligands are desirable as catalysts for a number of reactions because of their greater stability, activity and regio- and stereo-selectivity compared to complexes of the untethered ligands. 1-3 Except for two examples of intermolecular functionalization of metal-bound η²-cyclopentadienyl ligands,4 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 η²-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,5 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 η¹κ²C₅-cyclopentadienyl-phosphine complexes of rhodium and iridium.6-7 The cationic complexes [Cp*MCl₂κ²PR₂C₅F₅]⁺ and [Cp*MClκ²P(L)-(C₅F₅)PR₂-L]⁺ yielded [(η²κ²P-L-C₅Me₂CH₂₂C₆F₄PR₂-MCl)]⁺ and [(η²κ²P-L-C₅Me₂CH₂₂C₆F₄PR₂-L)MCl]⁺ (L = Lewis basic ligand or moiety) respectively on treatment with proton sponge. However, our attempts to synthesize complexes of tethered η¹κ²C₅-cyclopentadienyl-NHC ligands using this route have been unsuccessful: [Cp*RhCl₂κ-C(MeNC₅H₅)₂C₆H₄NC₆F₄P₂], 1, and [Cp*RhCl(CNCMe₅)κ-C(MeNC₅H₅)₂C₆H₄NC₆F₄]BF₄ were found to undergo no reaction on treatment with proton sponge, even at an elevated temperature for an extended period, and [Cp*RhCl₂κ-C₅H₅CH₂₂NC₅H₄NC₆F₄N-4)] afforded [Cp*RhCl₂κ-C₅-C₅H₅CH₂₂NC₅H₄NC₆F₄N-4-(OH)-2)] on treatment with base.8 Here we report the formation of a rhodium complex of an η¹κ²-cyclopentadienyl-NHC ligand by an intramolecular addition reaction.

Our recent observation of carbon-fluorine bond activation on treatment of [Cp*IrCl₂κ-C(MeNC₅H₅)₂C₆H₄NC₆F₄P₂] with silver(I) oxide, which decomposes to silver on stirring,9 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 [[(η²κ²C₅Me₂CH₂₂C₆F₄CH₂NC₅H₄[NMe]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 pentfluorophenyl 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 [[(η²κ²P-L-C₅Me₂CH₂₂C₆F₄PR₂-MCl)]⁺ and related complexes.6 Further, the ¹³F 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-diens.10
nism for similar reactions, it is suggested that the reaction and Silver(I) Oxide.

\[ \text{C}(11) - \text{Rh} - \text{C}(17) 82.3(2), \ 2.107(6), \ \text{Cp}^* - \text{Rh} - \text{Cl} 122.6(3), \ \text{Cp}^* - \text{Rh} - \text{C}(11) 126.3(3), \ \text{Cp}^* - \text{Rh} - \text{C}(17) 128.3(3), \ \text{Cl} - \text{Rh} - \text{C}(11) 95.8(2), \ \text{Cl} - \text{Rh} - \text{C}(17) 89.9(2), \ \text{C}(11) - \text{Rh} - \text{C}(17) 82.3(2). \]

Based on the observations and a previously proposed mechanism of the reaction between 1 and Silver(I) Oxide

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](http://pubs.acs.org).

Experimental procedures, characterizing data, spectra and associated figures

Crystallographic data for 2

**AUTHOR INFORMATION**

Corresponding Author

* g.saunders@waikato.ac.nz

Author Contributions

†,‡, HPT, ACM, PJM and GCS contributed equally.

Notes

The authors declare no competing financial interests.

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