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Template synthesis of an intermediate in silver salt metathesis using a calix[4]arene-based diphosphine ligand

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The synthesis and solid-state characterisation of the heterobimetallic rhodium(III)/silver(I) complex \([\text{Rh(2,2’-biphenyl)}](\text{CxP}_2)\text{Cl}] \supset \text{Ag}^+\) is described, where CxP₂ is a trans-spanning calix[4]arene-based diphosphine and the silver cation is dative bound to the chloride ligand within the cavity of the macrocycle.

The activation of transition metal complexes by abstraction of halide ligands using silver(I) salts is a widely employed strategy in organometallic chemistry and catalysis. Mechanistic work on by Mattson and Graham in 1981 substantiated a reaction sequence involving complexation of the silver(I) cation to the halide atom, before nucleophilic substitution and precipitation of the argentate salt from solution. Building on work by Reed and co-workers using weekly coordinating carborane anions, the first intermediate silver(I) halide adduct, \([\text{CpMo(CO)}_3\text{I}](\mu-\text{Ag})\)₃, was structurally corroborated in the solid-state by single crystal X-ray diffraction by Weller and co-workers in 2000. Notwithstanding facile onward reactivity, it is surprising to note that there have been only a handful of further well-defined examples over the intervening decades.

As part of our group’s ongoing interest in cavitand-based ditopic ligands, we have recently become engaged in exploring the coordination chemistry of Kubas’ calix[4]arene diphosphine ligand CxP₂. In a proceeding paper we described the preparation of mononuclear rhodium(III) aqua complex \([\text{Rh(2-biphenyl)}](\text{CxP}_2)\text{OH})\)\([\text{Al(OR)}_3]\) \(1\text{-OH}_2\); biph = 2,2’-biphenyl; \(R^f = \text{CF}_3\)) by substitution of \(\text{trans-}[\text{Rh(biph)(PPh}_3)\text{OH})\]\([\text{Al(OR)}_3]\) with CxP₂ in THF. Seeking to access water-free, low-coordinate Rh\[biph\] derivative 1, preparation and subsequent silver(I)-based halide abstraction of \(1\text{-Cl}\) was targeted. During the course of this work, we discovered that the silver(I) cation templates assembly of heterobimetallic rhodium(III)/silver(I) complex \([\text{Rh(biph)}](\text{CxP}_2)\text{Cl}] \supset \text{Ag}^+\) \(1\text{-ClAg}\), which is a rare well-defined example of an intermediate in silver salt metathesis reactions.

Monomeric rhodium(III) complex \([\text{Rh(biph)}](\text{dtbpm})\text{Cl}]\) \((\text{dtbpm} = \text{bis(di-tert-butylphosphino)methane})\) is an effective source of the \([\text{Rh(biph)}]\text{Cl}\) fragment in solution and was reacted with CxP₂ in CH₂Cl₂ at RT. Substitution of dtbpm was observed alongside generation of a sparingly soluble product that exhibits a \(31\text{P}\) resonance at \(\delta 29.9\) \((J_{\text{Rh-P}} = 114\text{ Hz})\) and is assigned as dimeric \([\text{Rh(biph)}]\text{Cl}]\)\(\text{Cl}^+\text{Ag}^-\) on the basis of a low-quality X-ray structure determination (Fig 1A). Whilst not the desired outcome, coordination of CxP₂ in this manner is consistent with earlier reports.

Reasoning that chelation of CxP₂ could still be induced upon chloride abstraction, 2 was carried forward and reacted with two equivalents of Ag[Al(OR)_₃] in dichloromethane under argon at RT. Analysis of the resulting suspension by NMR spectroscopy indicated clean conversion into a new complex within 48 h rather than the expected dichloromethane adduct \(1\text{-DCM}\) \((\delta_{31\text{P}} 4.4, J_{\text{Rh-P}} = 117\text{ Hz})\). This new organometallic is characterised by a sharp \(31\text{P}\) resonance at \(\delta 13.9\) \((J_{\text{Rh-P}} = 120\text{ Hz})\) significant downfield shifts of the aromatic \(1\text{H}\) resonances of the calix[4]arene scaffold relative to 2 \((p-\text{Ar}^a, 6.02 \rightarrow 7.32; m-\text{Ar}^a, 5.63 \rightarrow 7.11, m-\text{Ar}^a, 6.22 \rightarrow 6.50)\), and assigned to mononuclear \(1\text{-ClAg}\), where the CxP₂ ligand adopts the desired trans-spanning coordination mode and the silver cation is bound within the cavity of the calix[4]arene scaffold (Fig 1A). This species is persistent at RT under argon or dinitrogen, but incredibly moisture sensitive. Repeated attempts to isolate analytically pure samples were frustrated by facile and irreversible reaction with adventitious water, resulting in the formation of aqua complex \(1\text{-OH}_2\) with concomitant...

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precipitation of AgCl. Indeed, on a preparative scale, deliberate addition of a slight excess of water to in situ generated 1-ClAg enabled isolation of the considerably more robust, air and moisture stable 1-OH₂ as an orange solid in 77% yield from 2.

Consistent with the assigned structure of 1-ClAg, only a slight perturbation to the ¹H and ³¹P resonances occurs on formation of 1-OH₂ (δ 13.2, J_{RhP} = 120 Hz), alongside appearance of a distinctive 2H singlet at δ 0.84 for coordinated water. Most notably, one of the two unique OCH₂ groups is shifted from 4.49 → 4.12 and we account for this change by coordination of the associated aryl ether to silver in 1-ClAg.

Fortuitously, we have been able to structurally characterise 1-ClAg in the solid state through analysis of a co-crystalline sample formed with 1-OH₂ (58%:42% relative occupancy; Fig. 1B). From the crystallographic disorder model, silver was identified within the cavity and found to exhibit a pseudo T-shaped metal coordination geometry with a Ag1–Cl1 distance of 2.490(2) Å and two dative bonding interactions with the flanking aryl ether units of the calix[4]arene scaffold. Chelation of CₓP₂ to rhodium is promoted by Cl⇀Ag⁺ bonding (Fig. 1A) and thereafter silver chloride is lost upon reaction with water, adventitious or deliberately added. This sequence further corroborates Mattson and Graham’s mechanistic proposal for silver salt metathesis reactions, underscores the multifaceted ability of silver(I) cations to activate late transition metal complexes, and highlights the propensity of donor-functionalised cavitand ligands to orchestrate unusual metal-based reactivity.

Based on our observations, we propose conversion of 2 into 1-OH₂ is initiated by capture of silver within the calix[4]arene scaffold. Chelation of CₓP₂ to rhodium is promoted by Cl⇀Ag⁺ bonding (Fig. 1A) and thereafter silver chloride is lost upon reaction with water, adventitious or deliberately added. This sequence further corroborates Mattson and Graham’s mechanistic proposal for silver salt metathesis reactions, underscores the multifaceted ability of silver(I) cations to activate late transition metal complexes, and highlights the propensity of donor-functionalised cavitand ligands to orchestrate unusual metal-based reactivity.

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Conflicts of interest

The authors declare no conflicts of interest.
Notes and references


10 In line with the solution phase stability of the rhodium(III) dinitrogen analogue [Rh(biph)(CXP2)(N2)][Al(OR)4] (1-N2, ref. 8).