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One-pot synthesis of cationic rhenium (V) carbyne complexes by phosphine attack on coordinated alkyne

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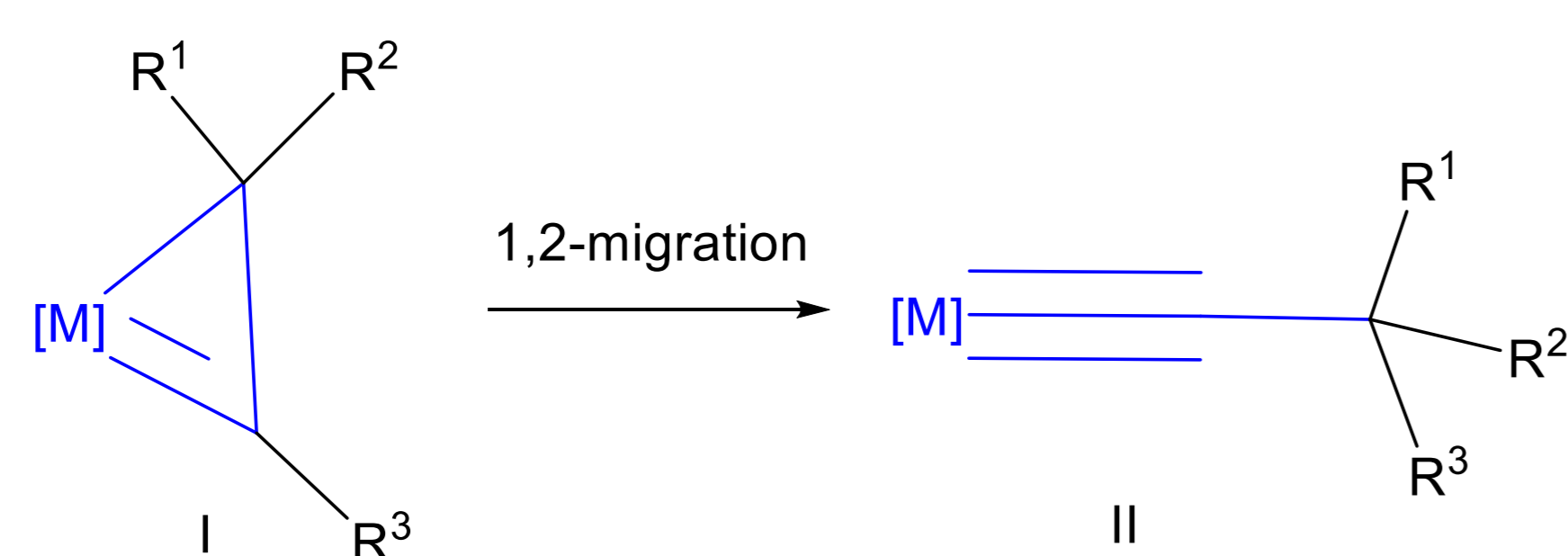
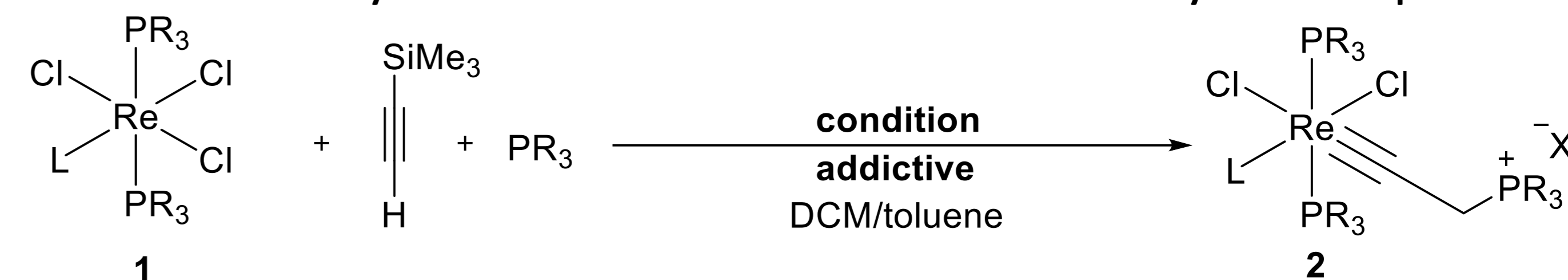
Introduction

Rhenium(V) carbyne complexes are potential alkyne metathesis catalysts with the advantage of robustness to water and wide range of substrates. One of the limitations of these catalyst candidates is the time-consuming and tedious preparation of their rhenium carbyne precursor. We have recently found that one-pot reactions of the rhenium(III) phosphine starting materials **1** with phosphine and TMS-C≡CH can give cationic rhenium(V) carbyne complexes **2** with decent yields (Scheme 1).

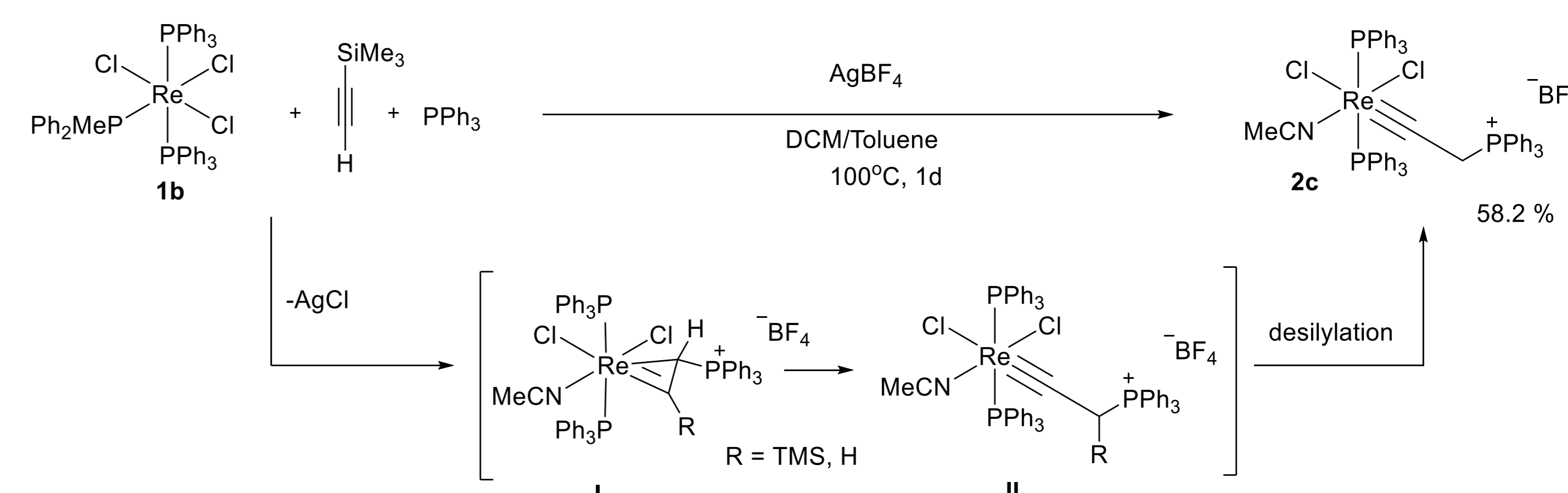
Synthesis and mechanism

The reaction (synthesis of **2c** is shown in Scheme 3 as an example) involves 1,2-H (or TMS) shift of a transient rhenium η^2 -vinyl intermediate, generated by the nucleophilic phosphine attack on a coordinated alkyne. The labile TMS group was hydrolyzed by residual water to give a TMS-free carbyne species **2**.

In the reaction that gives **2b**, the resulted Re(IV) counterion (as shown in Fig. 1) may be originated from the oxidation of Re(III) species **1b**, triggered by free chloride coordination. As a result, chloride scavenger AgBF₄ was used to synthesize the diamagnetic species **2c** for better atom economy.

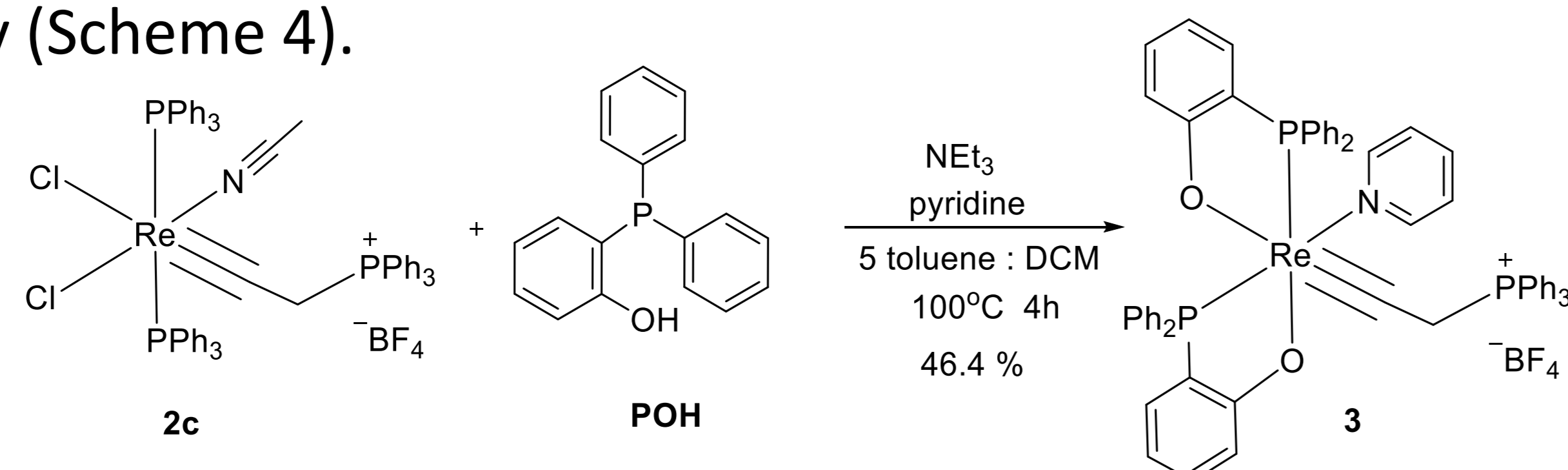
Scheme 2. The 1,2-migration of η^2 -vinyl complex to give a carbyne complex.Scheme 1. The synthesis of cationic rhenium carbyne complexes **2**.

1	PR ₃	L	Condition	Additive	Yield%	2	X
a	PMePh ₂	PMePh ₂	100 °C	/	63.0	a	Cl
b	PPh ₃	NcMe	80 °C	/	39.6	b	Re(PPh ₃)Cl ₅
b	PPh ₃	NcMe	100 °C	AgBF ₄	58.2	c	BF ₄

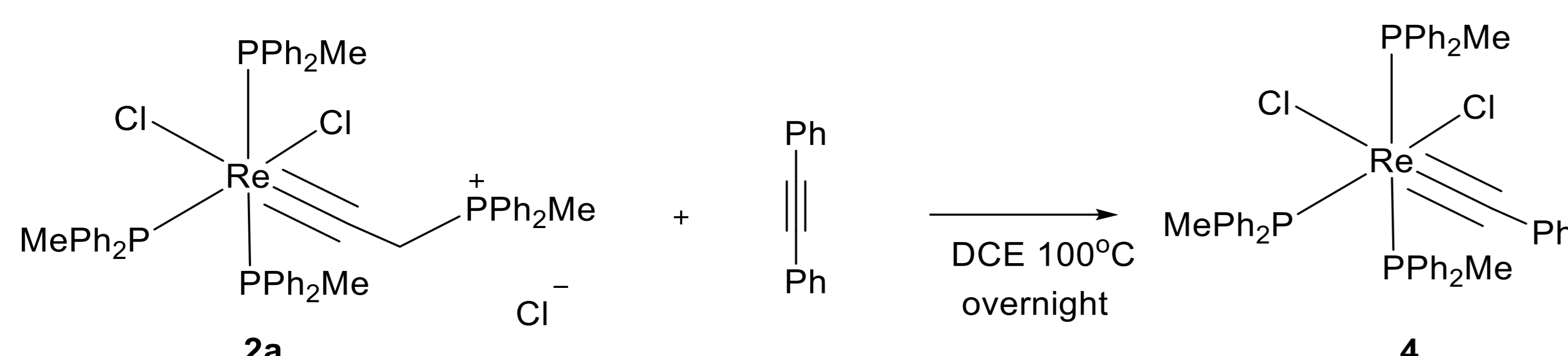
Scheme 3. A plausible mechanism to give complex **2c** with AgBF₄.

Reactions with cationic rhenium carbyne complexes

Cationic rhenium carbyne complexes were tested for ligand substitution. The complex **2c** reacted with the bidentate ligand (2-hydroxyphenyl)diphenylphosphine (**POH**) to give the complex **3** successfully (Scheme 4).

Scheme 4. The reaction of complex **2c** with a **POH** and pyridine to give complex **3**.

Stoichiometric alkyne metathesis was also examined for cationic rhenium carbyne complexes. The complex **2a** reacted with diphenylacetylene to give the expected metathesis product **4** (Scheme 5).

Scheme 5. The stoichiometric alkyne metathesis reaction of complex **2a** with diphenylacetylene to give product **4**.

X-Ray crystallography

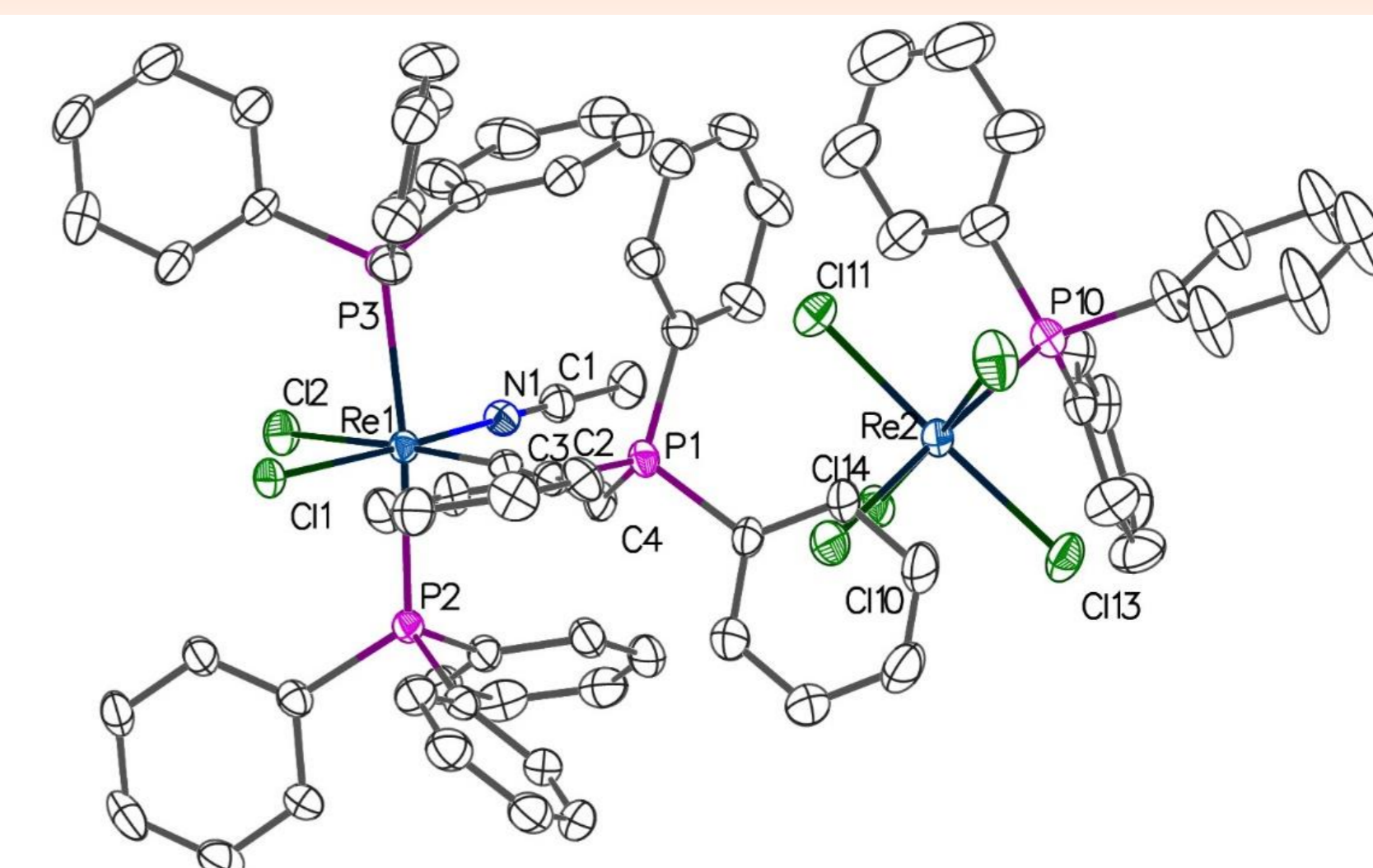


Fig 1. The crystal structures of the complex **2b**. Selected bond parameters for the structure of [A] and [o] : Re(1)-Cl(1) 2.4457(10), Re(1)-Cl(2) 2.5140(10), Re(1)-P(2) 2.4538(10), Re(1)-P(3) 2.4851(10), Re(1)-N(1) 2.072(4), Re(1)-C(3) 1.760(4), P(2)-Re(1)-C(3) 88.25(13), N(1)-Re(1)-C(3) 89.63(18).

Conclusion

We have developed a one-pot synthesis of rhenium carbyne complexes for potential alkyne metathesis catalyst precursor. The reactivities of these cationic carbyne species in ligand substitution and alkyne metathesis reactions have been tested and demonstrated.