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Metathesis reactions of Re(v) carbyne complexes with functionalized terminal alkynes†

Byeongsoo Park, [ID] Wei Bai, Lam Cheung Kong, Herman H. Y. Sung, Ian D. Williams [ID] and Guochen Jia [ID] *

Alkyne metathesis is a cornerstone reaction in synthetic chemistry. However, metathesis of terminal alkynes remains a rare accomplishment, both catalytically and stoichiometrically. To overcome this challenge, we explored reactions of non-d^0 carbyne complexes with terminal alkynes. It was found that d^2 Re (v) carbyne complexes, specifically Re($\equiv$CR)Cl$_2$(PMePh$_2$)$_3$, can undergo stoichiometric metathesis with a range of terminal aryl and aliphatic alkynes (HC$\equiv$CR'), yielding substituted carbyne complexes Re($\equiv$CR') Cl$_2$(PMePh$_2$)$_3$ and HC$\equiv$CR. These stoichiometric metathesis reactions are compatible with functional groups such as aldehydes, alcohols, esters, and even unprotected carboxylic acids. Density Functional Theory (DFT) calculations indicate that the formation of substituted carbyne complexes is both thermodynamically and kinetically more favorable than that of methylidyne complexes.

Introduction

Metathesis of transition metal carbyne (or alkylidyne) complexes with alkynes is a fundamentally important transformation that plays a key role in catalytic alkyne metathesis reactions.[1] The reactivity is now well-documented for internal alkynes.[2–4] On the basis of this reactivity, a library of catalysts have been invented for metathesis reactions of internal alkynes, including those based on well-defined or *in situ* generated high valent d^0 W(vi)[5] and Mo(vi)[6] carbyne complexes, and d^2 Re(v)[7] carbyne complexes. With these catalysts, alkyne metathesis is finding growing practical applications in areas such as organic synthesis,[8] polymerization[3a,9,10] as well as dynamic covalent chemistry.[11]

Terminal alkynes are highly attractive substrates for alkyne metathesis reactions due to their common use in organic synthesis and their accessibility compared to internal alkynes, such as methyl-capped alkynes.[12] Despite their potential, catalytic metathesis reactions involving terminal alkynes are rarely reported.[13] Competent catalysts for these reactions are restricted to a few high-valent d^0 Mo(vi) and W(vi) carbyne catalysts, for example, Mo($\equiv$CC$_6$H$_4$-*p*-OMe)(OSiPh$_3$)$_3$,[12,14,15,16,17,6l] W($\equiv$CMes){OCMe$_2$(CF$_3$)}$_3$,[18] Mo($\equiv$CMes){OCMe(CF$_3$)$_2$}$_3$,[19–22] and [MesC$\equiv$Mo{OSi(O*t*Bu)$_{3−n}$Ph$_n$}$_3$] (*n* = 1, 2).[23] More often,

terminal alkynes polymerize when exposed to a typical high-valent carbyne catalyst.[1a,6b,24,25,26,27]

To advance the development of new catalysts for terminal alkyne metathesis, it is crucial to identify carbyne complexes that can readily undergo metathesis reactions with terminal alkynes including those with different functional groups. Additionally, understanding of the activity and selectivity of metathesis reactions of carbyne complexes with terminal alkynes is essential. However, these issues remain largely unaddressed. Notably, well-defined stoichiometric metathesis reactions of terminal alkynes are exceedingly scarce. They have only been described for reactions of Mo($\equiv$C*t*Bu){OCMe$_2$(R)}$_3$ (R = Me, CF$_3$) with simple alkynes HC$\equiv$CR' (R' = *n*Pr, iPr, Ph) to give Mo($\equiv$CR'){OCMe$_2$(R)}$_3$,[28] and for the slow (in two weeks) reaction of HC$\equiv$C*t*Bu with W($\equiv$CMe)Cl(PMe$_3$)$_4$ to give W($\equiv$C*t*Bu)(η^2-HC$\equiv$CMe)Cl(PMe$_3$)$_2$.[29]

We herein report our recent findings that d^2 Re(v) carbyne complexes, specifically Re($\equiv$CR)Cl$_2$(PMePh$_2$)$_3$, can undergo stoichiometric metathesis with a range of terminal alkynes. For the first time, metathesis reactions of carbyne complexes have been demonstrated for terminal alkynes with functional groups including aldehydes, alcohols, esters, and unprotected carboxylic acids.
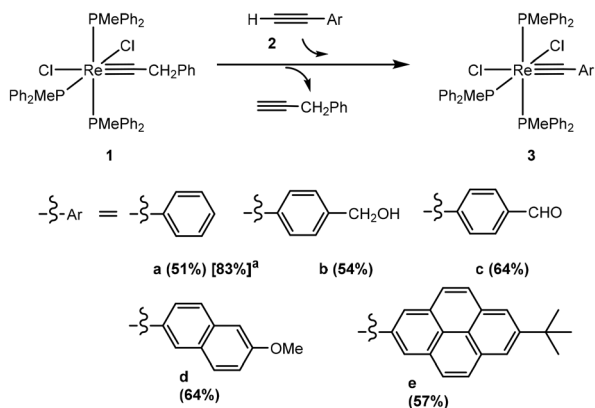
Results and discussion

Reactions of Re($\equiv$CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$ with terminal aryl alkynes HC$\equiv$CAr

Inspired by the recent discovery that d^2 Re(v) carbyne complexes can catalyse metathesis of internal alkynes,[7] we decided

Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. E-mail: chjiag@ust.hk

Scheme 1 Metathesis reactions of Re($\equiv$CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$ (**1**) with terminal aryl alkynes HC$\equiv$CAr (**2a–e**) in toluene. Reaction conditions: 4 equiv. of HC$\equiv$CAr, 100 °C, 2 h. The isolated yields are given in parenthesis. ^{a}**3a** could also be isolated in 83% yield from the reaction with 20 equiv. of HC$\equiv$CAr at r.t. for 30 h.

Scheme 2 Metathesis reactions of Re($\equiv$CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$ with terminal alkyl alkynes HC$\equiv$CR (**4a–d**) in toluene. Reaction conditions: 10–20 equiv. of HC$\equiv$CR, r.t., 24–30 h or 4 equiv. of HC$\equiv$CR, 45–90 °C, 2–5 h. The isolated yields are given in parenthesis for reactions at 45–90 °C, and in bracket for reactions at r.t.

Scheme 3 Metathesis reactions of Re($\equiv$CR)Cl$_2$(PMePh$_2$)$_3$ (R = Ph, (CH$_2$)$_4$OH) with 4 equiv. of terminal alkyl alkynes HC$\equiv$CR in toluene at 100 °C for 2 h. The ratio refers to molar ratio estimated by *in situ* NMR.

to explore their potential in metathesis reactions with terminal alkynes. In this work, we focus on stoichiometric alkyne metathesis reactions of Re(v) carbyne complexes (see Schemes 1–3 below). We began by investigating the reaction of phenylacetylene with Re($\equiv$CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$ (**1**), a complex that can be easily prepared on a large scale.[4b]

As monitored by NMR spectroscopy (see Fig. S1†), the complex **1** can undergo metathesis reaction with phenylacetylene in toluene at room temperature. With 20 equivalents of HC$\equiv$CPh, the reaction produced the expected metathesis product, Re($\equiv$CPh)Cl$_2$(PMePh$_2$)$_3$ (**3a**), in approximately 22% yield after 6 hours, 57% after 12 hours, and 86% after 24 hours (Scheme 1). In contrast, no metathesis product was observed for the reaction of **1** with 20 equivalents of the internal alkyne PhC$\equiv$CPh even after 48 hours. A higher temperature (*e.g.*, 110 °C) is required for the metathesis reaction of PhC$\equiv$CPh to proceed.[4b] The observations suggest that terminal alkynes are significantly more reactive than internal alkynes in alkyne metathesis.

As anticipated, the metathesis reaction of **1** with PhC$\equiv$CH proceeded at a higher rate at higher temperatures. When the reaction was carried out at 100 °C with four or less equivalents of PhC$\equiv$CH, the complex **1** was consumed completely within two hours to give the expected metathesis product Re($\equiv$CPh)Cl$_2$(PMePh$_2$)$_3$ (**3a**) as the major product. When five or more equivalents of PhC$\equiv$CH was used, the reaction at 100 °C produced a mixture of unidentified side products.

More interestingly, complex **1** can also undergo metathesis reactions with functionalized terminal aryl alkynes (Scheme 1). For example, it reacted with the aryl terminal alkynes **2b** bearing a CH$_2$OH group and **2c** bearing an aldehyde group to give the corresponding metathesis products **3b** and **3c**, respectively. The formation of **3b** and **3c** indicate that the metathesis reaction can tolerate OH and CHO groups. The result is interesting as OH and CHO functional groups are often incompatible or reactive with typical high valent d^0 carbyne complexes.
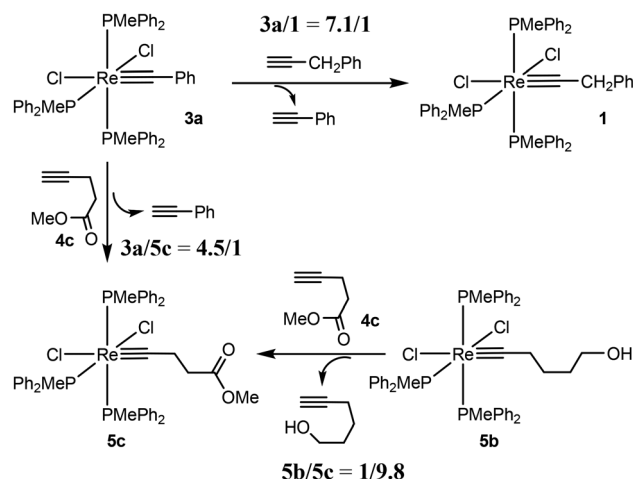
Metathesis products were also obtained by treating the complex **1** with terminal alkynes bearing polyaromatic rings. For example, the complexes **3d** and **3e** were formed from the metathesis reactions of the naphthalene derivative **2d** and the pyrene derivative **2e** respectively. Notably, complex **3e** is a rare example of a metal carbyne complex with a large extended aromatic system.

The metathesis products **3a–e** are air-stable solids. The complex **3a** is a known compound and has been fully characterized by NMR as well as X-ray diffraction as described previously.[4b] The structures of **3b–3e** can be readily assigned on the basis of their spectroscopic data. For example, the ^{31}P{^{1}H}

NMR spectrum of **3c** showed a triplet at −3.2 ppm and a doublet at −12.4 ppm. The $^{13}C\{^1H\}$ NMR spectrum showed the carbyne signal at 258.8 ppm and that of CHO at 192.2 ppm.

The structure of the complex **3d** has also been confirmed by X-ray diffraction. As shown in Fig. 1, it adopts an octahedral geometry with the carbyne ligand trans to one of the chloride ligands. The naphthalene group of the carbyne ligand lies almost in the same plane containing the rhenium metal center and the two chloride atoms. The Re≡C bond distance is 1.773(3) Å, and the Re–C(1)–C(2) angle is 171.2(3)°, which are typical for rhenium carbyne complexes.[30] The structural feature of the coordination sphere of **3d** is similar to that of **3a**.

Reactions of Re(≡CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$ with terminal alkyl alkynes HC≡CR

Encouraged by the successful metathesis reactions of **1** with terminal aryl alkynes, we expanded our exploration to include terminal aliphatic alkynes (Scheme 2). As indicated by the *in situ* $^{31}P\{^1H\}$ NMR spectrum (see Fig. S2†), the complex Re(≡CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$ (**1**) reacted with 10 equivalents of 1-hexyne, HC≡C(CH$_2$)$_3$Me (**4a**), in toluene at room temperature to give the expected metathesis product Re(≡C(CH$_2$)$_3$Me)Cl$_2$(PMePh$_2$)$_3$ (**5a**) in yields of *ca.* 40% in six hours and nearly 65% in 24 hours. The metathesis product Re(≡C(CH$_2$)$_3$Me)Cl$_2$(PMePh$_2$)$_3$ (**5a**) was isolated as a yellow solid. Similarly, the alkyne HC≡C(CH$_2$)$_2$CO$_2$Me (**4c**), bearing an ester group, reacted with complex **1** to yield the metathesis product Re(≡C(CH$_2$)$_2$CO$_2$Me)Cl$_2$(PMePh$_2$)$_3$ (**5c**), which was isolated as an orange solid (see Fig. S3†).

The alkynol HC≡C(CH$_2$)$_3$CH$_2$OH (**4b**) also undergoes a smooth metathesis reaction with the complex **1** to yield Re(≡C(CH$_2$)$_3$CH$_2$OH)Cl$_2$(PMePh$_2$)$_3$ (**5b**), indicating that the metathesis reaction is compatible with protic functional groups. Most impressively, complex **1** also reacted with the alkyne HC≡C(CH$_2$)$_2$CO$_2$H (**4d**), bearing a unprotected carboxylic acid group, to afford the metathesis product Re(≡C(CH$_2$)$_2$CO$_2$H)Cl$_2$(PMePh$_2$)$_3$ (**5d**), which can be isolated as an orange-yellow solid.

The metathesis products **5** are all stable in the solid state and can be stored under ambient condition for months without deterioration. Their structures can be readily assigned on the basis of their spectroscopic data. The structures of **5b–d** have also been confirmed by X-ray diffraction. The molecular structure of **5d** is presented in Fig. 2, and those of **5b** and **5c** are given in the ESI (see Fig. S15 and S16†). The structural features of **5b–d** in the coordination sphere are similar to that of **1**. Their NMR data are fully consistent with the solid-state structures.

In general, the reactivity of aliphatic and aryl terminal alkynes towards complex **1** is similar. Both types of alkynes react to produce the substituted carbyne Re(≡CR′)Cl$_2$(PMePh$_2$)$_3$ as the major product, along with minor unidentified side products that exhibit $^{31}P\{^1H\}$ signals around 24 ppm. However, *in situ* NMR experiments indicate that aliphatic terminal alkynes are slightly more reactive than aryl alkynes in the early stages of the reaction. For example, the reaction of PhC≡CH (20 equiv.) with complex **1** yielded **3a** in 22% after 6 hours, while the reaction of *n*-CH$_3$(CH$_2$)$_3$C≡CH (10 equiv.) with complex **1** produced **5a** in 38% yield over the same period.

Metathesis reactions of Re(≡CR)Cl$_2$(PMePh$_2$)$_3$ (R = Ph, (CH$_2$)$_4$OH)

In addition to complex **1**, other complexes of the type Re(≡CR)Cl$_2$(PMePh$_2$)$_3$ could also undergo metathesis reactions with terminal alkynes (Scheme 3 and Fig. S4†). For example, the aryl carbyne complex **3a** reacted with excess HC≡CCH$_2$Ph to give the complex **1**, and with HC≡C(CH$_2$)$_2$CO$_2$Me to give the complex **5c** (Scheme 3). The alkyl complex **5b** reacted with
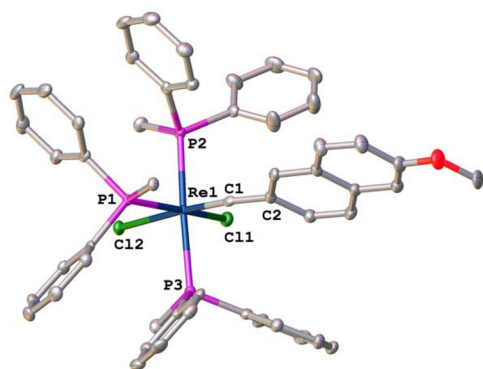
Fig. 1 The molecular structure of Re(≡C–C$_{10}$H$_6$-6-OMe)Cl$_2$(PMePh$_2$)$_3$ (**3d**). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re(1)–Cl(1) 2.4635(8), Re(1)–Cl(2) 2.5367(8), Re(1)–P(1) 2.4128(8), Re(1)–P(2) 2.4525(8), Re(1)–P(3) 2.4476(8), Re(1)–C(1) 1.773(3), C(1)–C(2) 1.444(5), Cl(1)–Re(1)–Cl(2) 81.55(3), P(3)–Re(1)–P(2) 168.59(3), Re(1)–C(1)–C(2) 171.2(3).
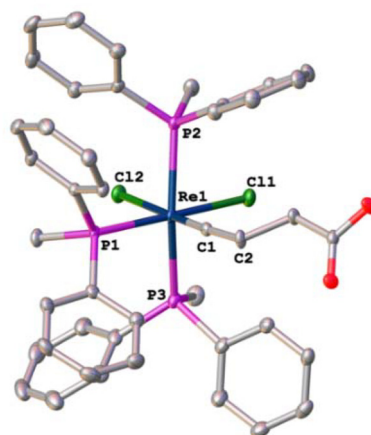
Fig. 2 The molecular structure of Re(≡C(CH$_2$)$_2$CO$_2$H)Cl$_2$(PMePh$_2$)$_3$ (**5d**). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re(1)–C(1) 1.746(2), Re(1)–Cl(1) 2.5074(5), Re(1)–Cl(2) 2.5369(5), Re(1)–P(1) 2.3804(5), Re(1)–P(2) 2.4443(5), Re(1)–P(3) 2.4765(6), C(1)–C(2) 1.488(3), Re(1)–C(1)–C(2) 174.72(17), P(2)–Re(1)–P(3) 161.319(19), Cl(1)–Re(1)–Cl(2) 87.170(17).

HC≡C(CH$_2$)$_2$CO$_2$Me to give the complex **5c** (Scheme 3 and Fig. S4†).

The metathesis reactions of **1** are noteworthy as well-defined stochiometric metathesis reactions of terminal alkynes are rare and have seldom been demonstrated with both high valent and non-d^0 carbyne complexes. To the best of our knowledge, well-defined metathesis products have been only reported for the reactions of high valent d^0 Mo(VI) complexes Mo(≡CtBu){OCMe$_2$(R)}$_3$ (R = Me, CF$_3$) with HC≡CR′ (R′ = nPr, iPr, Ph, TMS)[25] and the reaction of the d^2 W(IV) complex W(≡CMe)Cl(PMe$_3$)$_4$ with HC≡CtBu.[26] The reactions reported here represents the first example of stoichiometric metathesis reactions of carbyne complexes with terminal alkynes with functional groups such as alcohol, ester, aldehydes and unprotected carboxylic acid.

It is more common for carbyne complexes[31] to react with terminal alkyne to give non-metathesis products. For example, high valent d^0 carbyne complexes often react with terminal alkynes to give metallacyclobutadienes and deprotiometallacyclobutadienes,[32] which can initiate the polymerization of terminal alkynes. Carbyne complexes of types L$_n$MR(≡CR′) can react with terminal alkynes R″C≡CH to give carbene complexes L$_n$M(=CRR′)(η^2-R″C≡CH),[33] or L$_n$M(≡CR′)(CH=CRR″).[34] Strained carbynes such as osmallapentalynes can undergo [2 + 2] cycloaddition reactions with terminal alkynes to afford metallacyclobutadienes derivatives.[35] Reactions of alkynes with CO-containing carbyne complexes can give products derived from coupling of the alkyne with carbyne and CO ligands.[36] The square-planar derivatives OsX(≡CPh)(IPr)(PiPr$_3$) (X = Cl, F) reacted with HC≡CR (R = Ph, CO$_2$Me) to give carbene complexes Os(C≡CR)Cl(=CHPh)(IPr)(PiPr$_3$).[37]

The functional group compatibility of the present metathesis reactions is remarkable, considering the reported reactivity of high-valent d^0 carbyne complexes. These complexes are known to undergo Wittig-like reactions with compounds bearing a C=O double bond, for example, ketones, aldehydes, esters and even CO$_2$.[38] Additionally, they react acidic HX substrates, such as water and phenols, to form alkylidene complexes or products derived from further protonation of the alkylidene intermediates.[39]

Theoretical studies on the selectivity of terminal alkyne metathesis reactions

Scheme 4 show a plausible mechanism for the metathesis of complexes Re(≡CR)Cl$_2$(PMePh$_2$)$_3$ (**6′**) with alkynes HC≡CR′ to give Re(≡CR′)Cl$_2$(PMePh$_2$)$_3$. A complex Re(≡CR)Cl$_2$(PMePh$_2$)$_3$ (**6′**) could undergo a substitution reaction with HC≡CR′ to give the alkyne–carbyne complex Re(≡CR)(η^2-HC≡CR′)Cl$_2$(PMePh$_2$)$_2$ (**7′**) which could evolve to the metallacyclobutadiene complex **8′(β)**. Subsequent cyclo-reversion of **8′(β)** would produce the alkyne–carbyne complex **9′**, which could react with PMePh$_2$ to give the substituted carbyne complex **6″**. In principle, the alkyne–carbyne complex Re(≡CR)(η^2-HC≡CR′)Cl$_2$(PMePh$_2$)$_2$ (**7′**) could also undergo a cycloaddition reaction to give the isomeric metallacyclobutadiene complex **8′(α)**,
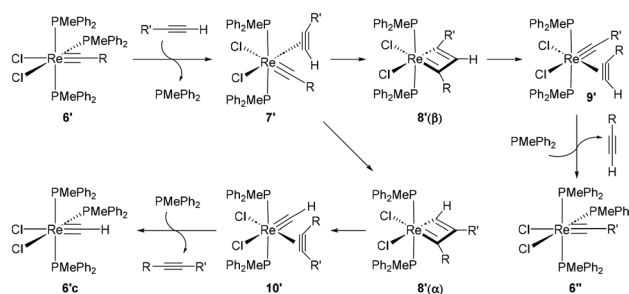
Scheme 4 Two pathways for the metathesis reactions of Re(≡CR) Cl$_2$(PMePh$_2$)$_3$ with terminal alkynes HC≡CR′.

which would evolve to the methylidyne complex Re(≡CH) Cl$_2$(PMePh$_2$)$_3$ (**6′c**) via the alkyne–carbyne complex intermediate Re(≡CH)(η^2-RC≡CR′)Cl$_2$(PMePh$_2$)$_2$ (**10′**). However, the expected methylidyne complexes were never detected in our experiments.

To understand the selectivity of the metathesis reactions, we have studied the reaction profiles for metathesis reactions of terminal alkynes with model carbyne complexes of the type Re(≡CR)Cl$_2$(PMe$_3$)$_3$. The ligand PMePh$_2$ was modeled by PMe$_3$ in the study in order to reduce the computational cost.[40]

Fig. 3 shows profiles for the reaction of the model alkyl carbyne complex Re(≡CMe)Cl$_2$(PMe$_3$)$_3$ (**6a**) with the terminal aryl alkyne HC≡CPh.[41] The profiles clearly indicate that the reaction leading to the phenylcarbyne complex Re(≡CPh) Cl$_2$(PMe$_3$)$_3$ (**6b**) and the terminal alkyne HC≡CMe is both thermodynamically (by 6.84 kcal mol^{-1}) and kinetically (by 4.4 kcal mol^{-1}) favored over that to the methylidyne complex Re(≡CH)Cl$_2$(PMe$_3$)$_3$ (**6c**) and the internal alkyne PhC≡CMe. The formation of phenylcarbyne complex Re(≡CPh)Cl$_2$(PMe$_3$)$_3$ (**6b**) is thermodynamically favored (by 3.56 kcal mol^{-1}), while that of the methylidyne complex Re(≡CH)Cl$_2$(PMe$_3$)$_3$ (**6c**) is thermodynamically unfavored by 3.28 kcal mol^{-1}. The reactions of Re(≡CPh)Cl$_2$(PMe$_3$)$_3$ (**6b**) with HC≡CPh, Re(≡CMe)Cl$_2$(PMe$_3$)$_3$ (**6a**) with HC≡CMe, and Re(≡CCH$_2$Ph)Cl$_2$(PMe$_3$)$_3$ (**6d**) with PhC≡CH show similar profiles (see Fig. S6, S8, and S12†). The computational results are aligning well with our
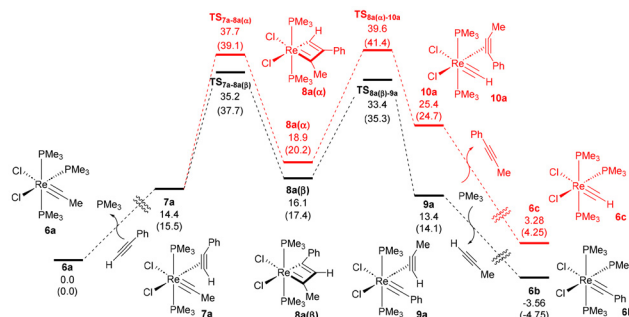
Fig. 3 The calculated energy profile for the metathesis reactions of the complex Re(≡CMe)Cl$_2$(PMe$_3$)$_3$ (**6a**) and HC≡CPh. The relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

experimental observations that the methylidyne complex Re($\equiv$CH)Cl$_2$(PMePh$_2$)$_3$ was not detected in the reactions Re($\equiv$CR)Cl$_2$(PMePh$_2$)$_3$ with terminal alkynes HC$\equiv$CR′.

The thermodynamic preference for forming substituted carbyne complexes (*e.g.*, **6b** and **9a**) over methylidyne complexes (*e.g.*, **6c** and **10a**) may be due to the lower stability of methylidyne complexes. As indicated by hydrogenation enthalpy values, internal alkynes are generally more stable than terminal alkynes due to stabilization through hyperconjugation, inductive, and conjugation effects.[42] The higher stability of substituted carbyne complexes relative to methylidyne complexes can be attributed to similar effects.

In general, the metallacyclobutadienes (the β-isomers, *e.g.* **8a(β)**) that evolve to substituted carbyne complexes were found to be more stable than the isomeric metallacyclobutadienes (the α-isomers, *e.g.* **8a(α)**) that evolve to methylidyne complexes. The relative stability of the isomeric metallacyclobutadiene intermediates can be partially attributed to steric effect. β-Isomers (*e.g.* **8a(β)**) contain a β-H and two substituents on two α-carbons. α-Isomers contain an α-H and two substituents on two adjacent carbons. Thus, α-isomers are sterically less favorable due to the steric repulsion of the neighbouring substituents. In agreement with the hypothesis, difference in the stability between the isomeric metallacyclobutadienes derived from reactions of Re($\equiv$CR)Cl$_2$(PMe$_3$)$_3$ with PhC$\equiv$CH is increased from 2.8 for R = Me to 5.3 kcal mol^{-1} for R = CH$_2$Ph (see Fig. S10 and S12†).

Conclusion

In summary, we have successfully demonstrated that d^2 Re(v) carbyne complexes Re($\equiv$CR)Cl$_2$(PMePh$_2$)$_3$ can undergo metathesis reactions with terminal aryl and aliphatic alkynes HC$\equiv$CR′ to selectively give substituted carbyne complexes Re($\equiv$CR′)Cl$_2$(PMePh$_2$)$_3$ and HC$\equiv$CR. Remarkably, this is the first time that stoichiometric metathesis reactions have been shown to work with terminal alkynes bearing reactive functional groups, including aldehydes, alcohols, esters, and unprotected carboxylic acids. These findings highlight the potential for further exploration of non-d^0 carbyne complexes in the development of catalysts for terminal alkyne metathesis.

Author contributions

G. J. conceived the project and supervised the findings of this work. B. P. and W. B. carried out the syntheses and characterizations. L. C. K. performed the computations. H. H. Y. S. and I. D. W. performed the XRD. G. J., P. B., W.B. wrote the manuscript and all authors contributed to the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Crystallographic data for **3d** (CCDC no. 2413226), **5b** (CCDC no. 2413480), **5c** (CCDC no. 2413479), and **5d** (CCDC no. 2413227) have been deposited at The Cambridge Crystallographic Data Centre, and can be obtained from https://www.ccdc.cam.ac.uk/structures/.†

Acknowledgements

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