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Robust Alkyne Metathesis Catalyzed by Air Stable d^2 Re(V) Alkylidyne Complexes

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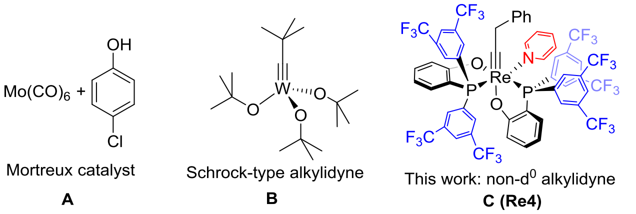
ABSTRACT: We report in this communication the first example of catalytic alkyne metathesis reactions mediated by well-defined non-d^0 alkylidyne complexes. The air-stable d^2 Re(V) alkylidyne complex **Re4**, bearing two PO-chelating ligands and a labile pyridine ligand, could catalyze homo-metathesis of internal alkynes with a broad substrate scope, including alcohols, amines and even carboxylic acids. The catalyst can tolerate heating, air and moisture in both solid and solution states and the catalytic metathesis reactions could proceed normally in wet solvents.

Alkyne metathesis has shown great potential in synthesis of natural products,[1] functional polymers[2,3] and supramolecular materials.[4] Classical homogeneous alkyne metathesis catalysts could be classified into two categories: the “in situ” catalytic system based on $Mo(CO)_6$/phenol or “Mortreux catalyst” (e.g. Scheme 1, **A**)[5,6] and well-defined high valent d^0 Schrock-type alkylidyne complexes (e.g. Scheme 1, **B**).[7] The former has the advantage of user-friendliness. The latter displays remarkable efficiency and a broader substrate scope, which was more commonly used and studied in the past 4 decades.[8] Modifications on Schrock-type alkylidyne catalysts have been carried out continually aiming to obtain more robust systems with high efficiency and broader substrate scope to benefit the wide popularity of alkyne metathesis.[9] Many valuable ideas emerged during this period and remarkable improvements in the efficiency and stability of alkyne metathesis catalysts based on high valent d^0 alkylidyne complexes have been achieved. Examples of the newly developed novel systems include Mo(VI) alkylidyne catalysts with tridentate ligands,[10,11,12,13,14,15] pyridine or phenanthroline stabilized bench-stable Mo(VI) precatalysts,[16,17,18] silica supported heterogeneous Mo(VI) alkylidyne catalysts,[19,20] and Mo(VI) or W(VI) alkylidyne complexes bearing imidazolin-2-iminato ligands,[21] NHC ligands[22] or silyloxy ligands.[23] Some of the systems can even efficiently promote the metathesis of challenging terminal alkynes.[24]

Although alkyne metathesis reactions mediated by high valent d^0 alkylidyne complexes are now well established and many non-d^0 alkylidyne complexes are known,[25,26] to the best of our knowledge, catalytic alkyne metathesis reactions mediated by well-defined non-d^0 alkylidyne complexes have not been reported yet. In contrast, olefin metathesis could be promoted by both d^0 metal (e.g. Ta(V), Mo(VI)) alkylidenes and d^4 Ru(IV) carbenes (a carbene ligand is viewed as a dianionic ligand).[27] Herein, we report the first example of alkyne metathesis reactions catalyzed by a non-d^0 metal alkylidyne complex, specifically, the d^2 Re(V) alkylidyne complex **Re4** (Scheme 1, **C**).

Scheme 1. Selected Homogeneous Transition Metal Catalysts for Alkyne Metathesis Reactions.



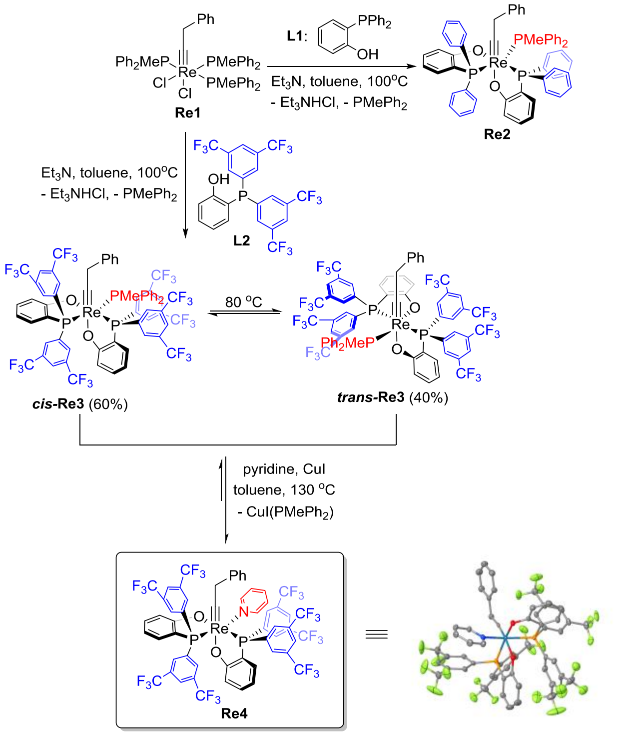
It was recently reported that the air stable d^2 Re(V) alkylidyne complexes $Re(\equiv CR')Cl_2(PR_3)_3$ (R' = aryl, alkyl; PR_3 = $PMePh_2$, PMe_2Ph) could undergo stoichiometric metathesis reactions with alkynes.[28,29] The interesting observation promoted us to explore the potential of Re(V) alkylidyne complexes for catalytic alkyne metathesis reactions.

The catalytic property of $Re(\equiv CCH_2Ph)Cl_2(PMePh_2)_3$ (**Re1,** Scheme 2) was firstly evaluated by using the self-metathesis reaction of *p*-tolyl-1-propyne (**1a**) as the model reaction. The complex **Re1** only showed marginal activity at 150 °C with neat **1a** or very poor activity at 100 °C in 0.1 M toluene (Table 1, entries 1, 2). The complex $Re[\equiv CCH_2(o\text{-}C_6H_4Br)]Cl_2(PMe_2Ph)_3$ behaved similarly (Table S1, entry 2).

In an alternative way to modify the catalytic property of Re(V) alkylidyne complexes, the ligand substitution reaction of **Re1** with the bidentate ligand, (2-hydroxyphenyl)diphenyl phosphine (Scheme 2, **L1**) was carried out to obtain the Re(V) alkylidyne complex **Re2** with two PO bidentate ligands. Subsequent experiments showed that the complex **Re2** displayed significantly improved catalytic activity in self-metathesis reaction of **1a** (Table 1, entry 3). **Re2** also has appreciable activity in promoting the model reaction in a toluene solution at 100 °C (Table 1, entry 4).

It was suspected that association of the mono phosphine ligand $PMePh_2$ in **Re2** may increase the reaction barrier for the catalytic metathesis reaction. Thus, catalytic reactions in the presence of CuI (which could act as a phosphine sponge) were performed. As expected, the **Re2**-catalyzed self-metathesis reaction of *p*-tolyl-1-propyne (**1a**) was accelerated in the presence of CuI. After heating of neat **1a** at 100 °C for 8 h in the presence of 2 mol% of **Re2** and 2 mol% of CuI, the conversion reached to 47% (Table 1, entries 5, 6).

Scheme 2. Synthesis of Rhenium (V) Alkylidene Catalysts.

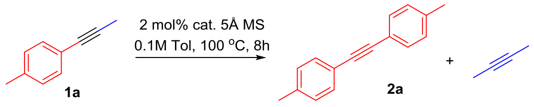


The above observation hinted that analogs of **Re2** free of PMePh$_2$ ligand may be catalytically more active. Attempts have been made to prepare the pyridine (py) complex Re(≡CCH$_2$Ph)Cl$_2$(*o*-OC$_6$H$_4$-PPh$_2$)$_2$(py) complex by reacting **Re2** with pyridine in the presence of CuI. The in-situ NMR experiments indicated that the desired pyridine complex might be formed.[30] Unfortunately, pure samples of the desired alkylidyne complex from the reaction could not be obtained due to the difficulty in completely removing the Cu-containing side product.

To facilitate the isolation of pyridine-coordinated alkylidyne complexes, the PO ligand was modified by introducing two CF$_3$ groups to the phenyl groups (Scheme 2, **L2**), which was expected to differentiate the solubility of the pyridine-coordinated alkylidyne complex from CuI(PMePh$_2$) in non-polar solvents. The reaction of **Re1** with the modified ligand [bis(3,5-bis(trifluoromethyl)-phenyl)phosphanyl] phenol (**L2**) at 100 °C for 3 h gave a mixture of isomers ***cis*-Re3** and ***trans*-Re3**, which can be separated by recrystallization. The isomers ***cis*-Re3** and ***trans*-Re3** can interconvert with each other when heated above 80 °C in toluene, giving an equilibrium mixture with a molar ratio of 3 : 2. Subsequent ligand exchange reaction of **Re3** with pyridine in the presence of CuI produced the desired pyridine supported complex **Re4**, which could then be easily separated from the Cu-containing side product CuI(PMePh$_2$) by diethyl ether extraction. The complex **Re4** has been characterized both spectroscopically and crystallographically. It is an air-stable golden-yellow solid that can be stored in air for months in the solid state and for weeks in solutions without appreciable decomposition. In addition, the complex **Re4** remain unchanged after heating in wet degassed toluene-d_8 at 100 °C for 16 hours as indicated by in-situ NMR spectroscopy.

Subsequent experiments showed that the performance of **Re3** in catalytic self-metathesis reaction of *p*-tolyl-1-propyne (**1a**) is similar to that of **Re2** (Table 1, entry 7). On the other hand, the pyridine complex **Re4** has a significantly improved activity compared with **Re1** - **Re3**. The model reaction of **1a** was essentially completed within 8 hours at 100 °C in toluene solution with 2 mol% of **Re4** (Table 1, entry 8).

Table 1. Rhenium (V) Alkylidenes Catalyzed Homo-metathesis of *p*-Tolyl-1-propyne

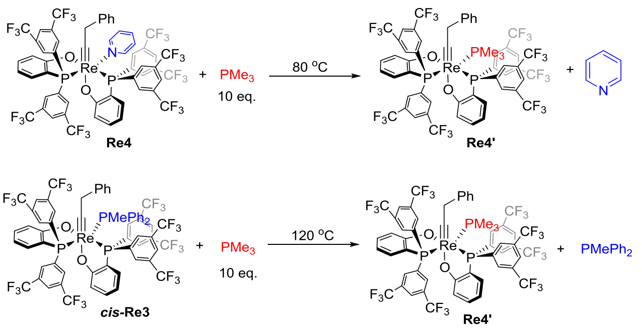


entry	catalyst(s)	solvent	T (°C)	t (h)	yield[d] (%)
1[a]	**Re1**	neat	150	8	19
2[b]	**Re1**	toluene	100	8	trace
3[a]	**Re2**	neat	150	2	60
4[b]	**Re2**	toluene	100	8	15
5[a]	**Re2**	neat	100	8	21
6[a]	**Re2/CuI**	neat	100	8	47
7[b]	**Re3**	toluene	100	8	11
8[b]	**Re4**	toluene	100	8	98
9[b]	**Re4**	1,4-dioxane	100	20	82
10[b]	**Re4**	^{i}BuOH	100	20	85
11[c]	**Re4**	wet toluene	reflux	48	95
12[c]	**Re4**	wet ^{i}BuOH	reflux	48	96

[a]Condition: alkyne (0.2 mmol), catalyst (2 mol%), without 5 Å MS; [b]Condition: alkyne (0.2 mmol), catalyst (2 mol%), 5 Å MS (250 mg), 0.1 M; [c]Condition: alkyne (0.2 mmol), catalyst (2 mol%), without 5 Å MS, wet[31] solvents, 0.1 M, refluxed under N$_2$; [d]Conversions were determined by ^{1}H NMR using CH$_2$Br$_2$ as the internal standard.

The higher activity of the pyridine-coordinated complex **Re4** compared with that of the corresponding PMePh$_2$ analog can be attributed to the relative lability of pyridine and PMePh$_2$ for substitution reactions. This hypothesis was supported by ligand exchange reactions of **Re4** and ***cis*-Re3** (Scheme 3). The ligand exchange reaction of **Re4** with trimethylphosphine (PMe$_3$) (10 equiv.) occurred at 60 °C and was completed at 80 °C within 6 hours to give the PMe$_3$-coordinated complex **Re4'** (Figure S1). On the other hand, the ligand substitution reaction of ***cis*-Re3** with PMe$_3$ (10 equiv.) could only slowly take place at 100 °C and proceeded with an appreciable rate at 120 °C (Figure S2).

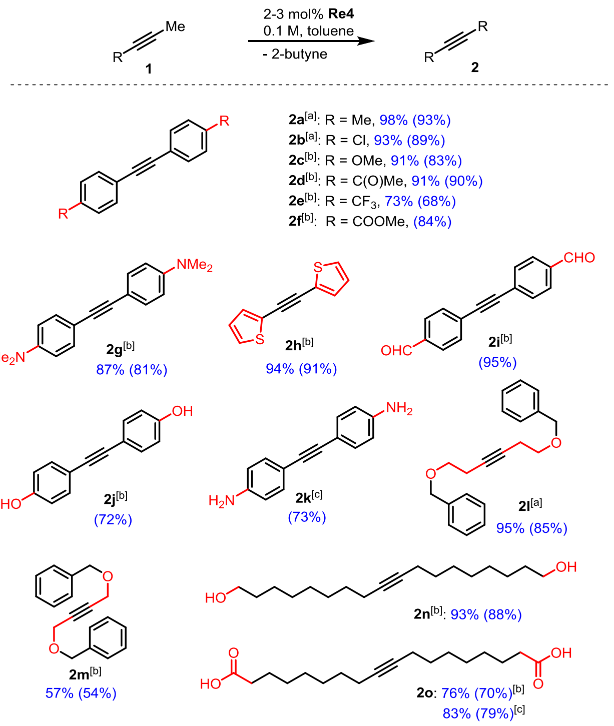
Scheme 3. Ligand Exchange Experiments of Re4 and *cis*-Re3.



The **Re4**-catalyzed reaction could proceed in strongly coordinating solvents like 1,4-dioxane with only slight decrease in the reactivity (Table 1, entry 9). Furthermore, the metathesis reaction promoted by **Re4** can tolerate protic solvents like isobutanol without significant decline in yield (Table 1, entry 10). Most interestingly, the catalytic metathesis reactions in wet[31] toluene or isobutanol could also take place (Table 1, entries 11, 12). Control experiments indicate that the catalyst **Re4** has nearly equal activity in wet and dry toluene. After refluxing the reaction mixtures containing **1a** and 2 mol% of **Re4** for 16 hours, the one in wet toluene gave 73% of NMR yield, while the one in dry toluene gave 77% of NMR yield (Table S1, entries 12, 13). The Re(V) alkylidyne catalytic system represents the first example of air and moisture stable alkylidyne catalysts with demonstrated metathesis activity for unstrained alkynes.[32]

The outstanding air and moisture stability of **Re4** hints that the catalyst has the potential to promote metathesis of substrates containing coordinating, polar or protic functional groups. The substrate scope of metathesis reactions mediated by **Re4** was next investigated, especially for substrates with potential problematic functional groups (Chart 1). In most cases, the catalytic reactions were conducted in dry toluene with 2 mol% of the catalyst and activated 5 Å MS as butyne absorber. Some reactions were carried out in wet toluene (e.g. **1k**, **1o**). For those substrates with strong coordination ability, higher catalyst loading (3 mol%) and prolonged reaction time (16 h) were employed.

Chart 1. Scope of Metathesized Alkynes Promoted by Re4.



[a]Conditions: alkyne (0.2 mmol), **Re4** (2 mol%), 5 Å MS (250 mg), dry toluene (2 mL), 100 °C, 8 h; [b]Conditions: alkyne (0.2 mmol), **Re4** (3 mol%), 5 Å MS (250 mg), dry toluene (2 mL), 100 °C, 16 h. [c]Conditions: alkyne (0.2 mmol), **Re4** (3 mol%), wet[31] toluene (2 mL), reflux, 48 h. Conversions were determined by ^1H NMR using CH_2Br_2 as the internal standard. Isolated yields are given in parentheses. Only isolated yields are provided for products with poor solubilities.

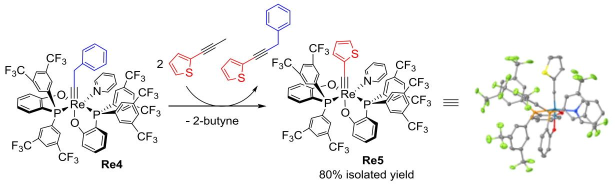
As shown in Chart 1, a variety of alkyne products can be obtained by **Re4**-promoted self-metathesis of internal alkynes. All of the products were isolated in moderate to excellent yields. The complex **Re4** is compatible with substrates containing functional groups such as ether (**1c**), ketone (**1d**), ester (**1f**) and tertiary amine (**1g**). The metathesis reaction of the more challenging substrate, 2-propynylthiophene (**1h**), also proceeded well and produced **2h** in excellent yield. 4-Propynylbenzaldehyde (**1i**), a tough substrate that was well-known to destroy some high valent d^0 alkylidyne catalysts,[11] could be metathesized by **Re4** efficiently to give **2i** in excellent yield.

Apart from aryl alkynes, metathesis reactions of alkyl alkynes were also tested. For example, the popular alkyl alkyne substate **1l** was metathesized by **Re4** to give **2l** in high isolated yield. Propargylic alcohol derivatives are another class of problematic substrates.[33] To the best of our knowledge, the self-metathesis reaction of the propargylic alcohol derivative **1m** has never been reported. With **Re4** as the catalyst, the substrate **1m** could be metathesized to give **2m** in moderate yield.

The metathesis of alkyne substrates with protic groups, such as hydroxy and amino groups, was well-recognized as a challenging task for high valent d^0 alkylidyne catalysts. Most catalytic systems reported before are either incompatible with such groups or show low efficiency. In contrast, the non-d^0 alkylidyne catalyst **Re4** is inherently tolerant to protic environments, and promotes self-metathesis reactions of protic substrates like 4-propynylphenol (**1j**) and 4-propynylaniline (**1k**) smoothly to give corresponding products in good isolated yields with only 3 mol% of catalyst loading. Moreover, the alkyl alkyne substrate **1n** with an "unhindered primary alcohol"[15] could also be metathesized normally by **Re4** to give the product **2n** in excellent yield. Encouraged by these successes, we extended the substrate scope to the unprotected carboxylic acid substrate **1o**. Surprisingly, the self-metathesis product **2o** was formed either in dry or wet toluene and isolated in good yields. To the best of our knowledge, **Re4** is the first catalyst with demonstrated metathesis activity for substrate with a carboxylic acid functional group.

The alkyne metathesis reaction mediated by **Re4** presumably proceeds through ligand dissociation, reversible cycloaddition of Re(V) alkylidyne intermediate with alkyne, and re-association of ligand.[28, 34] Consistent with the proposed mechanism, the in-situ $^{31}P\{^1H\}$ NMR spectra after catalytic reactions showed signals assignable to new Re(V) alkylidyne complexes analogous to **Re4**. For instance, **Re5** was isolated in 80% yield in the reaction of **Re4** with 5 equiv. of 2-propynylthiophene (**1h**), the structure of which was confirmed by X-ray diffraction (Scheme 4). The isolated complex, **Re5**, was found to be equally active as **Re4** for catalytic self-metathesis reaction of 2-propynylthiophene.

Scheme 4. Stoichiometric alkyne metathesis of Re4 with 2-propynylthiophene (1h).



In summary, this communication demonstrated the first example of alkyne metathesis reactions promoted by non-d^0 transition metal alkylidyne complexes. The d^2 Re(V) alkylidyne complex **Re4** prepared in this work has remarkable stability to both air and moisture and can effect metathesis of alkynes with a broad substrate scope, including alcohols, amines and even carboxylic acids. The results indicated that development of non-d^0 alkylidyne-based catalysts can provide an alternative approach toward user-friendly alkyne metathesis reactions. Fine-tuning of catalyst activity and elaboration of the mechanistic features of these systems are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional data and discussion of catalyst screening and ligand exchange experiments, experimental details, crystallographic data and NMR spectra (PDF).

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Notes

The authors declare no competing financial interests.

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(30) The $^{31}P\{^1H\}$ NMR spectrum of the crude product displays two signals at 46.3 and 30.9 ppm, in addition to a broad peak at -32.3 ppm assignable to $CuI(PMePh_2)$. The ^1H NMR spectrum shows characteristic peaks of Re≡CCH_2Ph at 2.88 (dt, *J* = 18.9, 3.2 Hz) and 2.58 (dt, *J* = 18.9, 3.6 Hz) ppm and a doublet at 8.31 (*J* = 5.7 Hz) ppm which is assignable to a pyridine ligand. The NMR data are similar to those of the isolated pyridine-coordinated complex **Re4**.

(31) Commercial A.R. grade toluene or isobutanol stored in air without any drying process was bubbled with N_2 for 10 minutes before use. Because 5Å MS cannot be employed to absorb 2-butyne in wet solvents, refluxing condition was utilized to remove the byproduct 2-butyne which will cause prolonged reaction times. See: reference 17.

(32) There's one example of moisture stable alkylidyne catalyst for ring opening alkyne metathesis polymerization. See: reference 14. Besides, it should also be mentioned that some $Mo(CO)_6$/phenol-based systems have been reported to operate without exclusion of air or moisture. See: references 6a, 6b and 6d).

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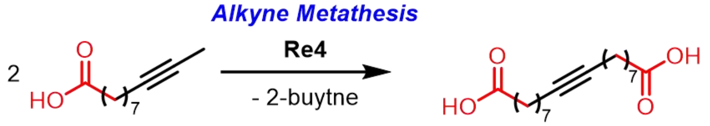

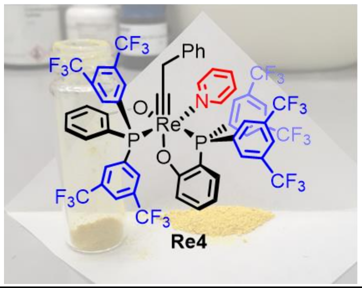

Non-d^0 alkylidyne complex

✓ Air & moisture stable

✓ User-friendly

✓ Protic solvent tolerance

✓ Broad substrate scope