Highlight Review

Cycloaddition Reactions of Transition Metal-containing Benzopyrylium and Related Zwitterionic Intermediates

Hiroyuki Kusama and Nobuharu Iwasawa*

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Abstract

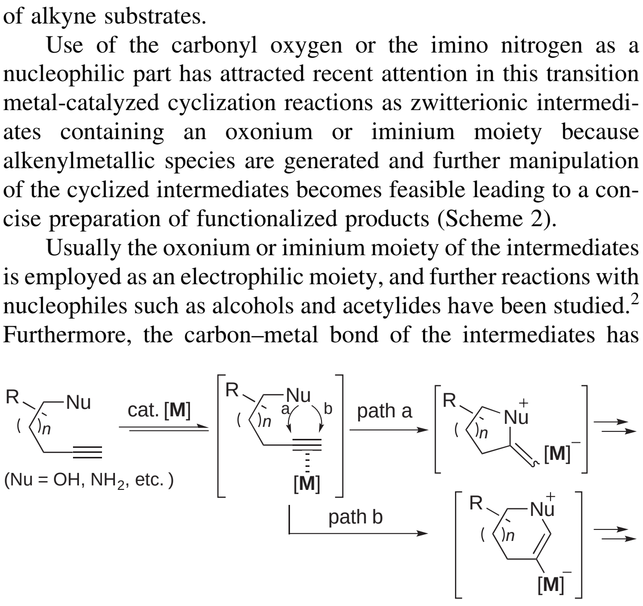
Recent advances in generation and cycloaddition reactions of transition metal-containing benzopyrylium and related zwitterionic intermediates from *o*-alkynylphenylcarbonyl or imine derivatives are summarized focussing on the difference of the two reaction pathways, that is, [3 + 2] and [4 + 2] cycloaddition reactions.

◆ Introduction

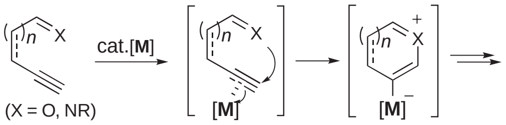
Recently, the transition metal-catalyzed electrophilic activation of alkynes towards the attack of nucleophiles has been a subject of extensive study due to their high utility as useful methods for the construction of carbon frameworks. In particular, the preparation of nitrogen- or oxygen-containing heterocycles utilizing the intramolecular variation of the reaction enhances the utility of the reaction, and a variety of methods for the preparation of useful compounds have been developed so far (Scheme 1).[1] Various kinds of electrophilic transition metals have been employed, and probably palladium(II) complexes have been the most common since the early stage of this chemistry. More recently, several other complexes such as Cu^{I}, Pt^{II}, Au^{I}, and Au^{III} have also been explored as a unique activator of alkyne substrates.

Use of the carbonyl oxygen or the imino nitrogen as a nucleophilic part has attracted recent attention in this transition metal-catalyzed cyclization reactions as zwitterionic intermediates containing an oxonium or iminium moiety because alkenylmetallic species are generated and further manipulation of the cyclized intermediates becomes feasible leading to a concise preparation of functionalized products (Scheme 2).

Usually the oxonium or iminium moiety of the intermediates is employed as an electrophilic moiety, and further reactions with nucleophiles such as alcohols and acetylides have been studied.[2] Furthermore, the carbon–metal bond of the intermediates has also been employed for further carbon–carbon bond formation such as coupling type reactions and the Heck reaction when Pd(II) complexes are employed as catalyst.[3] On the other hand, use of the zwitterionic intermediates as 1,3-dipole is quite limited. No cycloaddition reaction had been reported until we reported the first example of such reactions in 2001, that is, [3 + 2] cycloaddition of tungsten-containing carbonyl ylides generated from *o*-ethynylphenylcarbonyl compounds and $W(CO)_5(L)$.[4] In this review, we would like to summarize such cycloaddition reactions of transition metal-containing zwitterionic intermediates and discuss the difference of reactivity depending on the metal employed.



Scheme 1.



Scheme 2.

◆ Generation and [3 + 2] Cycloaddition Reactions of Tungsten-containing Carbonyl Ylides

Since 1997, we have been carrying out researches on the development of synthetic reactions utilizing the electrophilic character of (pentacarbonyl)tungsten species.[5] It has been known that when terminal alkynes are treated with (pentacarbonyl)metal species of group 6 metals, π-complexes are produced first, which further undergo 1,2-hydrogen migration to give vinylidene complexes. In these complexes, alkynes are activated electrophilically, and we have developed several useful synthetic reactions utilizing these characteristics. For examples, various kinds of intramolecular cyclization of the silyl enol ether moiety towards terminal alkynes have been realized with a catalytic amount of $W(CO)_5(L)$, and in the reaction of 7-siloxy-6-en-1-yne derivatives, either exo- or endo-selective cyclization has been achieved by the appropriate choice of the reaction conditions.[5b,5c] Furthermore, novel benzopyranylidene complexes **2** have been prepared as stable complexes, which undergo inverse electron-demand Diels–Alder reaction with electron-rich alkenes to give substituted naphthalenes **3** with simultaneous elimination of $W(CO)_6$ from the cycloadducts followed by elimination of an alcohol or an amine (Scheme 3).[6] We then thought of carrying out this naphthalene synthesis by a one-pot procedure. It was expected that by carrying out the reaction in the presence of an electron-rich alkene, formation of the benzopyranylidene complex and successive Diels–Alder reaction would proceed smoothly to give

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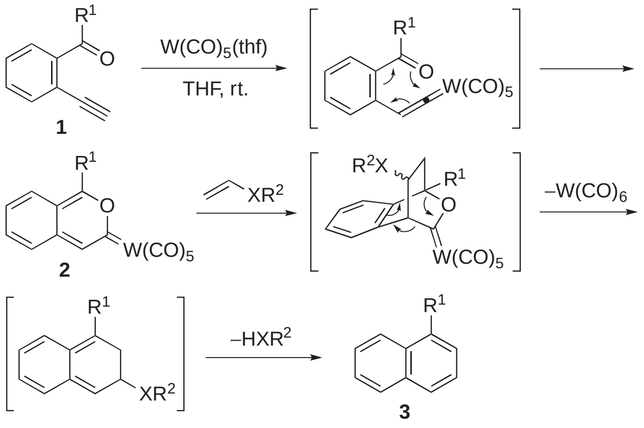
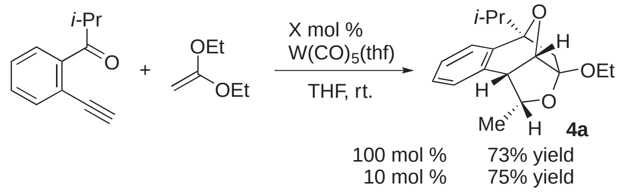
*Associate Prof. Hiroyuki Kusama, Prof. Nobuharu Iwasawa**
Department of Chemistry, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551
E-mail: niwasawa@chem.titech.ac.jp



Scheme 3.



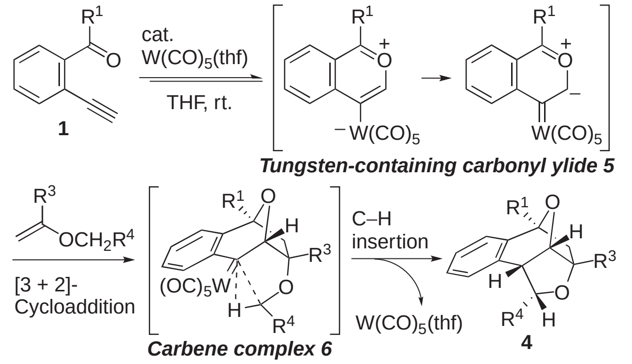
Scheme 4.

the corresponding naphthalene without the necessity of isolating the intermediate complex. This trial did not work as expected, but has led to the discovery of the novel tungsten-containing carbonyl ylide chemistry.[4]

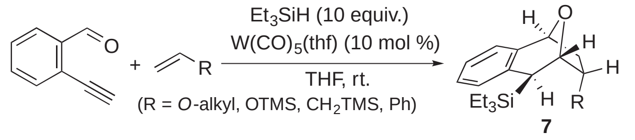
Thus, when a THF solution of *o*-ethynylphenylisobutyrophenone and 1,1-diethoxyethene was treated with a stoichiometric amount of $W(CO)_5(thf)$ at room temperature, an entirely unexpected oxygen-containing polycyclic compound **4a** was obtained in good yield. This reaction was found to proceed even with a catalytic amount of $W(CO)_5(thf)$ without lowering the yield (Scheme 4).

The mechanism of the reaction is proposed as follows: The alkyne moiety of *o*-ethynylphenyl ketone **1** is activated by $W(CO)_5$ electrophilically through π-complex formation. The 6-endo mode of the nucleophilic attack of the carbonyl oxygen onto the activated alkyne moiety generates a benzopyrylium-type zwitterionic intermediate **5**,[7] which readily undergoes [3 + 2] cycloaddition with the electron-rich alkene to give an unstabilized tungsten carbene complex **6**. Finally, the tungsten carbene moiety thus generated inserts into a carbon–hydrogen bond of the neighboring alkoxy group to give the product **4** with regeneration of $W(CO)_5$ species. Thus, the zwitterionic intermediate **5** could be regarded as tungsten-containing carbonyl ylide, a novel bifunctional metal-containing reactive species, and behaves both as a carbonyl ylide and as a carbene complex to realize construction of polycyclic carbon skeleton in a single operation (Scheme 5).

Not only ketene acetal but also *n*-butyl vinyl ether can be employed as an electron-rich alkene component to give the corresponding polycyclic products **4** stereoselectively in good yield even with 10 mol % of $W(CO)_5(thf)$. Several kinds of aryl ketones including an aryl aldehyde are suitable for this reaction. We also examined various transition-metal complexes such as Ir^I, Pt^{II}, Au^I, and Au^{III} as a catalyst, and found that tungsten(0) carbonyl was the most efficient for this reaction.



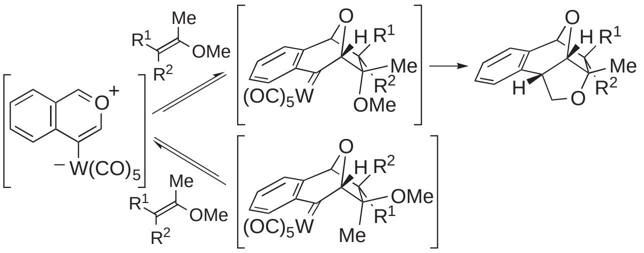
Scheme 5.



Scheme 6.

The intermediate carbene complexes could be trapped intermolecularly by carrying out the reaction in the presence of triethylsilane, giving the silicon-containing compounds **7** stereoselectively (Scheme 6). The formation of this silane-insertion product **7** clearly proved the existence of the tungsten–carbene intermediate **6** (see, Scheme 5). By using this protocol, the reaction could be extended to dipolarophiles containing no reactive C–H bond for intramolecular carbene insertion, and a silyl enol ether, allylsilane, and even styrene gave the corresponding silylated products **7** stereoselectively in good yield.[4b]

To obtain mechanistic information on the [3 + 2] cycloaddition step in detail, we further examined the reaction with stereochemically well-defined trisubstituted vinyl ethers in the presence or absence of triethylsilane, and found that the [3 + 2] cycloaddition proceeded in a concerted manner. Interestingly, the facial selectivity of the reactions in the presence or absence of triethylsilane differs considerably, which suggested reversible nature of this [3 + 2] cycloaddition reaction (Scheme 7).[4b]

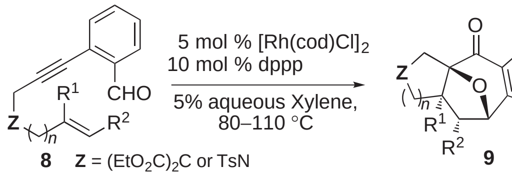


Scheme 7.

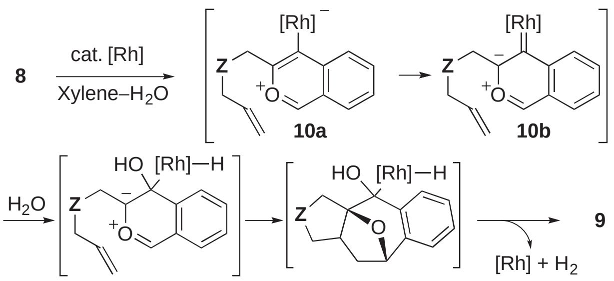
It is known that [3 + 2] cycloaddition of carbonyl ylides with alkenes is usually irreversible and only a few specific cases were reported for the retro cycloaddition reactions.[8] Therefore, the facile equilibrium observed here is a very rare example of such reaction and is the characteristic feature of the tungsten-containing carbonyl ylide.

♦ *Intramolecular Cycloaddition of Rh- or Au-containing Carbonyl Ylides*

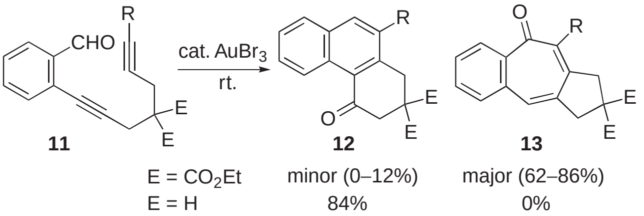
In 2005, Oh et al. reported the intramolecular [3 + 2] cyclo-



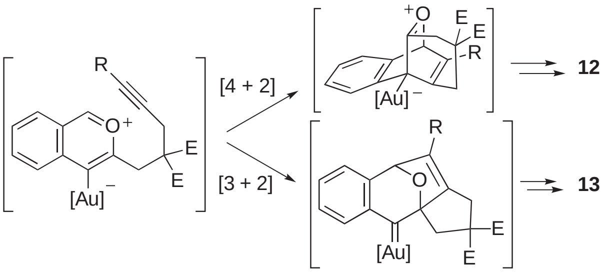
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

addition of the rhodium-containing benzopyrylium intermediates derived from *o*-alkynylbenzaldehyde bearing an olefinic moiety. Thus, treatment of **8** with a catalytic amount of [Rh(cod)Cl]$_2$ and dppp in aqueous xylene at 80–110 °C gave oxa-bridged polycyclic ketone **9** in good yield (Scheme 8).[9]

The proposed reaction mechanism is quite similar to those described in the former section. 6-Endo mode of nucleophilic attack of the carbonyl oxygen onto the rhodium-complexed alkyne moiety generated rhodium-containing benzopyrylium-type intermediate **10a**, which is equivalent to the carbonyl ylide having a rhodium carbenoid moiety **10b**. This species underwent intramolecular [3 + 2] cycloaddition reaction with an olefinic part to give the polycyclic compound **9** (Scheme 9). The authors mentioned that the carbonyl function of the product could be generated by addition of water to the carbene moiety followed by β-hydride elimination before or after the [3 + 2] cycloaddition step. Although the final product could be prepared by well-precedented 1,3-dipolar cycloaddition of the carbonyl ylide generated by the Rh-catalyzed reaction of diazoketone with a carbonyl group,[10] the present reaction seems to have an advantage in terms of availability of the starting material because an easily available alkyne moiety was employed instead of a diazoketone as a carbonyl ylide precursor.

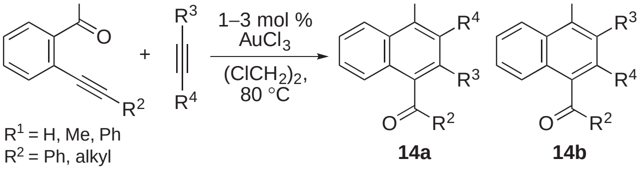
Oh et al. also reported that an allene could be employed as a dipolarophile in the same reaction, but in this case, AuCl$_3$ or its nanoparticles were found to be the best catalysts.[11]

Alkynes were also applicable as a dipolarophile in the intramolecular cycloaddition of gold(III)-containing benzopyrylium-type intermediates. Treatment of **11** with AuBr$_3$ at room temperature gave naphthalene derivative **12** or benzotropone derivative **13** in good yield.[12] The product distribution was highly dependent on the tether structure of **11** (Scheme 10). Thus, the substrate bearing a *gem*-diester group mainly gave the tropone derivatives **13**, formation of which was explained by the above-mentioned [3 + 2] cycloaddition mechanism. On the contrary, the reaction of **11** having no substituent on the tether exclusively gave the naphthalene **12** (Scheme 11). In this case, intramolecular [4 + 2] cycloaddition of the benzopyrylium intermediate followed by ring opening with regeneration of the catalyst was proposed to be a possible mechanism (Scheme 11), which was originally proposed by Yamamoto and Asao as described in the next section.

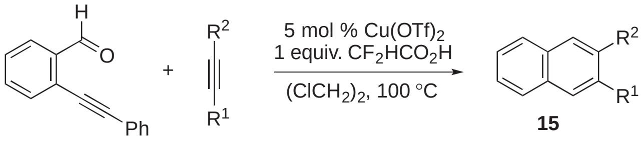
◆ *Benzannulation Reactions of Metal-containing Benzopyrylium Species*

In contrast to the above [3 + 2] cycloaddition of transition metal-containing carbonyl ylides, there have been reported several examples of the formal [4 + 2] cycloaddition of the same type of metal-containing pyrylium intermediates. In 2002, Yamamoto, Asao, and their co-workers reported the gold(III)-catalyzed novel benzannulation reaction.[13] Treatment of *o*-(phenylethynyl)benzaldehyde and an alkyne with a catalytic amount of AuCl$_3$ in dichloroethane at 80 °C gave naphthylketone derivatives **14** in moderate to high yield (Scheme 12). Although regioisomeric mixture of the products **14a** and **14b** could be formed, either of which was obtained as a major product depending on the structure of the alkyne employed. Variously substituted terminal and internal alkynes could be employed for this reaction, giving the corresponding naphthylketone derivatives **14** in good yield.

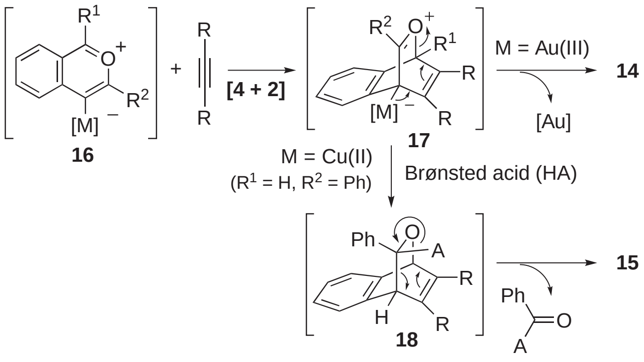
They also reported another type of benzannulation reaction: when a mixture of *o*-(phenylethynyl)benzaldehyde and an alkyne in dichloroethane was treated with a catalytic amount of copper triflate and an equimolar amount of CF$_2$HCO$_2$H at 100 °C, a deacylated naphthalene derivative **15** was obtained as an exclusive product in good yield (Scheme 13).[14] Appropriate choice of the proton source was essential for selective formation of the deacylated product **15**; for example, the reactions in the absence of pro-



Scheme 12.



Scheme 13.



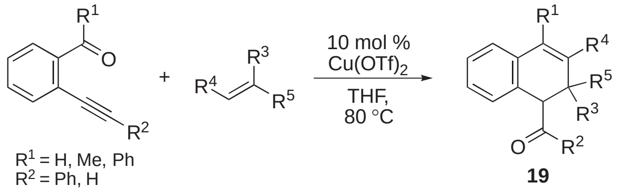
Scheme 14.

ton source or in the presence of a weak acid such as water and MeOH always accompanied formation of the naphthylketone derivatives **14** (10–20% yield). The gold(III)-catalyzed reaction gave a mixture of **14** and **15** even in the presence of CF_2HCO_2H.

As for the reaction mechanisms, they postulated [4 + 2] type cycloaddition between metal-containing benzopyrylium intermediate and an alkyne (Scheme 14, **16** to **17**). In the gold(III)-catalyzed reaction, the intermediate **17** would be converted to the naphthylketone **14** with regeneration of the catalyst. However, Straub's recent report on DFT calculation of the above gold-catalyzed reaction suggested that successive [3 + 2] cycloaddition–skeletal rearrangement would be the reasonable mechanism (see also, Scheme 19) rather than the [4 + 2] cycloaddition pathway shown in Scheme 14.[15,16]

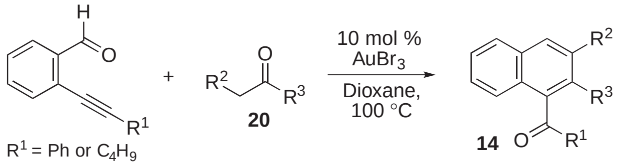
In the Cu^{II}-catalyzed reaction, the carbon–Cu bond of the Cu-containing cycloadduct **17** would be protonated by strong Brønsted acid to afford the intermediate **18**, which was easily converted to the deacylated product **15** with liberation of a benzoate derivative.

Yamamoto et al. extensively investigated this benzannulation chemistry and reported that alkenes could be utilized as a dienophile for the naphthylketone synthesis.[17] In this case, $Cu(OTf)_2$ exhibited higher catalytic activity than $AuCl_3$, giving the dihydronaphthalene derivatives **19** as a final product (Scheme 15).



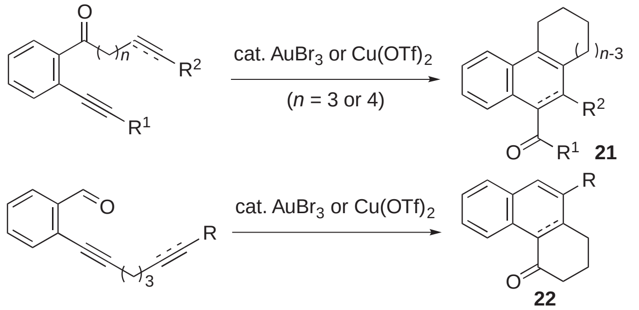
Scheme 15.

A quite similar reaction proceeded by using an enolizable ketone **20** instead of an alkene, but in this reaction, $AuBr_3$ was a suitable catalyst.[18] An enol generated by keto–enol tautomerism of the starting ketone reacted as a dienophile in the [4 + 2] cycloaddition to give a hydroxylated dihydronaphthalene intermediate, dehydration of which gave aromatized product, the naphthylketone derivatives **14**, in good yield (Scheme 16).



Scheme 16.

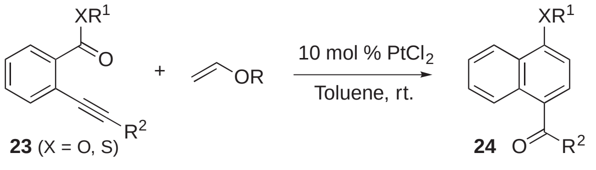
Yamamoto, Asao, and co-workers also demonstrated the intramolecular version of the above benzannulation by using two types of substrates; one is that the dienophile moiety is attached to the carbonyl group, and the other to the alkynyl group.[19] Both reactions were found to proceed smoothly by using Au^{III} or Cu^{II} catalyst to furnish the polycyclic ketones **21** or **22** in good yield (Scheme 17). These intramolecular reactions were successfully applied to total syntheses of rubiginone,[20] ochromycinone,[20] and heliophenanthrone.[21]



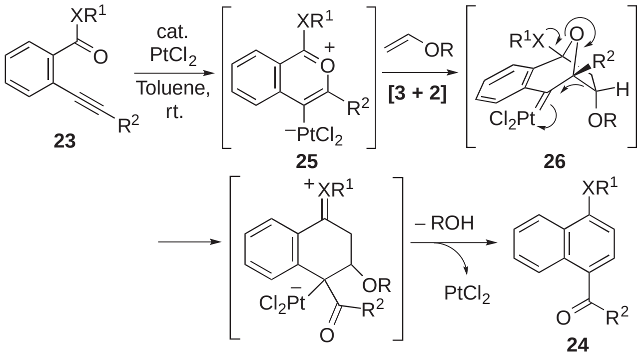
Scheme 17.

We also reported a similar type of Pt^{II}-catalyzed benzannulation reaction by employing *o*-alkynylbenzoate derivatives as a substrate.[22] When a mixture of *o*-ethynylbenzoate **23** and a vinyl ether was treated with $PtCl_2$ (10 mol %) in toluene at room temperature, 4-alkoxynaphthalene-1-carbaldehyde **24** was obtained in good yield (Scheme 18). Various benzoate esters and thioesters bearing a terminal or an internal alkyne moiety could be used as substrates. Noteworthy is that the present Pt^{II}-catalyzed reaction proceeds smoothly at room temperature, while the above-mentioned Au^{III}- or Cu^{II}-catalyzed benzannulation reactions normally require higher reaction temperature (80–100 °C).

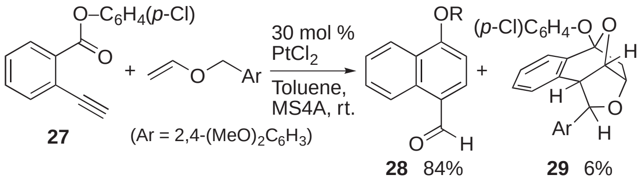
Concerning the reaction mechanism, we at present believe that the reaction proceeds through [3 + 2] cycloaddition of the platinum(II)-containing carbonyl ylides **25**, followed by 1,2-alkyl-migration of the produced carbene intermediates **26** as shown in Scheme 19 based on the following experimental evidences. When 2,4-dimethoxyphenylmethyl vinyl ether was employed as an electron-rich alkene, the C–H insertion product



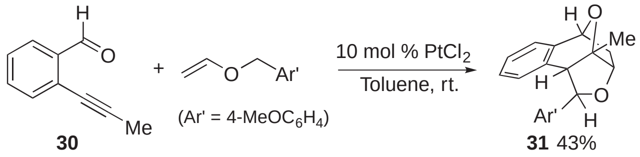
Scheme 18.



Scheme 19.



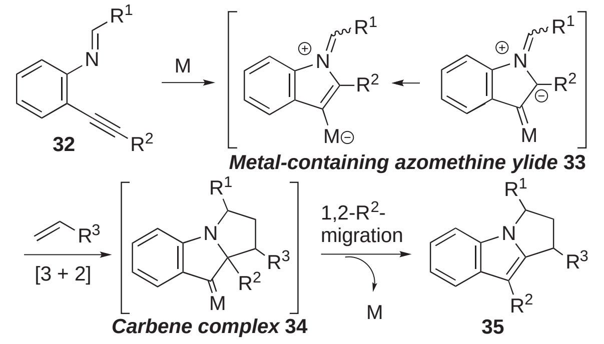
Scheme 20.



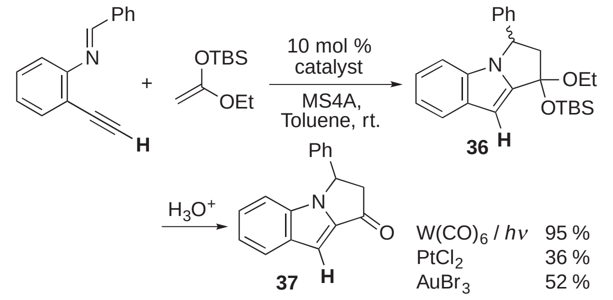
Scheme 21.

29 of the carbene intermediate **26** was obtained albeit in low yield along with alkoxynaphthalene **28** in 84% yield (Scheme 20). Furthermore, the platinum(II)-catalyzed reaction of *o*-(1-propynyl)benzaldehyde **30** with 4-methoxyphenylmethyl vinyl ether also gave the [3 + 2] cycloaddition–carbene insertion product **31** in reasonable yield (Scheme 21). These results strongly suggest that the naphthalene would be produced through [3 + 2] cycloaddition followed by 1,2-alkyl migration reaction. Probably the alkoxy group of the ester moiety facilitates 1,2-alkyl migration by electron donation to afford 4-alkoxy-1-naphthylcarbonyl compounds **24** as the product.

From the results described above, it is not necessarily easy to discriminate the two reaction pathways, that is, [3 + 2] versus [4 + 2] cycloaddition reactions of the metal-containing benzopyrylium intermediates. Furthermore, the difference of the electronic nature of dipolarophiles might have some effects on the course of the reaction. However, combined with the result of DFT-calculation by Straub,[15,16] the Au^{III}- and Pt^{II}-catalyzed reactions are likely to proceed via [3 + 2] cycloaddition followed by skeletal rearrangement.[23] The Cu^{II}-catalyzed reactions are less clear, and computational analysis of the Cu^{II}-containing benzopyrylium intermediates is thought to be required to clarify the exact reaction mechanism.



Scheme 22.



Scheme 23.

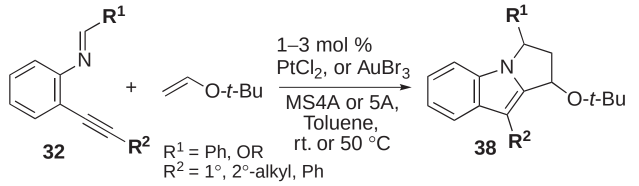
◆ Generation and Reactions of Metal-containing Azomethine Ylides

Based on our metal-containing carbonyl ylide chemistry, we then considered the possibility of generating metal-containing azomethine ylides **33** by 5-endo mode of nucleophilic attack of the imine nitrogen of the *N*-(*o*-alkynylphenyl)imine derivatives **32** onto the alkynyl group activated by electrophilic transition-metal complexes. The [3 + 2] cycloaddition of such ylides with electron-rich alkenes would afford a novel method for the construction of the polycyclic indole skeletons **35** found in various biologically active molecules (Scheme 22).[24]

The above consideration was realized as expected: treatment of a mixture of *N*-(*o*-ethynylphenyl)imine derivative **32** (R^1 = Ph; R^2 = H) and a ketene silyl acetal with a catalytic amount of $W(CO)_6$ under photoirradiation conditions afforded the tricyclic indole derivative **36** as a diastereomeric mixture, acidic treatment of which gave the corresponding ketone **37** in high yield (Scheme 23). The primary product **36** could be produced by [3 + 2] cycloaddition reaction of tungsten-containing azomethine ylide **33** with the electron-rich alkene followed by 1,2-hydrogen migration of thus-generated carbene complex intermediate **34**. Other metal complexes such as $PtCl_2$ and $AuBr_3$ also promoted this transformation, however, their catalytic activity was lower than that of the tungsten catalyst.

More interestingly, when *N*-(*o*-alkynylphenyl)imine derivatives **32** having an *internal* alkyne moiety (R^1 = Ph; R^2 = alkyl, aryl) were employed as substrate, a novel 1,2-migration of an alkyl or an aryl group was observed to give tricyclic indole derivatives **35** having a substituent at the 3-position of the indole nucleus in good yield. Careful examination on the reaction of the propynyl derivative **32** (R^2 = Me) enabled us to isolate the carbene complex intermediate **34** (R^2 = Me) along with the corresponding tricyclic indole **35**, and 1,2-Me migration of the isolated **34** occurred to give the final product **35** (R^2 = Me) quantitatively at room temperature;[24b] these findings strongly supported the proposed reaction mechanism.

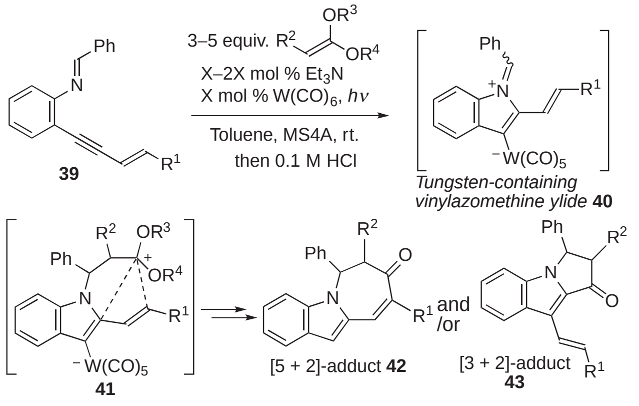
Although this internal alkyne protocol affords a highly effi-



Scheme 24.

cient method for the preparation of 3-substituted tricyclic indole skeletons such as mitomycins, the efficiency of the tungsten catalyst was moderate and a stoichiometric amount of $W(CO)_6$ was necessary to bring the reaction to completion. Therefore, we investigated various transition-metal complexes to realize highly efficient catalytic reactions employable for the substrates containing an *internal* alkyne moiety, and found that third-row transition-metal complexes, particularly $PtCl_2$ and $AuBr_3$, exhibited very high catalytic activity (Scheme 24).[25] As a substituent on the alkyne terminus of **32**, primary and secondary alkyls, heteroalkyl, and phenyl groups could be employed. Imidate derivatives also reacted smoothly to give the corresponding indole derivatives **38** having an *N*,*O*-acetal moiety, which could be useful precursors for synthesis of various natural products. Thus, this reaction could be applied for broad range of the *N*-(*o*-alkynylphenyl)imine derivatives by choosing the appropriate catalyst (W^0 for the *terminal* alkynes; Pt^{II} or Au^{III} for the *internal* alkynes).

This methodology was further applied to generation and reaction of metal-containing vinylazomethine ylide species. When *N*-arylbenzaldimine derivatives **39** bearing a conjugated enyne moiety was treated with a catalytic amount of $W(CO)_6$ and 3–5 molar amounts of sterically hindered ketene acetal (R^3 = TIPS or *i*-Pr, $R^4 = i$-Pr) in the presence of Et_3N under photoirradiation at ambient temperature, a novel intermolecular [5 + 2] cycloaddition of vinylazomethine ylide species **40** proceeded selectively to give azepino[1,2-*a*]indole derivatives **42** in good yield (Scheme 25).[26] On the contrary, the reactions with less hindered ketene acetal (R^3, R^4 = Et or $–CH_2CH_2–$) gave the pyrrolo[1,2-*a*]indole derivatives **43**, [3 + 2] cycloadducts, as a major product. These results indicate that steric hindrance around the reaction centers at the ring-closure step controls the reaction pathways, which realized selective preparation of either of the [3 + 2] or [5 + 2] adducts by appropriate choice of dipolarophile.



Scheme 25.

◆ Conclusion

Since the first example of the 1,3-dipolar cycloaddition of transition metal-containing benzopyrylium intermediate was reported in 2001, various reports on the generation and cycloaddition reactions of related metal-containing zwitterionic intermediates have appeared. They include [3 + 2], [4 + 2], and [5 + 2] cycloadditions, and in all cases, metal-containing cycloadducts further undergo the characteristic transformations depending on the substrate structure, metal catalyst, and reaction conditions, to give various types of polycyclic compounds by a one-pot procedure. Therefore, these methodologies will be useful and interesting tools for the synthesis of complex organic molecules.

References and Notes

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