Synthesis of $[RhCl(CO)(cyclopentadienone)]_2$ from $[RhCl(cod)]_2$ and a 1,6-diyne under CO: application to Rh(I)-catalyzed tandem [2 + 2 + 1] carbonylative cycloaddition of diynes and Claisen rearrangement†

Sang Ick Lee, Yoshiya Fukumoto and Naoto Chatani*

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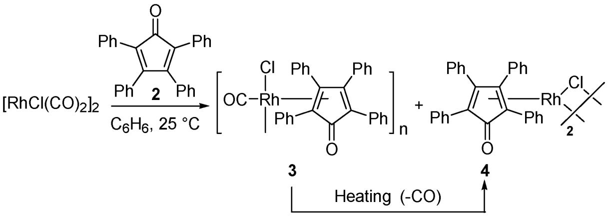
Although Rh(I)Cl(CO)(cpd) (cpd = cyclopentadienone) complexes were identified more than 40 years ago, their exact structures have not been determined because of the polymeric nature of these complexes. We determined the structure of $[Rh(I)Cl(CO)(cpd)]_2$, which was formed by the reaction of $[Rh(cod)Cl]_2$ with a 1,6-diyne under CO. In addition, based on determination of the structure of the $[Rh(I)Cl(CO)(cpd)]_2$ complex, we identified a new catalytic tandem reaction—the Rh-catalyzed [2 + 2 + 1] carbonylative cycloaddition of phenoxide-substituted diynes and Claisen rearrangement.

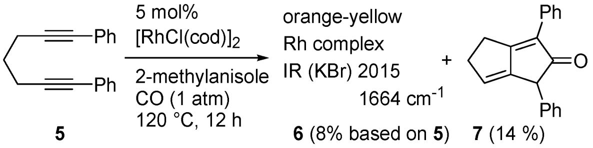
Transition-metal-catalyzed carbonylative cycloaddition is a powerful method for the enhancement of molecular complexity and the construction of polycyclic carbonyl compounds.[1] A typical example of this type of reaction is the carbonylative [2 + 2 + 1] cycloaddition of enynes. This reaction, which is referred to as the Pauson–Khand (P–K) reaction, allows for the direct and efficient synthesis of cyclopentenones.[2] Since Jeong *et al.* first reported the catalysis of an intramolecular P–K reaction,[3] much attention has been paid to Rh catalysts for carbonylative cycloaddition.[4] Subsequently, Rh-catalyzed carbonylative cycloaddition has been widely studied through the use of structural analogues of various substrates, such as allenynes, dienynes, and trienes.[5] In contrast to the numerous studies of these substrates, Rh-catalyzed carbonylative cycloaddition of diynes has rarely been studied. This is somewhat surprising because Müller *et al.*[6] reported that diynes react efficiently with a stoichiometric amount of $RhCl(PPh_3)_3$ under CO to give CPDs (CPD = cyclopentadienone). CPD-containing compounds have received considerable attention due to their high reactivity in decarbonylative cycloaddition with alkynes, in which CPDs act as a dienophile.[7] Isolated CPDs have also been used as ligands in metal complexes, which are efficient catalysts for transfer hydrogenation reactions.[8] CPD–metal complexes have also been synthesized by the reaction of diynes (or two alkynes) with transition metal carbonyl compounds, such as $Fe(CO)_5$, $CpCo(CO)_2$, and $Os_3(CO)_{12}$. The structures of the CPD metal complexes have been characterized by X-ray crystallography.[9] Rh(I)Cl(CO)(cpd) complexes also have been known for a long time.[10] Maitlis and McVey reported the formation of a $[Rh(I)Cl(CO)(cpd)]_n$ complex (**3**) from $[RhCl(CO)_2]_2$ (**1**) and an alkyne[10a] or tetraphenylcyclopentadienone (**2**)[10b] more than four decades ago (Scheme 1). The exact structure of complex **3** remains unknown because of the poor solubility of polymeric complexes.



Scheme 1 McVey and Maitlis report.[10b]

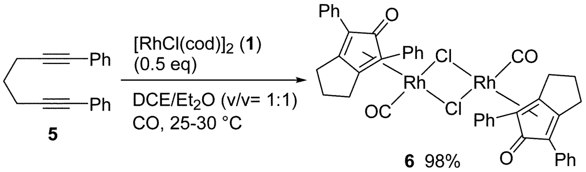
Here, we report our structural characterization by X-ray analysis of $[RhCl(CO)(cpd)]_2$, which was formed by the reaction of a 1,6-diyne with $[Rh(cod)Cl]_2$ under CO. In addition, based on the structural characteristics of the $[RhCl(CO)(cpd)]_2$, a new tandem carbonylative [2 + 2 + 1] cycloaddition of diynes and Claisen rearrangement was discovered.[11]

Carbonylation of diyne **5** in the presence of a catalytic amount of $[RhCl(cod)]_2$ gave the orange-yellow Rh complex **6** with concomitant formation of the bicyclo[3.3.0]octadienone **7** in 14% yield (eqn (1)).[12]



(1)

Because the Rh-complex **6** showed poor solubility in common organic solvents, spectral data for complex **6** were unavailable, except for the results of IR spectroscopy. The IR spectrum of **6** in KBr exhibited two sharp carbonyl-stretching frequencies at 2015 cm^{-1} and 1664 cm^{-1}, which corresponded to the terminal metal carbonyl and the organic C=O, respectively. Interestingly, when the amount of $[RhCl(cod)]_2$ loaded was increased to 50 mol% at 25 °C in 1,2-dichloroethane (DCE)/Et_2O, **5** was completely consumed and **6** was isolated as the sole product without formation of **7** (eqn (2)).



(2)

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan.
E-mail: chatani@chem.eng.osaka-u.ac.jp

† Electronic supplementary information (ESI) available: Spectral data for all new compounds and crystallographic data of **6** and **8**. CCDC 752604–752606. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000747a

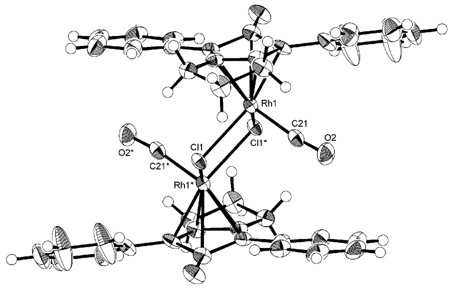
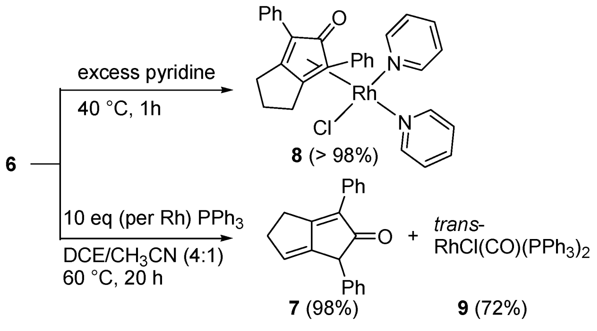


Fig. 1 X-Ray crystallography of the complex **6**.

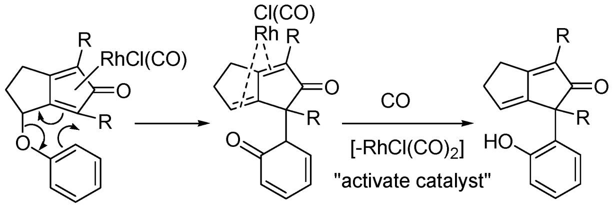
Fortunately, we were able to obtain a single crystal of **6** by slow diffusion of **5** into $[RhCl(cod)]_2$ (**1**) (see ESI†). X-Ray crystallography confirmed the structure of **6**, which was a chloro-bridged dimer of Rh(CO)(cpd) (Fig. 1). It is important to note that, as far as we know, this is the first structural characterization of a chloro-bridged Rh(I)–CPD carbonyl complex.[13] It is assumed that the poor reactivity of diynes toward Rh-catalyzed carbonylative cycloaddition might be due to the formation of a stable RhCl(CO)(cpd) complex, which deactivates the Rh-catalyst and prevents additional catalytic cycles. In fact, when **5** was reacted with a catalytic amount of $[Rh(cod)Cl]_2$ under CO even at 120 °C, 70% of **5** was recovered from the reaction shown by eqn (1).

Next, we investigated the thermal stability of **6** and its reactivity toward other ligands that might possibly be used as additives to catalyze the liberation of CPD. We envisioned that Rh(I)-catalyzed incorporation of CO into a diyne could be accomplished by liberation of CPD from Rh(I) metal. But, similar to other ML_n–CPD complexes, CPD was strongly coordinated to the rhodium center to fulfill 18e configuration. To our surprise, **6** exhibited high stability when exposed to high temperatures <200 °C. By contrast to the results reported by McVey and Maitlis,[10b] when **6** was heated at 130 °C for 20 h, the decarbonylation of complex **6** was not observed. Likewise, the liberation of **7** was not detected by GC analysis.

In the presence of excess pyridine (as a solvent), **6** was transformed into the $RhCl(cpd)(py)_2$ complex (**8**) in quantitative yield ($>98\%$) (Scheme 2). This result is similar to the pyridine coordination of a RhCl(CO)(cpd) complex described by McVey and Maitlis.[10b] The structure of complex **8** was also confirmed by X-ray analysis (see ESI†). When **6** was reacted with excess PPh_3, CPD was liberated from Rh, and **7** was isolated in high yield with the concomitant formation of *trans*-$RhCl(CO)(PPh_3)_2$ (**9**), as confirmed by ^1H and ^{31}P NMR and by IR spectroscopy.



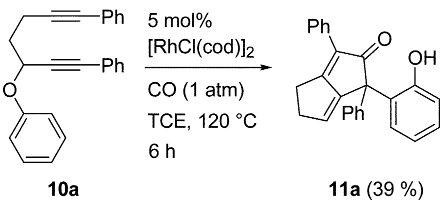
Scheme 2



Scheme 3 A working hypothesis.

Next, we focused our attention on substrate modification to achieve tandem catalytic reactions *via* an Rh–CPD intermediate.[14] We postulated that structural changes in CPD would liberate Rh metal from coordination, thereby making the reaction catalytic. We assumed that a metal coordinated to CPD would show properties similar to those of a metal coordinated to alkenes or alkynes. In transition metal-catalyzed [3,3]-sigmatropic rearrangement, the reaction becomes favorable by enhancing electrophilicity through metal coordination (Scheme 3). However, Rh-catalyzed Claisen rearrangement reactions are much less studied than Pd-catalyzed rearrangement.[15]

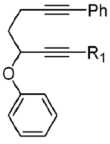
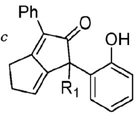
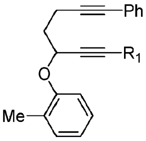
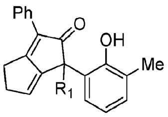
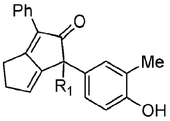
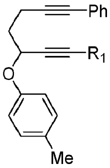
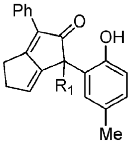
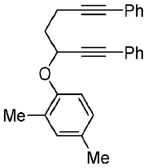
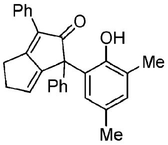
Based on these assumptions, we attempted Rh-catalyzed carbonylative cycloaddition of the phenoxide-substituted diyne **10a** under CO. We successfully isolated the bicycle-[3.3.0]octadiene derivative with an *ortho* substituted phenol **11a**, which was formed by tandem carbonylation and Claisen rearrangement (eqn (3)).



(3)

It should be noted that thermal Claisen rearrangement usually requires a high reaction temperature (>200 °C). Thus, formation of the RhCl(CO)(cpd) complex makes the Claisen rearrangement a favorable reaction. Encouraged by this positive result, we examined the scope of substrates for the Rh-catalyzed tandem $[2+2+1]$ carbonylative/Claisen rearrangement (Table 1). As expected, substrate reactivity was strongly influenced by the substituent (R_1) that was located in a sterically hindered environment (entries 1–4). The cyclopropyl-substituted substrate **10b** showed comparable reactivity (entry 2). But the substrate with the Pr group gave only a trace amount of the expected compound (entry 3). In the case of R_1 = H, a complicated mixture was obtained (entry 4). Next, we observed the effect of arene substituents. We expected that Claisen rearrangement would be accelerated by electron-donating substituents. Surprisingly, use of an *o*-methyl-substituted phenyl ring, as in **10e**, gave a mixture of *ortho* (45%)- and *para* (12%)-substituted phenol products, **11e** and **12e** (entry 5). However, use of R_1 = *c*-Pr selectively gave the *ortho*-substituted phenol product (entry 6). *Para*-substitution of the phenyl ring exclusively gave *ortho*-substituted phenol products (entries 7–9). We propose that the

Table 1 Rh(I)-catalyzed tandem carbonylative [2+2+1] cycloaddition and Claisen rearrangement[a]

Entry	Reactant	Product (%)[b]	
1	 **10a** (R_1=Ph)	 **11a** (39%)	
2	**10b** (R_1=*c*-Pr)[c]	**11b** (43%)	
3	**10c** (R_1=Pr)	**11c** (trace)	
4	**10d** (R_1=H)	**11d** (0%)	
5	 **10e** (R_1=Ph)	 **11e** (45%)	 **12e** (12%)
6	**10f** (R_1=*c*-Pr)	**11f** (67%)	**12f** (trace)
7	 **10g** (R_1=Ph)	 **11g** (48%)	
8	**10h** (R_1=*c*-Pr)	**11h** (29%)	
9	 **10i**	 **11i** (52%)	

[a] Reactant (0.5 mmol) and $[RhCl(cod)]_2$ (0.025 mmol) in TCE (2.5 mL, TCE = 1,1,2,2-tetrachloroethane) at 120–130 °C for 20 h. [b] Isolated yield. [c] *c*-Pr = cyclopropyl.

reaction proceeds *via* [2+2+1] carbonylative cycloaddition and [3.3]-sigmatropic rearrangement, as shown in Scheme 3.[16]

In conclusion, we isolated $[RhCl(CO)(cpd)]_2$ (**6**) from a 1,6-diyne and $[Rh(cod)Cl]_2$ at room temperature under CO. The complex showed high stability under thermal conditions. With the addition of ligands, such as pyridine or triphenylphosphine, $[RhCl(CO)(cpd)]_2$ was converted into either pyridine-coordinated complex **8** or bicyclo[3.3.0]octadienone **3**. The use of a tandem Claisen rearrangement to activate the Rh-catalyst in the Rh–CPD complex was studied. The structural modification of reactants successfully activated a new tandem catalytic carbonylative cycloaddition and Claisen rearrangement. Additional studies of both the scope and mechanism of the tandem reaction (*ortho*- and *para*-substitution) are in progress.

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16 The reaction mechanism, particularly that of the formation of the *para*-substituted product **12**, is not clear at the present time. A possible mechanism for the formation of the *para*-substituted product is the ion-pair mechanism. Although, in most cases, phenoxide nucleophiles undergo O-alkylation instead of C-alkylation, C-alkylation at the *para* position reportedly takes place when phenol is used as the nucleophile. Nevertheless, at the present time, we cannot comment on whether the Claisen rearrangement proceeds *via* a concerted or an ion-pair mechanism.