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一、中文摘要

金屬碳烯化合物的合成性質，雙胺碳烯配位體在金屬間的轉移。

關鍵詞：雙胺碳烯，金屬，配位體，轉移，

Abstract

Under mild conditions, reactions of group VI metal carbenes with Pd(II), Pt(II), Rh(I), Cu(I), Cu(II) and Ag(I) ions provide the corresponding diaminocarbene complexes via carbene ligand transfer. The Cu(I) and Ag(I) complexes readily undergo acid-induced M=C cleavage to yield the imidazolidin-2-ylidinium salts.

Keywords: diaminocarbene, ligands, transfer reactions, metal.

二、緣由與目的

Diamino-substituted carbenes are unusually stable due to the good σ-donating ligand. It occurred to us that the stable diaminocarbene makes them suitable for studying carbene transfer between metal ions. In a preliminary report, we showed that carbene complexes of Pd(II), Pt(II), Rh(I), and Au(I) were formed in high yields via the reaction of tungsten diaminocarbene complexes $[(CO)_5W{=}CNRCH_2CH_2NR]$ with $(PhCN)_2PdCl_2$, $(PhCN)_2PtCl_2$, $[(CO)_2RhCl]_2$, and $(Me_2S)AuCl$ under mild conditions, indicating that a carbene transfer reaction between transition metal complexes can be facilethe. In order to gain insight into such carbene transfer, an investigation of the reactvities of diaminocarbene complexes 1 - 4 toward other transition metal ions were conducted..

三、報告內容

Preparation of Carbene complexes. All carbene complexes were prepared by the method previously reported for the N-benzyl substituted complexes (**1c, 2c**, and **3c**). The p-coordinated diaminocarbene complex **4** is obtained thermally by heating 1b above 100 ^{o}C. Substitution reactions of 1a and 1c with triphenylphosphine or dppe proceeded cleanly at 120 ^{o}C to produce **5a -b** and **6a-b**, respectively, in excellent yields.

All the carbene complexes were isolated as stable solids and characterized by both spectral and elemental analyses. Some spectral data are summarized in Table 1. The facial geometry of complexes **6** and the cis arrangement in **5** were established by ^{31}P NMR chemical shifts and their IR carbonyl stretching patterns. X-ray single-crystal structures of **5b** and **6b** were obtained to provide confirmation

Carbene Transfer Reactions. The diaminocarbene unit of group VI metal carbonyl complexes **1-3** is readily transferred to the other transition metal ions. We reported earlier that reaction of 1a and 1b with $(PhCN)_2PdCl_2$, $(PhCN)_2PtCl_2$, $[(CO)_2RhCl]_2$, and $(Me_2S)AuCl$ results in the formation Pd(II), Pt(II), Rh(I) and Au(I) carbene complexes, respectively, in high yields. Further investigation showed that the chromium and molybdenum diaminocarbene complexes with different N-substituents behave similarly.

Carbene Transfer and Cleavage of M=C. Reaction of $[Cu(CH_3CN)_4]BF_4$ with an equimolar amount of **1a** in refluxing acetonitrile results in the cleavage of the carbene moiety to yield the imidazolidin-2-ylidinium salt quantitatively. A deuterated product at C2 is obtained when acetonitrile-d3 or a mixture of tetrahydrofuran and D_2O is used. This outcome suggests that the additional hydrogen originated from the solvent. Cleavage of metal carbene is also observed in the reaction of **1a** with Cu(II) or Ag(I) ions. Therefore, the reaction of 1a with an equimolar amount of $Cu(BF_4)_2.6\ H_2O$ or $AgBF_4$ in an acetonitrile solution provides 14a as the exclusive product. Other N-substituted complexes like 1b-c, as well as group VI carbene complexes 2a-b and 3a-c, undergo similar reactions to give N-substituted imidazolidin-2-ylidinium salts 14a-c, respectively. Treatment of 4 with an equimolar amount of $[(CH_3CN)_4Cu]BF_4$ in acetonitrle results in the cleavage of carbene ligand to yield 14b.

In order to understand the role of metal ions in these reactions, metal complexes from the reaction of 1a with $[Cu(CH_3CN)_4]BF_4$ were trapped by adding a three equimolar amount of (dppe) to the reaction mixture. A copper complex of formula of $[Cu(dppe)_2]BF_4$ was obtained in a quantitative yield based on the amount of copper reagent used, indicating that the copper ion retains its oxidation state. Tungsten products $W(CO)_4(dppe)$, $W(CO)_3(dppe)(CH_3CN)$ and other substitution complexes were identified by spectroscopic means. Hexacarbonyltungsten was recovered in up to 60 % yield (based on the carbene complex used) when the reaction was carried out in the presence of an atmosphere of carbon monoxide.

Copper- and Silver-Carbene Complexes. A NMR tube containing a freshly dried $CDCl_3$ solution of 1a and 0.5 mol equiv of $[Cu(CH_3CN)_4]BF_4$ was studied by both 1H and ^{13}C NMR. Clean spectra were observed, consisting of peaks due to two species: the biscarbene copper species 15a and a trace of N,N-dimethylimindazolinium salt 14a (less 5 % by integration). Selected ^{13}C NMR chemical shifts are summarized. The chemical shifts and splitting patterns of copper and silver biscarbene complexes are similar to that of the stable bis(imidazol-2-ylidene) copper complex 18a, which was isolated by Arduengo and coworkers.5b The range of chemical shifts for the carbene moiety in 15a-c and 16a-c is downfield of that in 18a-b, reflecting a difference in p-delocalization in these N-heterocyclic carbenes. Unlike 18a, the copper complexes in this work are highly sensitive toward air and moisture, and readily decompose. In fact, the copper carbene complexes 15a-c in dichloromethane readily convert into the corresponding cyclic urea when exposed to air. This may be due to the less steric bulkiness of the N-alkyl substituents and the non-aromaticity of the N-heterocyclic carbene ring. Due to the contamination of trace tungsten complexes and difficulty of purification, attempts to obtain acceptable elemental analysis of these carbene complexes failed, but these copper complexes were characterized spectroscopically. The mass spectrum (FABMS) of 15a gave cations at m/z 315, 317 in the ratio of 2:1, which accords with the ratio of natural abundance of 63Cu and 65Cu. Similar observation also appear with complexes 16b-c (Table 3). The observed coupling from 107Ag and 109Ag nuclei to the carbene-C suggests coordination of the carbene ligands to the metal center, which is in accordance with observations by Arduengo and coworkers concerning 18b.5b

Upon addition of a trace of water to the NMR samples, 1H NMR spectra showed only the N,N-disubstituted imindazolinium salt, indicating that the biscarbene species react with water. These results are consistent with the deuterium-labeled experiments. From the above observations, the pathway of carbene cleavage shown in scheme 2 is proposed. The first step involves a carbene transfer reaction to form the new metal carbene complex A.12 By dissociation, the diaminocarbene ligand acts as a base which receives a proton from the solvent to yield the product. It was demonstrated by theoretical calculations that the simple diaminocarbenes are strong bases, even stronger than the imidazolylidene (an aromatic heterocyclic carbene).18,6b Thus, when the reaction is carried out in acetonitrile, the carbene ligand deprotonates the a-proton of acetonitrile to form the organic salts 14.

Furthermore, the cleavage reaction is accelerated under acidic conditions. In tetrahydrofuran and 10 % aqueous HBF4, reaction of 1a with Cu(I) is complete within few minutes. A catalytic amount of copper ions (10 % mol) can accomplish the same reaction under acidic conditions. The reaction does not proceed in aqueous sodium hydroxide solution even with an excess of metal ion. When the reaction is carried out in air, the cyclic urea product and imidazolidin-2-ylidinium are obtained (Eq. 3), indicating that the formation of urea stems from the reaction of copper carbene with O_2.

Other Carbene Transfer Reactions. It was reported recently by Lin and coworkers that imidazol-2-ylidene silver complexes react with $(CH_3CN)_2PdCl_2$ to yield the corresponding palladium carbene. In our studies, we found that treatment of palladium complex 7b or platinum complex 10b with AgBF4 readily causes the cleavage of M=C to yield 14b. Presumably the formation of 14b is similar to the reaction of 1-3 with $AgBF_4$, e.g., the formation of silver carbene complex 16b, which then undergoes the cleavage reaction. No carbene ligand transfer from silver to palladium ion was observed. This result is attributed to the stronger basicity of the simple carbenes (non-aromatic heterocyclic carbene). Ligand Effect. The reactivity of the diaminocarbene moiety in the transfer reaction is sensitive to the ligands around the tungsten center. It was found that 1a, 1c and 4 do not react with excess of S8 in tetrahydrofuran under refluxing conditions. This is a consequence of the combination of the strongly donating character of diaminocarbene ligand and the strongly p-acid carbonyls around the tungsten center. The phosphine substituted complexes 5a-b and 6a-b readily react with sulfur to form the cyclic thiourea (Eq. 4). Apparently, the s-donating phosphine ligands change the electronic environment of metal center and allow the carbene ligand to be oxidized, which is similar to the oxidative cleavage of tetraamino-substituted olefins by sulfur to form thiourea.

By monitoring the product formation via NMR shifts, the relative rate of the cleavage of the diaminocarbene ligand by copper(I) ion was found to decrease in the order 1a > 4 ~ 5a > 6a. This may be due to the steric bulkiness of the phosphine substituent around the metal, which hinders the access of copper ion to the carbene ligand. In the carbene transfer reaction, monodenatate phosphine substituted carbene complexes 5a-b undergo a similar reaction, but the phosphine ligand shifts from tungsten to the new metal center to form the phosphine-carbene complex. Reactions of 5a-b with (PhCN)2PdCl2 and [(CO)2RhCl]2 gave a mixture of products which were not easy to purify. However, NMR showed the disappearance of the starting carbene 5a-b, indicating carbene transfer. In the bisphosphine substituted carbene complexes 6a-b, reactions gave the simple bisphosphine metal complexes 20 accompanied by formation of imidazolidin-2-ylidinium salt.

Summary

Diaminocarbene transfer from a group VI metal center to another metal (Pd, Pt, Rh, Au) has been shown to be a viable synthetic approach for the preparation metal carbene complexes. Copper and silver carbene species can be prepared similarly, but subsequently decompose to yield an iminium salt.

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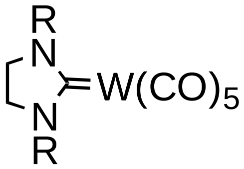

1 R= Et, Allyl, benzyl, 4=penteny