Diamino-substituted Carbene Transfer between Transition Metal Ions

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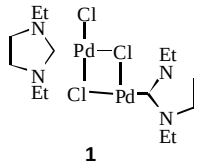
Diamino-carbene ligand transfer between various metal ions is studied, particularly with Pd(II) to Rh(I), Rh(I) to Au(I). Reactions of various carbene complexes with $AgPF_6$ result in the cleavage of the M=C bond to give the protonated carbene species, imidazolidin-2-ylidinium salt, indicating the presence of free carbene ligand in the reaction medium. When the carbene transfer process was carried out in tetrahydrofuran, the polymerization of tetrahydrofuran occurred.

INTRODUCTION

The carbene transfer is an interesting process in catalytic or metal-mediated reactions.[1] Fischer and coworkers reported the first example of such a transfer in the reaction of [Cp(CO)(NO)Mo=C(OMe)Ph] with $[Fe(CO)_5]$ in benzene solution upon irradiation to provide $[(CO)_4Fe=C(OMe)Ph]$.[2] Since then, few investigations involving carbene transfer between transition metal ions have occurred,[3-9] presumably due to the stabilization of carbene ligand by the metal ion. In a recent study, we found that diamino-carbene moiety can be easily transferred from group VI to Pd(II), Pt(II), Rh(I), Au(I), Cu(I) and Ag(I) ions. Such a result indicates that a carbene transfer reaction between transition metal complexes can be facile.[10,11] In view of the carbene transfer between other metal ions, the reactivity of palladium and platinum, as well as rhodium carbene substrates (**1-6**), are explored with the relevant metal ions.



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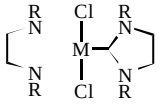
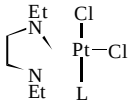


2 , M = Pd, R = allyl
3 , M = Pt, R = allyl



4 , L = CO
5 , L = PPh_3

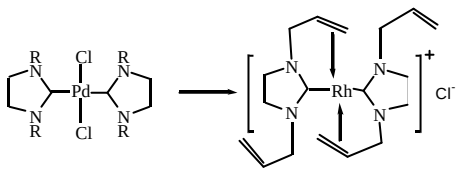
RESULTS AND DISCUSSION

Carbene transfer between transition metal ions

Pd(II) to Rh(I)

Palladium carbene complexes were prepared by the method previously reported.[9] The *N*-ethyl substituted palladium carbene complex **1** does not react with $[Rh(CO)_2Cl]_2$ in chloroform at room temperature. Even in the presence of pyridine or triphenylphosphine, there is no carbene transfer from **1** to the rhodium metal center, indicating the stable nature of the chloro-bridging palladium complex. However, the *N*-allyl substituted palladium complex **2** undergoes a carbene transfer reaction with $[Rh(CO)_2Cl]_2$ in chloroform at room temperature to yield the biscarbene rhodium complex **6**. The success of carbene transfer to the new metal center is presumably due to the coordinating assistance of the π-bond of the allyl substitutent, which has been illustrated in such a transfer between tungsten and palladium.[9,10]

Scheme I



2, R = allyl **6**

Pt(II) to Rh(I)

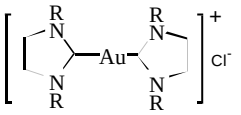
In contrast to the palladium complexes, platinum carbene complexes are inert toward the carbene transfer with $[Rh(CO)_2Cl]_2$. By monitoring the reaction with NMR, no reaction occurs between **3** and $[Rh(CO)_2Cl]_2$, nor with the complex **4** or **5.** This outcome indicates the stronger interaction of the Pt-C bond than that of the Pd-C.

Rh(I) to Au(I)

The *N*-allyl-substituted diamino carbene moiety read-

Dedicated to Professor Hsin, Shu-Ching ( ) (NTU) on the occasion of her 70th birthday.

ily un der goes trans fer from rho dium(I) to gold(I) cen ter under a mild con di tion. Thus an equimolar mix ture of **6** and $(Me_2S)AuCl$ in chlo ro form-d_3 was checked by ^1H NMR at room tem per a ture. The spec trum of the re ac tion mix ture showed a quan ti ta tive con ver sion into biscarbene gold complex **7**. How ever, the rel e vant ethyl-substituted com plex appears less re ac tive.

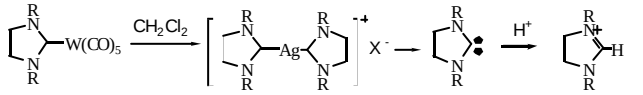


7, R = allyl

Carbene cleav age by sil ver(I)

In the pre vi ous in ves ti ga tion, we found that the tungsten com plexes **8** readily un dergo carbene trans fer in dichloro methane with Ag(I) or Cu(I) to form the cor re spond ing carbene complex, which then hydrolysizes to yield the imidazolidin-2-ylidinium salt (Scheme II).[10] Such ob ser vation is also true in some of the pal la dium com plexes. The metal-carbon bond is readily cleaved in the re ac tion of the biscarbene com plexes **1** or **2** with $AgPF_6$ in the pres ence of mois ture to form the cor re spond ing sub sti tuted imidazolidin-2-ylidinium salt **11**. Pre sum ably, the for ma tion of the or ganic salt is sim i lar to the re ac tion of tung sten-carbene with $AgBF_4$, e.g. the for ma tion of sil ver-carbene com plex **9**, which then undergoes the cleavage process. However, the platinum carbene com plexes be have dif fer ently. Com plexes **4** and **5** do not re act with $AgPF_6$ in chlo ro form or acetonitrile so lu tions, whereas the biscarbene com plex **3** un der goes the cleav age reac tion smoothly un der mild con di tions. As for the rho dium com plexes, com plex **6** readily re acts with $AgPF_6$ to yield the imidazolidin-2-ylidinium salt quan ti ta tively.

Scheme II



8a R = Et
8b R = allyl

9a R = Et
9b R = allyl

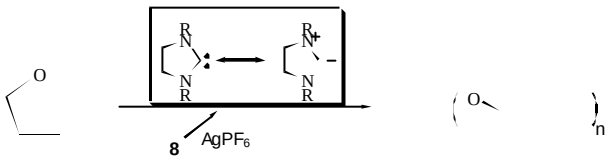
10a R = Et
10b R = allyl

11a R = Et
11b R = allyl

Poly mer iza tion of THF dur ing the carbene trans fer between tungsten(0) and silver(I)

As dis cussed in the pre vi ous sec tion, the carbene moiety can be cleaved by a sil ver(I) ion in the pres ence of mois-ture. In ter est ingly, when the re ac tion was car ried out in THF as the sol vent, a poly meric prod uct was ob tained (Scheme III). In a 10-mL round-bottom flask equipped with a re fluxing con denser, a mix ture of **8a** (or **8b**) and $AgPF_6$ in tetrahydrofuran (6 mL) was heated to re flux for 30 min. The re action mix ture be came vis cous and could not be stirred. The poly mer was pu ri fied by dis solv ing in di chloro methane and re-precipitated by meth a nol to yield a white solid. Both ^1H and ^{13}C NMR of the poly mer clearly il lus trated its struc ture and GPC anal y sis shows M_N = 43244 (M_W/M_N = 2.7). The for ma tion of such a poly mer is pre sum ably due to the base-catalyzed ring opening re ac tion. The dis so ci ated carbene ligand **10** from the gen er ated sil ver carbene spe cies be haves as a strong base and nucleophile, which cat a lyzes the polymer iza tion. In deed, there is no poly mer iza tion oc cur ring in the pres ence of a trace of wa ter. It has been re ported that the ba sic ity of 2,3-dihydro-1*H*-imidazol-2-ylidene is known as the stron gest or ganic Bronsted base.[13,14]

Scheme III



Carbene ligand trans fer be tween metal ions of fers another syn thetic ap proach to gen er ate the new carbene complexes. It ap pears that such a re ac tion tends to pro vide the more sta ble metal carbene com plexes. How ever, the sil ver carbene com plex un der goes ligand dis so ci a tion to gen er ate a free carbene, which can act as a base or nucleophile. In par tic-u lar, the *N,N'*-diethyl-2,3-dihydro-1*H*-imidazol-2-ylidene causes the poly mer iza tion of tetrahydrofuran.

EXPERIMENTAL SECTION

General Information

Sol vents were dried by stan dard pro ce dures. IR spec tra were re corded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were recorded on a Bruker ACE-200 or a ACE-300 spec trom e ter. For the ^{31}P NMR spec tra, the spec-

trom e ter fre quency at 81.015 MHz or 121.49 MHz was employed and chem i cal shifts are given in ppm (δ) rel a tive to 85% H_3PO_4 in $CDCl_3$. Values up field of the stan dard are defined as neg a tive. The cor re spond ing fre quen cies for ^{13}C NMR spec tra were at 50.32 MHz or 75.47 MHz for re spec tive spec trom e ters. Mass spec tro met ric anal y ses were col lected on a JEOL SX-102A spec trom e ter. El e men tal anal y ses were done on a Perkin-Elmer 2400 CHN an a lyzer. Com plexes **1-6** were pre pared ac cord ing to the method pre vi ously re ported *via* carbene transfer reaction.[10] Metal complexes such as $[Rh(CO)_2Cl]_2$ and $AgPF_6$ were ob tained com mer cially and used with out fur ther pu ri fi ca tion.

Carbene Trans fer Re ac tion be tween Pd(II) and Rh(I)

To a mix ture of Pd(II) carbene com plex was added an equimolar amount of $[Rh(CO)_2Cl]_2$ in dichloromethane. Prog ress of re ac tions was mon i tored by the ^1H NMR till the start ing ma te rial dis ap peared. The re ac tion mix ture was filtered through a small amount of sil ica to re move the metal res i due and the fil trate was con cen trated to yield the de sired com plexes. Rho dium carbene com plex **6** was ob tained as a yel low solid: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.65 (m, 2H), 5.19 (m, 4H), 4.45 (m, 2H), 3.94 (m, 4H), 3.65-3.40 (m, 12H), 3.12 (d, J = 11.8 Hz, 2H), 2.85 (d, J = 8 Hz, 2H), which is es sen tially iden ti cal to the sam ple preapred from the re ac tion of $[(CO)_5W{=}CN(allyl)CH_2CH_2N(allyl)]$ with $[Rh(CO)_2Cl]_2$.[11] Studies of the carbene transfer between Pt(II) and Rh(I) are essentially fol low the pro ce dure described for the Pd(II) com plexes.[12]

NMR Studies of Carbene Cleavage by Silver(I)

Into a NMR tube was placed an equimolar amount mixture of pal la dium or plat i num com plex and $AgPF_6$. The tube was flushed with ni tro gen gas and chlo ro form-d_1 (0.7 mL) was added. Prog ress of the re ac tion was checked by ^1H NMR spec tros copy. Re ac tion was com pleted within 30 min ~ 1 h. NMR sig nals of the carbene cleav age prod uct (*N*-Substituted imidazolidin-2-ylidinium salt) are iden ti cal to the sam ple previous reported.[11,12]

Poly(tetrahydrofuran)

A mix ture of **8a** (0.44 mmol) [or **8b**] and $AgPF_6$ (0.44 mmol) in de gassed THF (6 mL) was heated to re flux un der N_2 for 30 min. The re ac tion mix ture was dis solved in di chloromethane (10 mL) to form a clear so lu tion. Slow ad di tion of meth a nol (200 mL) to the above so lu tion re sulted in the forma tion of a white solid. Fil tra tion give the de sired poly mer (2.56 g, 48% based on THF used): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.63 (br, 2H), 1.56 (br, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 70.5, 26.4; GPC M_W = 116798, M_N = 43244, M_W/M_N = 2.7.

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Key Words

Carbene transfer; Diaminocarbenes; Transition metal ions.

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