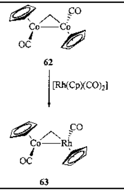
Carbene transfer reactions between transition-metal ions



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Carbene transfer processes are often involved in catalytic or metal-mediated reactions, however, a limited number of works concerning such transfer between transition metal complexes appear in the literature. This article presents an overview of the progress of this chemistry with an emphasis on examples with well-defined structures. A few studies, which are discussed in some detail, provide an insight of what has been achieved as well as an indication of the future work.

1 Introduction

Since the first discovery of stable transition metal carbene complexes by Fischer and Maasböl,[1] metal carbenes have become an important area of organometallic chemistry. A number of synthetic approaches for the preparation of carbene complexes have been reported in the last three decades, conversion of carbonyls or isocyanide groups into carbene ligands and cleavage of electron rich alkenes to give metal carbenes amongst them.[2,3] However, there are a few instances where carbene complexes are prepared from other metal carbene species by a simple transfer reaction of the carbene ligand itself.[4–21]

The use of carbenes in various synthetic methodologies, particularly metal mediated reactions, is frequently employed in their transformation into useful organic products.[22, 23] Formation of metal carbene intermediates has been postulated and observed in many catalytic processes, such as olefin metathesis and the Fischer–Tropsch reactions. In fact, the cyclopropanation of alkenes is one of the most widely studied reactions and metal carbene species are known to be key intermediates in transferring the carbene moiety, but the source of the carbene is generally restricted to the organic carbenoid.[24] Simple transfer of a carbene ligand from one metal to another metal centre is rare. The difficulty in transferring is presumably due to the stabilization of carbene ligands *via* the metal centre in these presynthesized carbene complexes. In spite of that there are some examples demonstrating carbene transfer between metal ions, in particular with diamino-substituted carbene complexes.[14–16] This article seeks to summarize such transfer processes between metal ions and illustrates the interesting feature of this type of reaction in possible further applications.

2 Carbene transfer between simple metal ions

The first example of a carbene ligand transfer between metal ions was reported by Fischer and his coworkers.[4] Reaction of [Mo(Cp)(CO){C(OMe)Ph}(NO)] (**1a**) with [Fe(CO)$_5$] in benzene solution under photochemical conditions affords the iron carbene complex [Fe(CO)$_4${C(OMe)Ph}] (**2a**). In this study, the authors suggested that the carbene transfers might proceed *via* two possible pathways: one involving a free carbene as an intermediate which then transfers to iron, and the other by the coordination of molecule **1a** with the [Fe(CO)$_4$] fragment followed by migration of carbene from molybdenum to iron. Later studies demonstrated that arylalkoxy- and aryldialkylamino-carbenes (**1b** and **1c**) also can be transferred from the corresponding molybdenum carbene complexes [eqn. (1)].[5]

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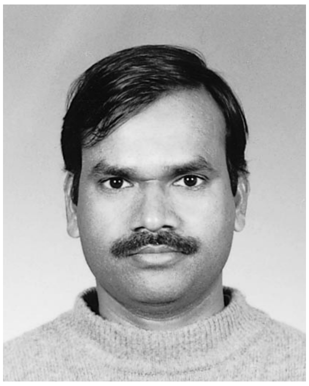

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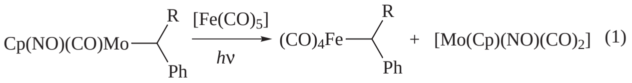
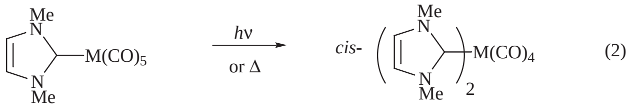


1a R = OMe
1b R = OEt
1c R = NMe$_2$

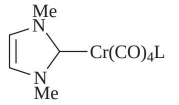
2a-c

Under irradiation conditions, pentacarbonyl(1,3-dimethyl-4-imidazolin-2-ylidene)chromium (**3a**) yields a biscarbene chromium complex **4a** in boiling THF [eqn. (2)].[6] It is also found that the analogous molybdenum and tungsten complexes (**4b** and **4c**) can be prepared by thermal reaction from the corresponding carbene complexes **3b** and **3c** respectively.[7] Here carbene transfer between the metal atoms is expected to proceed through the initial formation of a tetracarbonyl metal carbene intermediate, which subsequently reacts with **3** to generate *cis*-biscarbene complexes **4**. Formation of ligand substituted products **5** upon treating **3a** with $P(C_6H_5)_3$ or $C_6H_{11}NC$ indicates that the unsaturated metal intermediate can be trapped in the presence of a donor ligand. Of course, generation of a free carbene as the intermediate is excluded in this investigation.



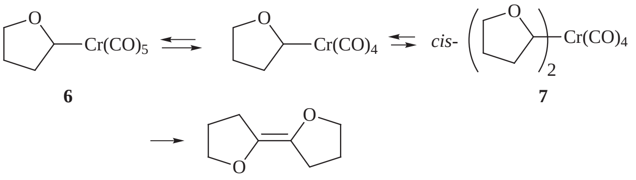
3a M = Cr
3b M = Mo
3c M = W

4a-c



5 L = PPh_3, $C_6H_{11}NC$

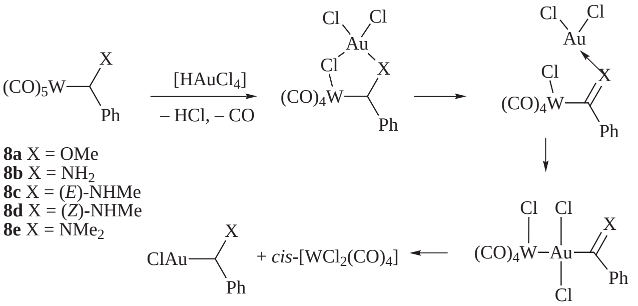
The dissociation of a carbene ligand from the metal centre is proposed to occur through a free carbene intermediate in certain cases based on the formation of alkene products. In the thermolysis of $[Cr(CO)_5\{C(OMe)R\}]$ (R = Ph, Me), the authors suggested that the formation of alkene product (MeO)RC=CR(OMe) (R = Ph, Me) was due to the dimerization of the dissociated carbene species.[25] However, evidence against such an argument has been demonstrated from an authentic preparation of 2-oxacyclopentylidene, which was found to yield dihydrofuran and cyclobutanone as the major products upon thermolysis instead of dimerization.[8] The absence of the formation of cyclobutanone in the thermolysis of the chromium carbene complex **6** rules out intervention of the free carbene in this reaction. Based on a simple kinetic investigation the reaction pathway was proposed as in Scheme 1. This shows that the alkene product comes from the elimination of the biscarbene chromium complex **7**, which is presumably formed *via* a carbene transfer reaction. In addition, compound **6** undergoes simple carbene transfer upon reaction with $[W(CO)_6]$ generating the corresponding complex (2-oxacyclopentylidene)-$W(CO)_5$, which supports the possibility of carbene transfer between the metals.



Scheme 1 Mechanism for the formation of the alkene from the metal carbene.

In addition, Lappert showed that the electron rich alkenes themselves could be the intermediates in such types of reaction.[3] Thermolysis of $[Mo(CO)_5(L^{Me})]$ giving *cis*-$[Mo(CO)_4(L^{Me})_2]$ $\{L^{Me}$ = 1,3-dimethylimidazolidinylidene$\}$ which was prepared under the same conditions using the corresponding electron rich alkenes (enetetraamines) and $Mo(CO)_6$, indicating the possibility of formation of alkenes *via* the heteroatom-stabilized metal carbene complexes.

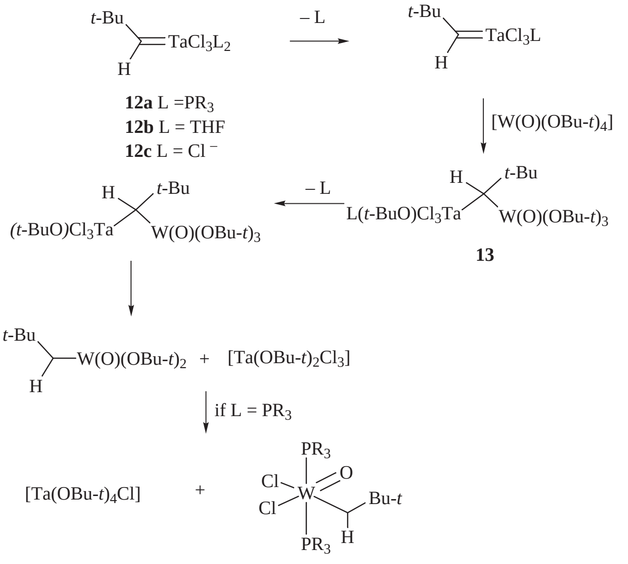
Using a carbene ligand transfer reaction, gold(I) carbenes of the type $[AuCl\{C(R)Ph\}]$ (**9a–d**) were prepared by reaction of the corresponding tungsten carbene complexes $[W(CO)_5\{C(R)Ph\}]$ (**8a–d**) with $HAuCl_4$ (Scheme 2).[9] Transfer of the carbene in these redox reactions is found to proceed at 0 °C and the resulting complexes are stable at room temperature. However, upon heating up to 200 °C the carbene ligand dimerizes with the formation of metal chlorides. Dimerization of the carbene moiety at 200 °C after carbene transfer from tungsten to gold indicates that the stability (kinetic or thermodynamic) of the resulting carbene complex dictates the carbene cleavage process. A possible reaction pathway (Scheme 2) for the formation of gold(I) carbene complexes involves the coordination of the gold centre to form a chloride-bridged dinuclear species, which allows the carbene ligand to shift from tungsten to gold and a *cis*-arrangement around the tungsten ought to be the thermodynamic result. It is noticed that the oxidation state of gold is reduced from III to I during the transfer reaction.



Scheme 2 Reaction pathway of carbene transfer between tungsten and gold.

In the study of these gold carbene complexes, the authors found that the substituent on the carbene ligand affected the transfer reaction. In the case of dimethylamino substituted carbene complex **8e** the reaction proceeds similarly, but yields a mixture of $[AuCl\{C(NMe_2)Ph\}]$ (**9e**) and $[AuCl_3\{C(NMe_2)Ph\}]$ (**10**), in which compound **10** retains the oxidation state III unlike the previous reaction shown in Scheme 2.[10] However, the reaction of $[W(CO)_5\{C(NMe_2)Ph\}]$ with $[HAuBr_4]$ yields only $[AuBr\{C(NMe_2)Ph\}]$, which upon oxidation by Br_2 yields the corresponding gold(III) complex. The above examples show that the simple carbene transfer from Group 6 metal complexes to the gold centre is accompanied by a redox reaction at tungsten. Similar transfer forming a binuclear gold(I) carbene complex $[Au_2Cl_2\{CPhNH(CH_2)_nNHCPh\}]$ (n = 2, 6) is accomplished by treatment of the tungsten complexes $[(W(CO)_5)_2\{C(Ph)NH(CH_2)_nNHC(Ph)\}]$ with 2 equiv. of $[HAuCl_4]$.[11] Concerning the redox chemistry of the carbene transfer in gold complexes, there is no further investigation.

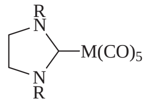
The first example of a carbene transfer in which the carbene is not stabilized by a heteroatom substituent was reported in the preparation of $[Mn(Cp)(CO)_2\{CPh_2\}]$ (**11**) (Cp = η^5-C_5H_5).[12] Thermolysis of $[W(CO)_5\{CPh_2\}]$ in the presence of $[Mn(Cp)(CO)_2(THF)]$ results in the formation of the manganese carbene complex **11**, which shows diphenylcarbene transfer from tungsten to manganese. In addition, a number of tungsten oxoneopentylidene complexes were readily obtained by alkylidene transfer from tantalum to tungsten.[13] Thus, treatment of the tantalum complexes [Ta(=CHCMe$_3$)Cl$_3$L$_2$] (**12a**) (L = PMe$_3$, PEt$_3$, PMe$_2$Ph) with [W(O)(OCMe$_3$)$_4$] in pentane resulted in the formation of the corresponding tungsten oxoneopentylidene complexes [W(O)(CHCMe$_3$)Cl$_2$L$_2$] **(14)**. A crystallographic study of [W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)$_2$] showed that these species are approximately octahedral with the arrangement of *trans*-phosphine and *cis*-halide ligands. Scheme 3 illustrates the possible pathway of the carbene transfer from tantalum to tungsten. It appears that a phosphine ligand dissociates from tantalum to generate a penta-coordinated intermediate which allows a *tert*-butoxide ligand to bridge between tungsten and tantalum. Subsequent ligand transfer generates a μ-neopentylidiene species **13**, which permits carbene ligand transfer to tungsten. When the starting tantalum complexes have the coordinating phosphine, ligand replacement continues until all the *tert*-butoxide ligands are transferred from tungsten to tantalum exchanging neopentylidene and *tert*-phosphine ligands. In the absence of *tert*-phosphines the reaction stopped after the transfer of the second *tert*-butoxide, yielding [Ta(OCMe$_3$)$_2$Cl$_3$] and [W(O)(CHCMe$_3$)(OCMe$_3$)$_2$] as shown in Scheme 3.



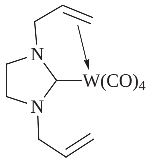
Scheme 3 A possible mechanism for neopentylidene ligand transfer.

For the last few years, research concerning diaminocarbene ligands has received much attention.[26] This type of carbene is a strong σ-donor towards various metal ions and is found to be readily transferred between metal centres.[14–16] In addition, it is observed that the ligands surrounding the metal and *N*-substitution in complexes **15–20** affect the carbene transfer dramatically in both the reaction rate and structural change.[15]

As shown in Scheme 4, complex **15a** reacts with [PdCl$_2$(PhCN)$_2$] to yield a chloro-bridged dipalladium carbene complex **21a**, whereas complexes **15b–d** give the biscarbene palladium species **21b–d** in high yields. ^{13}C NMR clearly indicates the formation of Pd–carbene compounds, shifts of carbene carbon appeared around 198–199 ppm, which are shifted upfield compared to the analogous Group 6 metal complexes (in the range 207–209 ppm). The *trans*-biscarbene palladium complexes then isomerize to the thermodynamically more stable *cis*-form.



15a M = W, M = W, R = Et
15b M = W, M = W, R = Allyl
15c M = W, M = W, R = Benzyl
15d M = W, M = W, R = Pent-4-enyl
16a M = Mo, M = Mo, R = Et
16b M = Mo, M = Mo, R = Allyl
17a M = Cr, M = Cr, R = Et
17b M = Cr, M = Cr, R = Allyl
17c M = Cr, M = Cr, R = Benzyl



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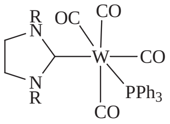
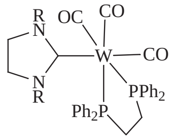
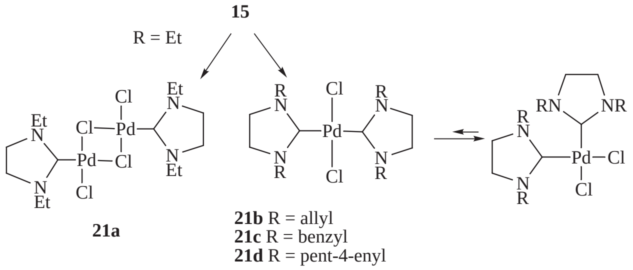


19a R = Et
19b R = benzyl

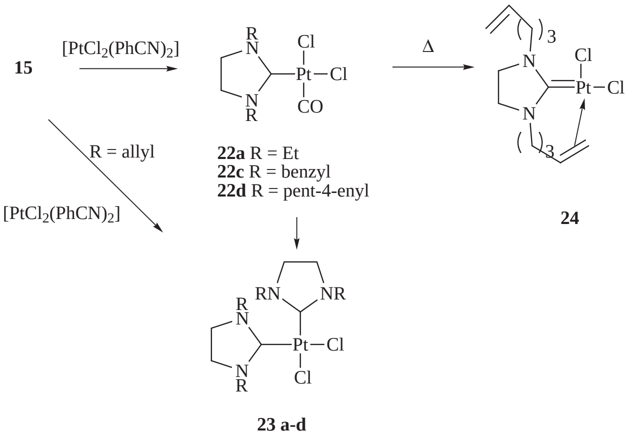


20a R = Et
20b R = benzyl



Scheme 4 Formation of palladium carbene complexes *via* the reaction of **15a–d** with [PdCl$_2$(PhCN)$_2$].

Unlike palladium complexes, both carbene and carbonyl ligands are transferred from tungsten to platinum in several cases (Scheme 5). Reactions of **15a**, **15c** and **15d** with [PtCl$_2$(PhCN)$_2$] in dichloromethane solution result in the formation of **22a**, **22c** and **22d** respectively. The infrared carbonyl absorptions around 2100–2110 cm^{-1} are essentially identical with those reported in *cis*-[PtCl$_2$(CO)(R$_3$P)].[27] Such spectral data imply the donating properties of diaminocarbene are similar to that of trialkylphosphines. Treatment of these carbonyl–carbene complexes **22a**, **22c** and **22d** with Me$_3$NO provides the corresponding biscarbene complexes **23a**, **23c** and **23d**, respectively. Apparently, the formation of biscarbene complexes proceeds *via* a ligand re-distribution reaction, *i.e.*, carbene transfer takes place between platinum metals to provide the thermodynamically more stable biscarbene complexes. The



Scheme 5 Preparation and reactions of platinum carbonyl–carbene complexes.

N-allyl substituted biscarbene complex **23b** was obtained directly from the reaction of **15b** with $[PtCl_2(PhCN)_2]$ in refluxing chloroform solution. It is evident that the π-bond (η^2-bond) *via* the *N*-allyl substituent assists the carbene transfer, but inhibits the transfer of the carbonyl ligand. However, the chain length of the *N*-substituent influences the nature of the reaction. Complex **15d** undergoes both carbonyl and carbene transfer to form **22d** followed by thermally induced intramolecular substitution to yield an alkene substituted complex **24**. The chemical shifts of the carbene carbon (166–174 ppm) for mono and biscarbene platinum complexes appear to be much more upfield than the corresponding palladium–carbene complexes, which is a trend in these metal carbene complexes. The ^{13}C chemical shifts of the carbene carbon have become a convenient tool to investigate these metal carbene species.

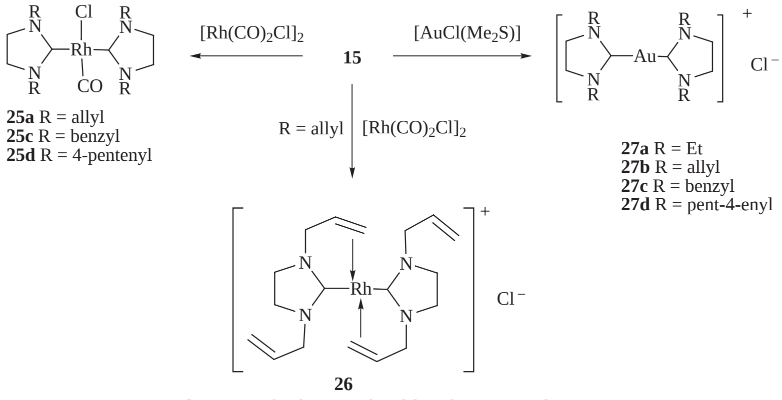
Similar to Pt(II) and Pd(II) complexes, carbene ligand transfer reactions are also observed with rhodium(I) and gold(I) metal ions. Reactions of **15a**, **15c**, **15d** with $[RhCl(CO)_2]_2$ gave biscarbene rhodium complexes **25a**, **25c** and **25d** respectively (Scheme 6). In the case of the *N*-allyl substituted carbene **15b**, the π-coordinated product **26** was obtained directly under the same conditions. The ^{13}C NMR chemical shifts for the carbene carbon appeared around 200–215 ppm with a rhodium–carbon coupling $J_{\text{Rh-C}} \sim 35$ Hz. As for the gold biscarbene complexes **27a**–**d**, which are similar to those prepared by the ligand substitution reactions of LAuCl (L = PPh_3, Me_2S) with *C*-imidazolyllithium,[28] was formed by the reaction of **15a**–**15d** with $[AuCl(Me_2S)]$ in dichloromethane at room temperature. ^{13}C NMR resonances for the carbene carbon appear in the range 203–205 ppm which is comparable to other related gold carbene complexes.

Further studies verify the diaminocarbene transfer from tungsten to copper and silver complexes. Reactions of **15** with $[Cu(MeCN)_4][BF_4]$ or $[AgBF_4]$ in dichloromethane or chloroform yield the corresponding copper(I) and silver(I) complexes (**28** and **29**). However, the resulting complexes are sensitive to oxygen and moisture and readily decompose to yield the *N*,*N*-dialkylimidazolidin-2-ylidinium salts, *i.e.*, cleavage of the metal–carbene bond followed by protonation. Nevertheless, these copper and silver carbene complexes generated *in situ* in $CDCl_3$ have been characterized by ^1H NMR, ^{13}C NMR and mass spectroscopy under anhydrous conditions. ^{13}C NMR shows signals around 197–199 ppm for the corresponding Cu–C(carbene) carbon and 202–204 ppm for the Ag–C(carbene) with the isotope coupling values ranging from 168–170 Hz for ^{107}Ag–C and 192–196 Hz for ^{109}Ag–C.

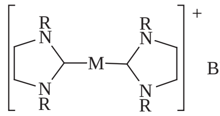
In fact, reactions of Group 6 diaminocarbene complexes with $[Cu(MeCN)_4][BF_4]$ or $[AgBF_4]$ in the presence of water provide the corresponding imidazolidin-2-ylidinium salt directly. Scheme 7 shows the possible reaction pathway for the cleavage of the metal–carbene bond from the tungsten carbene complexes **15**. The diaminocarbene ligand is initially transferred to the copper or silver metal and then dissociates and behaves as a strong base, which is protonated to yield the iminium salt. It has been demonstrated by theoretical calculations that the simple diaminocarbenes are strong bases, even stronger than the *N*,*N*-disubstituted imidazolylidenes (an aromatic heterocyclic carbene).[29] Formation of C2 deuterated product in acetonitrile-d_3 or a mixture of THF and D_2O indicates that the proton comes from the solvents. Furthermore, this cleavage reaction is accelerated under acidic conditions. Reaction of **15a** with Cu(I) is complete within a few minutes in 10% HBF_4 solution. Even a catalytic amount of copper ions (10% mol) can accomplish the same reaction in acid media. Such a cleavage process is also observed in the reactions of the biscarbene palladium and platinum complexes **21** and **23** with $[AgBF_4]$ or $[Cu(MeCN)_4][BF_4]$ in the presence of water. These results show the possibility of diaminocarbene transfer among the late transition metal ions.

The metal ions, molybdenum- and chromium-diaminocarbene complexes (**19** and **20**) follow the same general trend as tungsten. In terms of substituent effect, the π-bond functionality on the nitrogen atom accelerates the carbene transfer and influences the structure of the products as shown in Schemes 4–6. In the case of palladium, the rate of formation of the biscarbenes **21b**–**d** is faster than that of the chloro-bridged carbene complex **21a**. Ligands on the Group 6 carbene complexes also influence the nature of carbene transfer. The π-coordinated tungsten carbene complex **18** does not undergo carbene transfer with Pd and Pt, whereas the triphenylphosphine substituted tungsten carbenes **19a**–**b** readily undergo carbene transfer with $[PtCl_2(PhCN)_2]$ and result in the formation of platinum carbene phosphine complex [eqn. (3)]. Bisphosphine ligand transfer was observed upon the reaction of **20a**–**b** with $[MCl_2(PhCN)_2]$ (M = Pd or Pt) as shown in eqn. (4). Here, the carbene moiety is believed to transfer to the platinum initially, however in the presence of a bidentate phosphine ligand carbene–metal bond cleavage occurs. These reactions suggest that diaminocarbenes are as good σ-donors as phosphines. Such phosphine ligand transfer from tungsten to palladium was also observed in the tungsten–neopentylidine complexes. Reaction of $[W(O)(=CHMe_3)Cl_2(PMe_3)_2]$ with 0.5 or 1 equiv. of $[PdCl_2(PhCN)_2]$ generates $[PdCl_2(PhCN)(PMe_3)]$ and $[PdCl_2(PMe_3)_2]$ demonstrating phosphine transfer from W to Pd. However, no carbene transfer was observed in the latter example.[13]

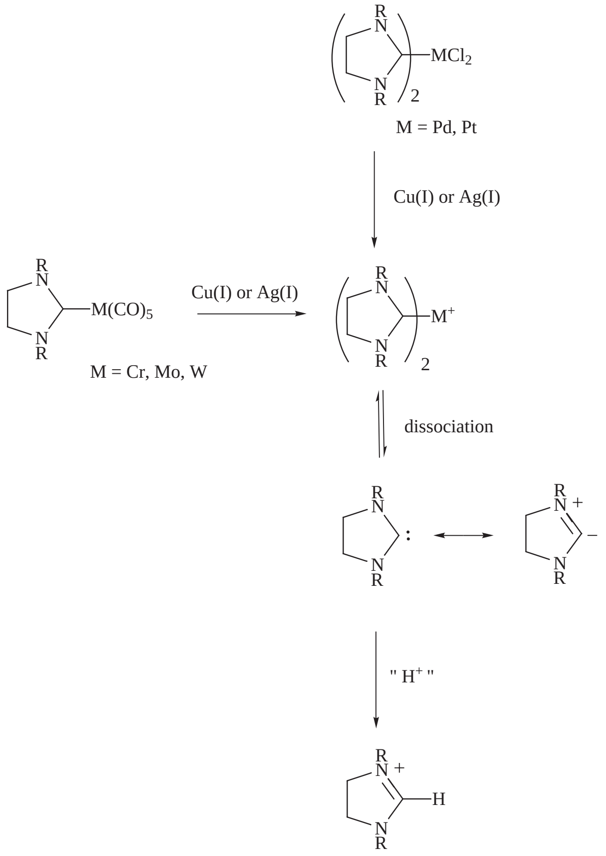
Ligands around the metal centre are also important for the carbene transfer reactions. It is found that $[PdCl_2(CH_3CN)_2]$, $[PdCl_2(Ph_3P)_2]$, $[PdCl_2(COD)]$ or $[PdCl(Me)(COD)]$ do not react with the tungsten diaminocarbene complexes **15.** On the other hand chromium and tungsten complexes of 1,3-thiazolin-2-ylidene (**30**) are found to undergo carbene transfer upon treating with $[PdCl_2(COD)]$ to give the *trans*-biscarbene palladium complexes **31** [eqn. (5)],[17] which indicates that the coordinating ability of heteroatom-substituted carbene complexes affects the reactions.



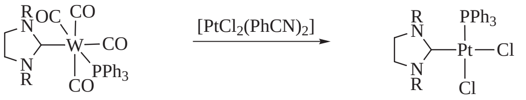
Scheme 6 Rhodium and gold carbene complexes.



28a M = Cu, R = ethyl
28b M = Cu, R = allyl
28c M = Cu, R = benzyl
29a M = Ag, R = ethyl
29b M = Ag, R = allyl
29c M = Ag, R = benzyl

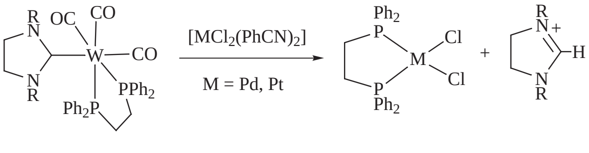


Scheme 7 Reaction pathway of M=C cleavage by Cu(I) and Ag(I).



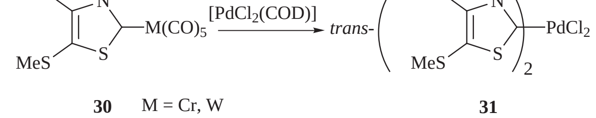
(3)

19a R = Et
19b R = benzyl



(4)

20a R = Et
20b R = benzyl

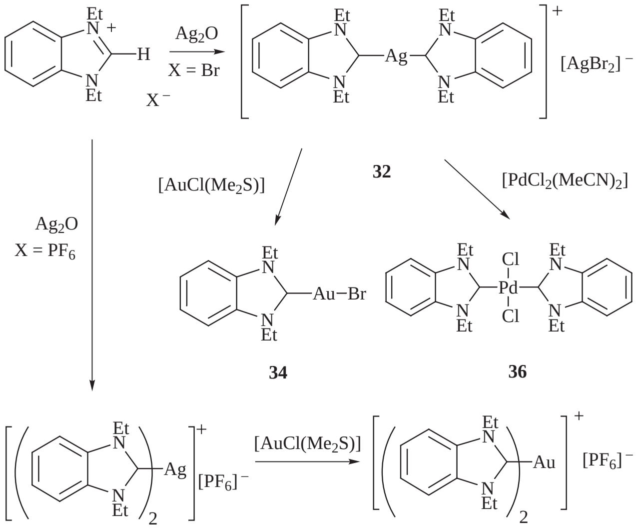


(5)

30 M = Cr, W **31**

All the above examples illustrate the ability of the diaminocarbene ligand to transfer among various metal complexes. Formation of diaminocarbene complexes can be represented as the adduct of a strong Lewis-base carbene and a Lewis-acid organometallic fragment. The diaminocarbene transfer between transition metals in these reactions is likely to be the thermodynamic product. The pathway of such transfer processes may occur through the initial coordination of the nitrogen atom of the carbene moiety to the unsaturated metal centre followed by the carbene shift to form the product. However, the intermediates have not been isolated to verify the mechanism of these diaminocarbene transfer reactions. Qualitative studies by NMR spectroscopy show that the relative rate of the cleavage of the diaminocarbene ligand by the copper(I) ion was found to decrease in the order **15a** > **21** ~ **22a** > **23a**. This may be due to the steric bulk of the phosphine which hinders the access of copper to the carbene ligand, indicating the possibility of weakening the coordination of the heteroatom toward copper to assist the transfer.

The diaminocarbene complexes of Pd(II), Pt(II), Rh(I), Au(I), Cu(I) and Ag(I) complexes resulting from transfer from Group 6 metal complexes do not undergo the reverse transfer reaction with [M(CO)$_6$] (M = Cr, Mo, W), *i.e.* no carbene transfer from Pd(II), Pt(II), Rh(I), Au(I), Cu(I) and Ag(I) to W(0) is observed. In contrast to this trend, a carbene transfer from silver to gold and palladium metal ions is reported with 1,3-dimethylbenzimidazol-2-ylidene (Et$_2$-Bimy) ligand, a heterocyclic aromatic carbene.[16] Treatment of silver complexes **32** and **33** with [AuCl(SMe$_2$)] in a 1 : 1 molar ratio results in the formation of the mono and biscarbene gold complexes [AuBr(Et$_2$-Bimy)] (**34**) and [Au(Et$_2$-Bimy)$_2$][PF$_6$] (**35**) respectively (Scheme 8).



Scheme 8 Carbene transfer from silver to gold and palladium complexes.

However, compounds **34** and **35** could not be obtained directly from the carbene precursor and the metal complex under basic phase transfer catalytic conditions. *trans*-[PdCl$_2$(Et$_2$-Bimy)$_2$] (**36**) was also obtained in high yield by the reaction of [PdCl$_2$(MeCN)$_2$] with **32** in 1 : 1 molar ratio in dichloromethane.

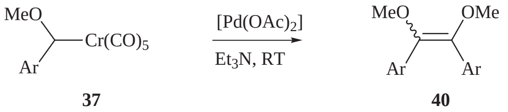
Formation of carbene transfer intermediates is also proposed in certain catalytic reactions. Recently Sierra and co-workers found that palladium acetate catalyzes the carbene ligands of chromium(0) complex to undergo self-dimerization and C–H insertions under mild conditions.[31] In this work, they found that addition of catalytic amounts of [Pd(OAc)$_2$] to a THF solution of chromium carbene complexes **37** and **38** and triethylamine resulted in the formation of the alkene products **40–41** as shown in eqns. (6) and (7). For aminocarbenes **39** the transfer reaction to palladium is accelerated in the presence of acrylate or acrylonitrile and the carbene moiety is then incorporated into these unsaturated substrates to yield the addition product **42** [eqn. (8)]. In all these reactions, the palladium carbene complex **43** *via* the transfer process from tungsten is believed to be the key intermediate for the catalytic cycles. A synthetic approach leading to **44** is achieved by adopting this technique [eqn. (9)].

3 Carbene transfer in di- and poly-nuclear complexes

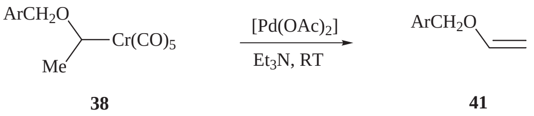
3.1 Carbene transfer resulted in the formation of di- and poly-nuclear complexes

Although numerous di- and poly-nuclear carbene complexes appear in the literature, there are only a few instances where they are synthesized by a carbene transfer reaction from the mononuclear carbene complex. A trinuclear carbene species prepared by such an approach was achieved by Fischer and co-workers in the photochemical reaction of $[MoCp(CO)\{C(OMe)Ph\}(NO)]$ with tetracarbonylnickel(0) in benzene solution, resulting an unstable trinuclear nickel carbene complex $[Ni_3(CO)_3\{\mu\text{-}C(OMe)Ph\}_3]$.[4] It is clear that the cluster is formed *via* a carbene transfer process from the molybdenum to the nickel followed by the construction of metal–metal bonds.

Stone and co-workers discovered various carbene-bridged di- and tri-nuclear complexes which were formed by the reaction of $[M(CO)_5\{C(OMe)Ph\}]$ [M = Cr, or W] with $[Pt(C_2H_4)_2(PR_3)]$ $\{R = PBu^t{}_2Me$ or $P(c\text{-}C_6H_{11})\}$ involving the carbene transfer process.[18] Scheme 9 summarizes the study of these reactions. Reaction of $[Pt(C_2H_4)_2(PR_3)]$ with tungsten carbene **45** provides a triangular WPt_2 cluster **50** as the exclusive product, whereas the chromium carbene **46** produces a $CrPt_2$-trinuclear complex (**51**) and a mixture of platinum di- and tri-nuclear species (**52** and **53**) under similar conditions. Rationalization of the formation of these metal–metal bonded species is shown in Scheme 9 and the bridging carbene species **47** generated *via* the coordination of the carbene to '$Pt(C_2H_4)(PR_3)$' ought to be the key intermediate. Such species undergo either dissocation of



(6)



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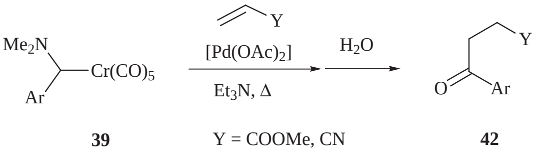

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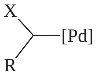

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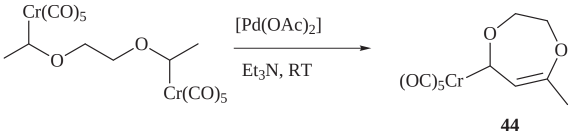

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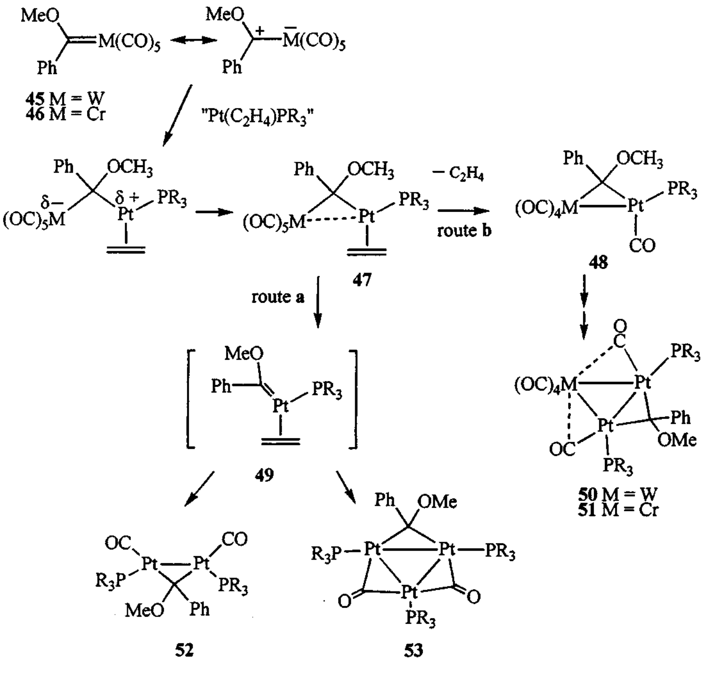
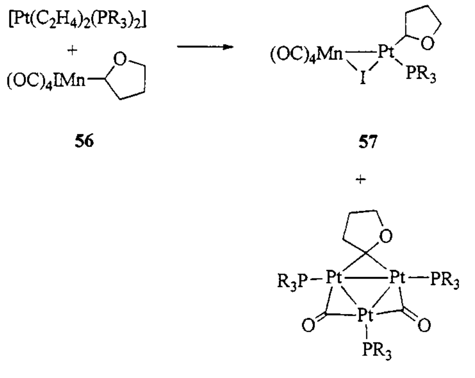


Scheme 9 Formation of carbene-bridged clusters.

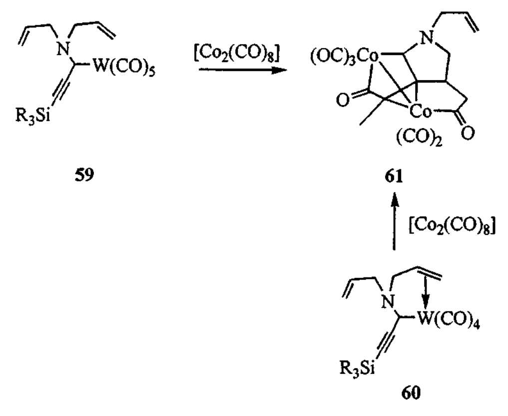
'M(CO)$_5$ fragment' to yield **49** (a carbene transfer product, route **a** in Scheme 9) which leads to the formation of homonuclear platinum carbene complexes, or the rearrangement of the ligand to construct the heteronuclear species **48** (route **b**) which reacts with '$Pt(C_2H_4)(PR_3)$' to yield **50.** From the product distribution, it appears that the ease of carbene transfer depends on the metal, *i.e.* the chronium carbene is able to proceed through route **a**, but not the tungsten carbene.

Reaction of $[Mn(Cp)(CO)_2\{C(OMe)Ph\}]$ with $[Pt(C_2H_4)_2(PR_3)]$ produces a mixture of homonuclear platinum carbene complexes $[Pt_3\{\mu\text{-}C(OMe)Ph\}_3(PMe_3)_3]$ (**54**) and $[Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}CO)(PR_3)_3]$ (**55**), without the formation of any compound containing bridging carbene across Pt–Mn bonds, indicating that the transfer of a carbene group from the manganese complex to platinum is easier than those from chromium and tungsten. On the other hand, the reaction of the 2-oxacyclopentylidene–manganese complex **56** with $[Pt(C_2H_4)_2(PR_3)]$ (R_3 = $Bu^t{}_2Me$) affords a mixture of $[MnPt(C_4H_6O)(CO)_4(PR_3)I]$ (**57**) and $[\{Pt(\mu\text{-}CO)(PPR_3)\}_3]$ (**58**). The carbene moiety in **57** is exclusively bonded to the platinum centre [eqn. (10)],[19] which illustrates the expected stronger interaction of the Pt–C bond than the Mn–C.



56 **57** **58** (10)

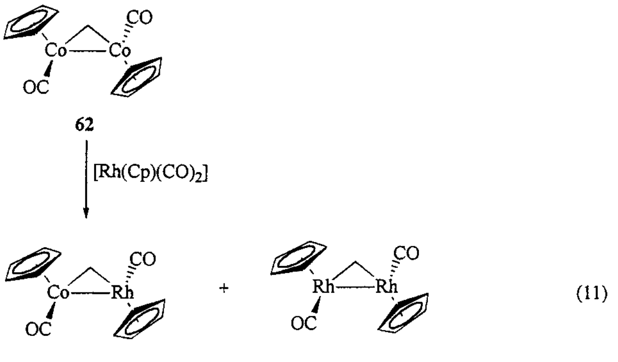
The recent work on the Pauson–Khand type of reaction with the substrate of trimethylsilylalkynyl tungsten carbene **59** reported by Moreto and co-workers was the only example involving carbene transfer reaction.[20] Treatment of tungsten complex **59** or the π-coordinated form **60** with $Co_2(CO)_8$ provides a carbene transfer product **61** (Scheme 10). Structurally, it shows that the carbene group shifts from tungsten to cobalt leading to the dicobalt complex **61**. Unlike the chemistry of diaminocarbene transfer between tungsten and platinum, the π-coordination at the tungsten metal centre has no effect on the transfer.



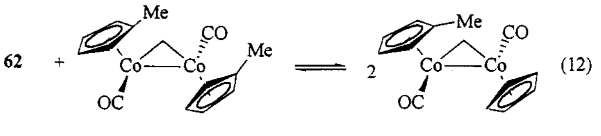
59 **61** **60**

Scheme 10 Carbene transfer in the Pauson–Khand reaction.

In addition to the carbene transfer between mononuclear complexes as discussed in the previous section, bridging carbenes are also able to undergo a similar reaction in binuclear systems. Bergman and Theopold discovered that a μ-CH_2 unit of the dicobalt complex **62** is transferred to form a new bridging dinuclear carbene complex in the reaction of **62** with $[Rh(Cp)(CO)_2]$ [eqn. (11)].[21] It is also found that an equimolar mixture of **62** and its MeCp analogue **65** in benzene at 63 °C produces a statistical ratio of **62, 65** and the mixed dimer **66** [eqn. (12)], indicating the equilibration between these species.



62 **63** **64** (11)



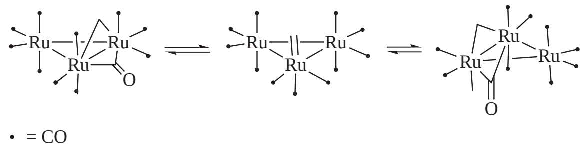
65 **66** (12)

This observation suggests a reversible transfer of the carbene ligand between complexes.

3.2 Carbene migration in di- and poly-nuclear complexes

Migration of the carbene ligand in di- and poly-nuclear complexes is a common process in carbene transfer reactions as well as in metal induced catalytic processes, and indeed the direct observation of carbene migration is reported in some examples.

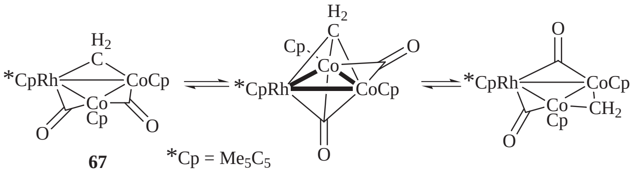
Interconversion of bridge-to-terminal carbene is an example of where the carbene is found to be in a dynamic state. Typical examples of this kind of isomerization appear in the complexes of $[Ru_2Cp(\mu\text{-}CO)(\mu\text{-}CMe_2)]$,[32] $[Co_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}dppm)]$[33] and $[CoRh(Cp)_2(CO)_2(\mu\text{-}CH_2)]$.[21] As for the cluster, Shapley and Holmgren reported that the fluxional behavior of $[Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)]$ can be attributed to the migration of bridging carbene and carbonyl ligands.[34] Scheme 11 illustrates the mechanism which involves the conversion of bridge-to-terminal carbene species.



Scheme 11 Carbene shift in tri-ruthenium cluster.

Another route involving carbene "migration" in the cluster was illustrated by Barnes and co-workers in the complex of

$[RhCp^*(CpCo)_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)]$ (**67**).[35] The crystal structure of **67** exhibits a triangular arrangement of the metal atoms with carbene ligand bridging the Rh–Co edge and the two carbonyl ligands bridging the remaining Rh–Co and Co–Co edges. Spectroscopic data of a CD_2Cl_2 solution of **67** at room temperature are consistent with this structure. However, upon standing overnight complex **67** isomerized to a new species with the carbene ligand bridging to the Co–Co edge. They observed additional signals from the other isomer in which the carbene is capped to the three metal units, which might be the intermediate for the carbene transfer (Scheme 12). All these experimental observations clearly indicate the labile nature and various bonding modes of the carbene ligands and these species are believed to be the intermediates for many catalytic processes.



Scheme 12 Migration of carbene moiety in metal cluster.

4 Summary

In this article examples of carbene or alkylidene ligand transfer between transition metals in an inter- or intramolecular fashion have been considered. These investigations illustrate the plausibility of such transfer between various transition metals. Some of these reactions proceed efficiently to generate the new carbene species, which is not easily achieved by a traditional approach. As mentioned, the carbene transfer might be an important catalytic process and more effort in mechanistic understanding could help to design better catalysts for relevant synthetic applications. Indeed, Sierra and co-workers demonstrated that palladium catalyzes the transformation of chromium(0) carbenes into useful organic products.

It is also appears that the driving force directing such transfers is not fully understood. Nevertheless, the resulting carbene transfer product ought to be the thermodynamically favored one. Indeed, a crystallographic study on the related species $[WPt(CO)_5(\mu\text{-}C(OMe)Ph)(PMe_3)_2]$, clearly shows that the bond distance of Pt–C [2.04(1) Å] is shorter than that of W–C [2.48(1) Å], *i.e.* the stronger bond of Pt–C, reflecting the tendency of the carbene ligand transferring from tungsten to platinum.[30] Of course, more experimental and theoretical studies may provide greater insight into these carbene transfer reactions.

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