

# Catalytic Transmetalation from Group 6 Fischer Carbene Complexes: An Emerging Powerful Tool in Organic Synthesis

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Received July 23, 2004

## ABSTRACT

The chemistry of metal carbene complexes has experienced an enormous development in the past decades. Despite this fact, the use of transition metals as catalysts in reactions involving group 6 Fischer carbene complexes was virtually neglected. Here, we describe how the reactivity of these compounds can be enhanced or modified in the presence of catalytic amounts of a transition metal, leading to new forms of reactivity and others offering clear advantages in terms of efficiency over the uncatalyzed reactions. The key step for these reactions is the transmetalation from the stoichiometric metal carbene reagent to the catalyst. This process generates a new metal–carbene complex that leads to enhanced reactivity of new reaction modes. Two examples of Fischer carbene complexes obtained by transmetalation to Pd and Cu have been isolated during the last 2 years, showing the flexibility if the mechanistic hypothesis for these reactions. The work presented in this Account shows how an area, which was practically unexplored 5 years ago, has emerged as a new and powerful field of research.

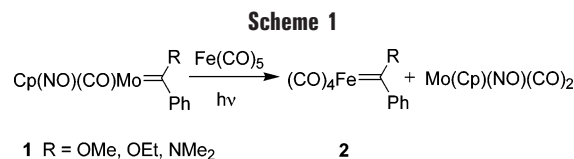
## Introduction

Since the discovery of stable transition-metal carbene complexes by Fischer and Maasböl,<sup>1</sup> these compounds have proven to be extremely valuable tools in organic synthesis.<sup>2</sup> The use of metal carbenes in metal-mediated reactions is relatively frequent, but despite the fact that transmetalation is one of the most important processes in organometallic chemistry,<sup>3</sup> the simple transfer of a carbene ligand from one metal to another metal center is still rare.<sup>4</sup> At the beginning of our work, the transition-

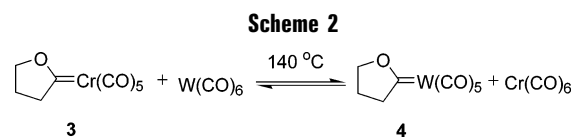
metal-catalyzed carbene transfer from a group 6 Fischer carbene complex was unknown.<sup>4</sup> Moreover, processes involving metal–metal–carbene transfer processes were scarce at that time. However, in the last 4 years, the study of catalytic processes involving carbene transfer reactions in transition-metal complexes has emerged as a new field of investigation that has opened new forms of reactivity for this type of compound. The possibility of carrying out new synthetically valuable transformations with metal–carbene complexes under very mild conditions, with high stereochemical control, makes metal-catalyzed carbene transfer reactions an emerging and very attractive research field. In this Account, we present an overview of these studies as well as an outlook on their perspectives in the near future.

## Background

The first example of a stoichiometric carbene ligand transfer between metal ions was reported by Fischer and co-workers<sup>5</sup> in the reaction of molybdenum carbene complexes **1** with photochemically generated Fe(CO)<sub>5</sub> to produce iron carbene complexes **2** in acceptable yields (Scheme 1).



The thermal equilibrium between chromium alkoxy-carbene complex **3** and W(CO)<sub>6</sub> to form tungsten alkoxy-carbene complex **4** and Cr(CO)<sub>6</sub> was also reported (Scheme 2).<sup>6</sup> Additionally, gold(I) carbenes of the type AuCl[C(R)Ph] were prepared by reaction of the corresponding tungsten carbene complexes W(CO)<sub>5</sub>[C(R)Ph] with HAuCl<sub>4</sub>.<sup>7</sup> Although initially the possible involvement of free carbenes as intermediates was considered, further studies clearly pointed to a carbene transfer reaction between the two metal centers as the key to explain the mechanism of the transmetalation process.<sup>6,8</sup>



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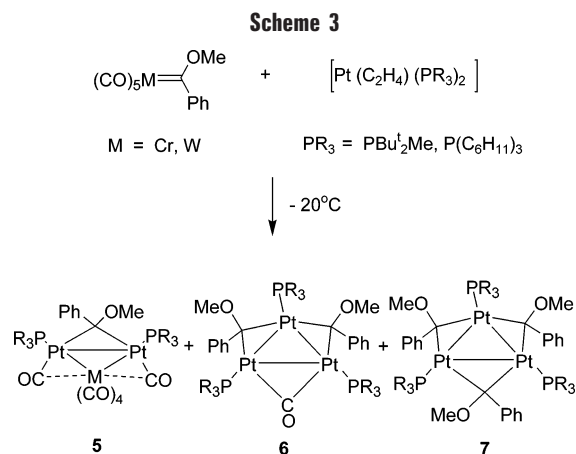
Mar Gómez-Gallego studied chemistry at the Universidad Complutense de Madrid (UCM) where she obtained her Ph.D. in 1987. She continued her scientific education with a Fleming Postdoctoral Fellowship with Prof. W. M. Horspool, and she returned to Madrid where she was appointed Prof. Ayudante in 1990 and then Prof. Titular in 1992. Her current research interests are focused on the development of new processes based on transition-metal complexes as well as in the development of new iron-chelating agents and the study of their environmental impact.

María José Mancheño studied Chemistry at the Universidad Complutense de Madrid (UCM) where she graduated in 1988 and obtained her Ph.D. in 1993. Then, she did a postdoctoral stay at the University of Maryland with Prof. P. Mariano. In 1992, she was appointed Prof. Ayudante at UCM, Prof. Asociado in 1997, and promoted to Profesor Contratado Doctor in 2003 at the same university. Her current research interests are focused in organic synthesis, organometallic chemistry, photochemistry, as well as environmental chemistry.

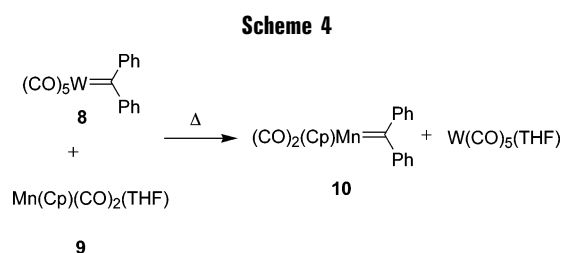
Miguel A. Sierra studied chemistry at UCM (Madrid) and received his Ph.D. in 1987, after which he was appointed to Assistant Professor. After a postdoctoral stay at Colorado State University (Prof. Louis Hegedus), he returned to Madrid where he was promoted to Professor in 1990. His research encompasses the development of new processes based on transition-metal complexes, the preparation of new bioorganometallic compounds tailor-made for specific applications in crop protection, and the study of environmental organic processes. He is the secretary of the Madrid regional division of the Spanish Chemical Society and member of the Scientific Advisory Board of the Organization for the Prohibition of Chemical Weapons (OPCW).

Stoichiometric transmetalation from ylide complexes has received a lot of attention in the last years.<sup>9</sup> *N*-heterocyclic carbenes are strong  $\sigma$  donors toward various metal ions and can be easily transferred between metal centers.<sup>10</sup>

Sometimes, the carbene transfer reaction from a mononuclear carbene complex results in the formation of di- and polynuclear carbene species. This is the case with the unstable trinuclear nickel carbene complexes obtained by Fischer<sup>5</sup> or the di- and trinuclear Pt clusters 5–7 reported by Stone (Scheme 3).<sup>11</sup>



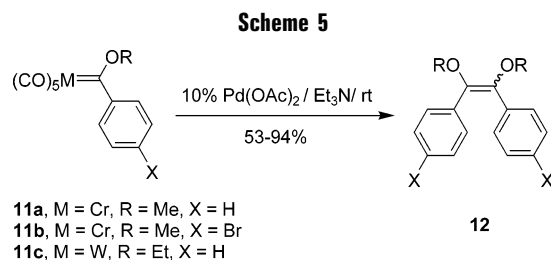
Finally, examples of carbene transfer in complexes in which the carbene complex is not stabilized by the presence of a heteroatom attached to the carbene ligand are less frequent. Thermolysis of **8** in the presence of Mn complex **9** results in the formation of **10**, which shows diphenylcarbene transfer from tungsten to manganese (Scheme 4).<sup>12</sup> Alkylidene transfer from tantalum to tungsten has also been reported.<sup>13</sup>



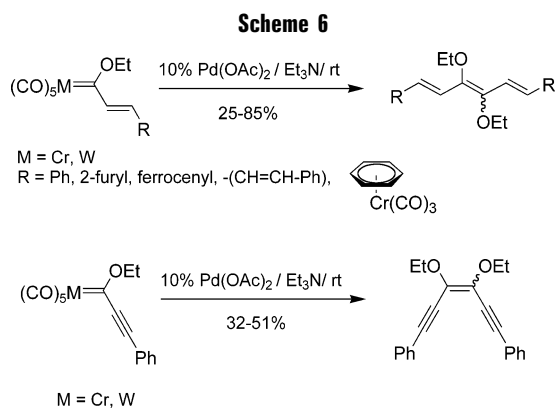
## Pd-Catalyzed Carbene Transfer Reactions

**Self-Dimerization Reactions of the Carbene Ligand.** Our first studies to determine the viability of metal-catalyzed carbene transfer from group-6-stabilized metal–carbene complexes were carried out by reacting pentacarbonyl[(aryl)(methoxy)carbene]chromium(0) complex **11a** and catalytic amounts of  $\text{Rh}_2(\text{OAc})_4$  at different temperatures. Although we observed that carbene ligand self-dimerization of the complex occurred around 100 °C, the procedure was not advantageous over the uncatalyzed process that occurs at temperatures above 130 °C.<sup>14</sup> After a broad study, we found Pd catalysts as the choice reagents. Reaction of carbene complex **11a** with 10 mol %  $\text{Pd}(\text{OAc})_2$  in the presence of  $\text{Et}_3\text{N}$ , using THF as the solvent and at room temperature (rt), led to 1,2-dimethoxydiphenylethene

**12a** as a 2:1 *E/Z* mixture. Complexes **11b** and **11c** also formed the corresponding dimers under the same reaction conditions (Scheme 5).<sup>15</sup>



These initial results demonstrated that the transfer of the carbene ligand was possible under catalytic conditions. In fact, as indicated in Scheme 6, different polyenes were obtained in fair to good yields from conjugated carbene complexes and  $\text{Pd}(\text{OAc})_2/\text{Et}_3\text{N}$ . The dimerization proved to be fully compatible with the presence of additional metallic centers in the starting material. Unsaturated tungsten–carbene complexes were also reactive, and no significant differences were found with respect to their chromium counterparts. The method was also applicable to the synthesis of higher conjugated polyenes and enediyne.<sup>16</sup>

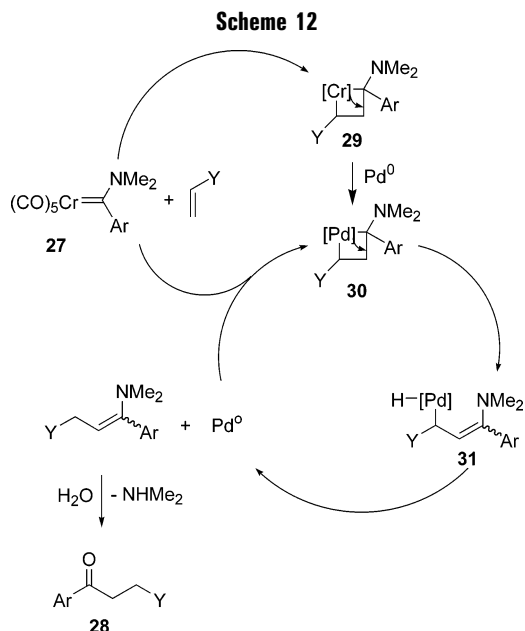


Lower loads of catalyst (2 mol %  $\text{Pd}(\text{OAc})_2/\text{Et}_3\text{N}$ ) resulted in longer reaction times and in an increase of the *E* selectivity of the dimers. The use of additives such as  $\text{PPh}_3$ ,  $\text{AsPh}_3$ , or  $\text{SbPh}_3$ , change of the solvent (THF, hexane, benzene,  $\text{Et}_2\text{O}$ , MeCN, or  $\text{CH}_2\text{Cl}_2$ ), or decreasing the temperature from rt to 0 °C had little effect either in the nature of the products or in the ratio of the isomers. Other  $\text{Pd}^{\text{II}}$  or  $\text{Pd}^0$  catalysts ( $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ ,  $\text{PdCl}_2(\text{MeCN})_2$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{PPh}_3)_4$ , and Pd on charcoal) were equally efficient in promoting the carbene ligand dimerization.<sup>16</sup>

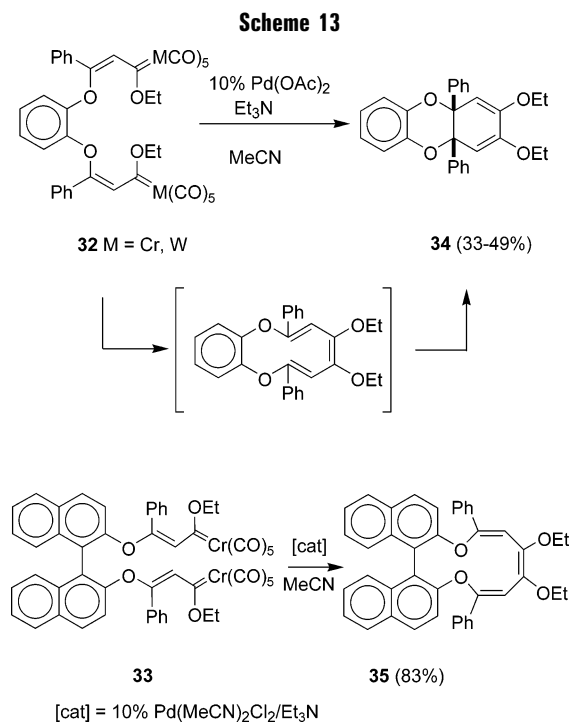
The nature of the reaction products strongly depends on the catalyst when the substituents on the carbene carbon are methyl groups. Thus, alkyl carbene complex **13** gave exclusively vinyl ether **14** in the presence of  $\text{Pd}(\text{OAc})_2/\text{NEt}_3$ , whereas other Pd catalysts ( $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ ,  $\text{PdCl}_2(\text{MeCN})_2$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{PPh}_3)_4$ , and Pd on charcoal) gave only the expected carbene ligand dimerization product **15** (Scheme 7).



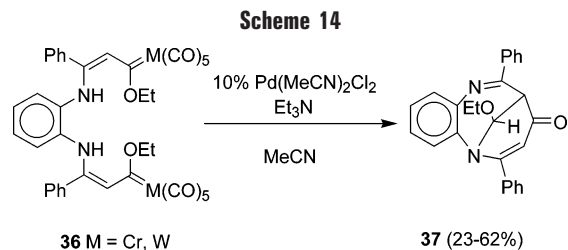
cyclobutane **29**.<sup>19</sup> Transmetalation to Pd from **29** could give intermediate **30**, which by transfer of a  $\beta$  hydrogen to the metal center and reductive elimination produces enamine **31**, precursor by hydrolysis of the  $\beta$  ketoderivatives **28** (Scheme 12).



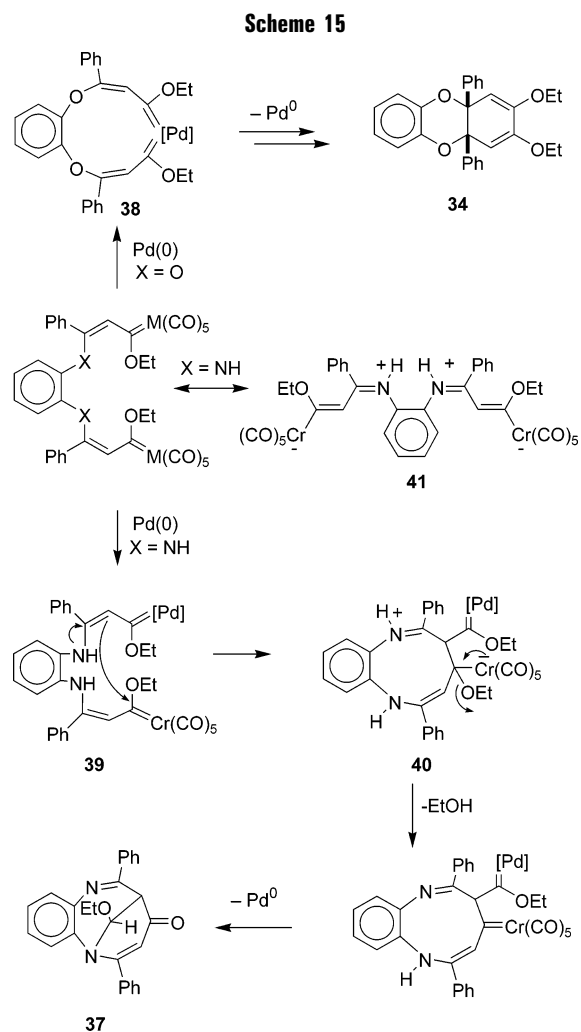
**Tandem Reactions.**<sup>20</sup> Catechol-derived biscarbene **32** react with 10 mol %  $\text{Pd}(\text{OAc})_2$  at rt to yield compound **34** arising from a cascade of reactions involving ligand dimerization followed by electrocyclic ring closure (Scheme 13). The dimerization product was also obtained by treatment of 1,1'-dihydroxybinaphthyl biscarbene complex **33** and  $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ . In this case, the hexatriene **35** is highly strained, and hence the electrocyclization stops at this stage.



The outcome of the reaction was different when complexes **36**, derived from *o*-diaminobenzene, were treated with  $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ . In this case, neither dimerization nor cyclization was observed, and tricycle **37** was obtained as the sole reaction product (Scheme 14).<sup>20</sup>

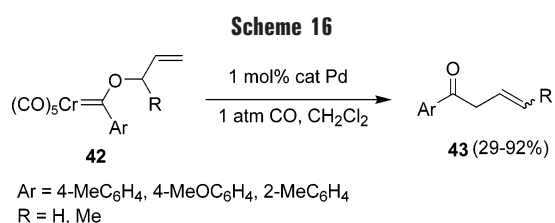


Differences in reactivity were explained depending on the heteroatom attached to the metalatetraene moiety in the starting complex (Scheme 15). When  $\text{X} = \text{O}$ , the reaction follows an intramolecular cyclization pathway through a mononuclear Pd–biscarbene complex such as **38**, but when  $\text{X} = \text{N}$ , the first transmetalation would form heterobimetallic intermediate **39**. Intramolecular attack of the nucleophilic enamine carbon<sup>21</sup> to the remaining chromium carbene carbon would yield intermediate **40** from which the final tricyclic product is formed. Now, the transmetalation from Cr to Pd not only enhances the

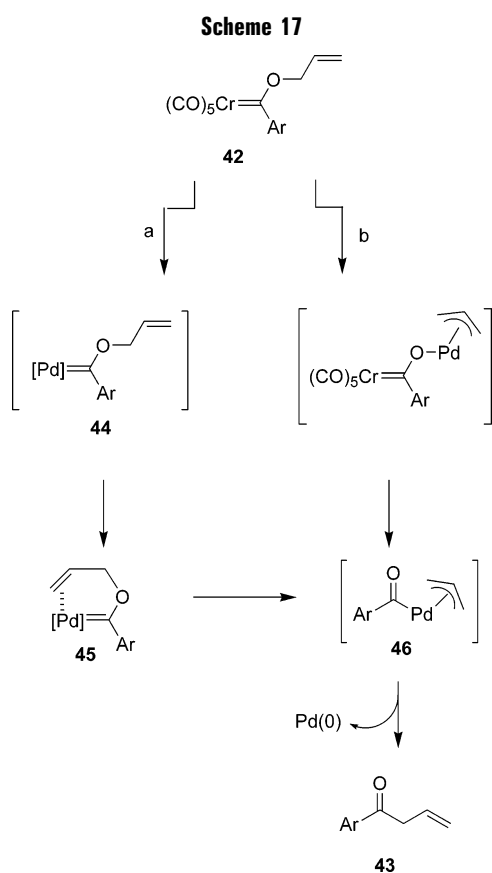


reactivity of group 6 Fischer carbene complexes in dimerization processes but also promotes unknown processes by decreasing the ability of the metal center to accept electrons.<sup>22</sup>

**Other Pd-Catalyzed Carbene Transfer Reactions.** Soon after we described our work, Narasaka and co-workers<sup>23</sup> reported the rearrangement of allyloxy(aryl)chromium carbene complexes **42** to allyl aryl ketones **43** catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub>. The reaction can be considered as a formal [2,3]-sigmatropic rearrangement of the Fischer carbene complex (Scheme 16).

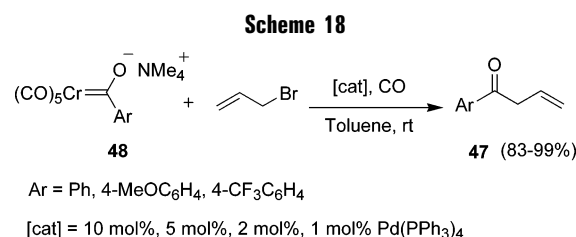


Two different reaction pathways were proposed to explain the outcome of the reaction (Scheme 17). The first one (path a) proposes the initial transmetalation to the chromium carbene complex to generate a palladium carbene complex **44**. After the formation of the palladium alkene-carbene complex **45**, aroyl  $\pi$ -allyl-palladium complex **46** is produced and is subsequently converted to the product **43** by reductive elimination, regenerating Pd<sup>0</sup> in the process. The other mechanism (path b) suggests that a  $\pi$ -allyl-palladium complex is initially produced to give a bimetallic complex, which in the presence of CO is



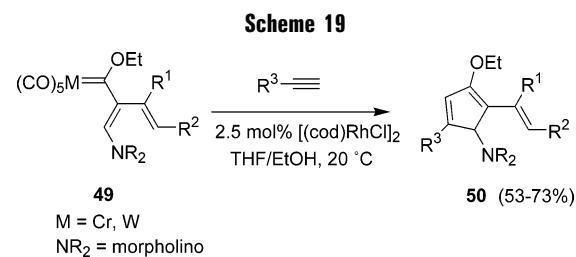
converted to the  $\pi$ -allyl-palladium intermediate **46** precursor of the final product (Scheme 17).

After these results, the same research group has reported different palladium-catalyzed cross-coupling reactions of acylchromate complexes. For example, ketones **47** are obtained in good yields by the coupling of allylic bromides and tetraalkylammonium acylchromate **48** (Scheme 18).<sup>24</sup> The reactions did not take place in the absence of the Pd catalyst, and they required to be carried out under CO pressure. Although these and related reactions<sup>25</sup> are catalytic in Pd, they have been interpreted through the formation of an acyl  $\pi$ -allyl-palladium complex (as in path b of Scheme 17) and do not involve a Cr-Pd transmetalation step.



## Rh-Catalyzed Transmetalation Reactions

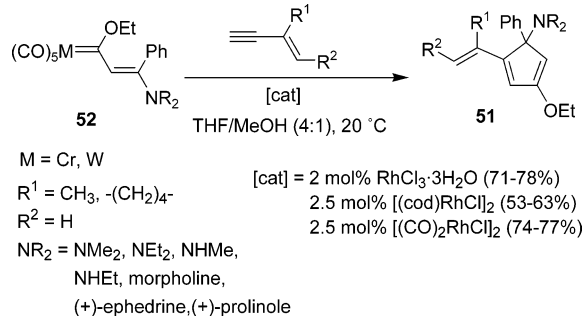
The first example in which a Rh catalyst had been successfully applied to enhance the reactivity of a Fischer carbene complex was reported by Aumann and co-workers in the reaction at rt between cross-conjugated metallahexatrienes **49** and alkynes to form vinylcyclopentadienes **50** catalyzed by [(cod)RhCl]<sub>2</sub> (Scheme 19).<sup>26</sup>



The thermal (noncatalyzed) condensation of alkynes with 4-amino-1-chromo-1,3-butadienes structurally related to **49** was a known process.<sup>27</sup> However, the reaction applies only to chromium but not to tungsten complexes, requires temperatures of 50–80 °C, and is strongly dependent on the substituents and conditions. The success of the rhodium-catalyzed synthesis rests on the fact that it could be made under very mild conditions and works well with both chromium and tungsten complexes.

Other rhodium catalysts have been successfully employed in the reaction. Thus, vinyl cyclopentadienes **51** can be obtained in good yields from conjugated aminocarbene complexes **52** and 1-alken-3-yne in the presence of RhCl<sub>3</sub>·3H<sub>2</sub>O, [(CO)<sub>2</sub>RhCl]<sub>2</sub>, or [(cod)<sub>2</sub>RhCl]<sub>2</sub> (Scheme 20). Among these, [(cod)<sub>2</sub>RhCl]<sub>2</sub> was somewhat less efficient in giving cyclopentadienes **51**, while [(CO)<sub>2</sub>RhCl]<sub>2</sub> proved to be almost as good as RhCl<sub>3</sub>·3H<sub>2</sub>O in THF/MeOH. The exact nature of the catalytically active species is not known. Rh<sup>I</sup> species are good candidates because

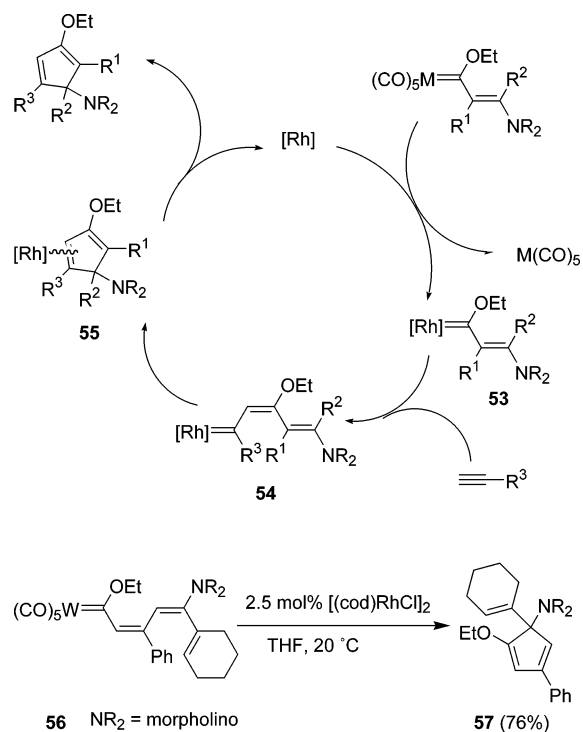
Scheme 20



$[(\text{CO})_2\text{RhCl}]_2$  is active in this reaction and the system  $\text{Rh}^{\text{III}}/\text{MeOH}$  is known to generate  $\text{Rh}^{\text{I}}$  in the presence of suitable ligands.<sup>28</sup>

On the basis of this hypothesis, the possible mechanism for the reaction is represented in Scheme 21. The process would start with a  $\text{Rh}^{\text{I}}\text{--Cr}$  (or tungsten) transmetalation step to give the corresponding rhodium carbene complex **53** from which a 1-rhoda-1,3,5-hexatriene **54** is derived by insertion of the alkyne. From a subsequent  $\pi$  cyclization of compound **54**, a vinyl cyclopentadiene rhodium complex **55** could be formed, and from this compound, the vinyl cyclopentadiene is finally extruded by regeneration of the catalytic active rhodium species.

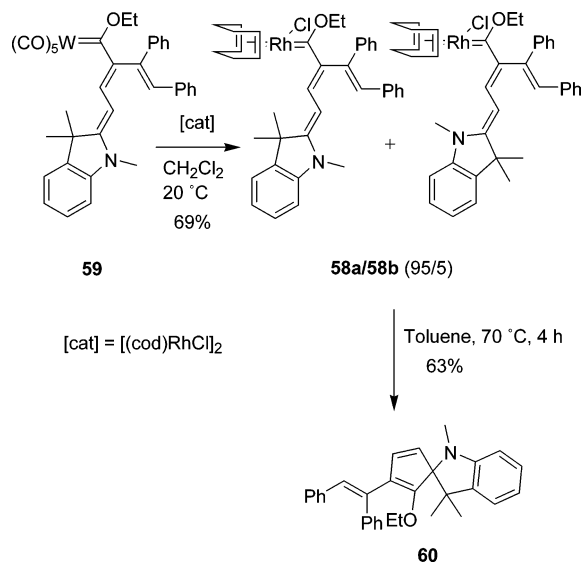
Scheme 21



As the key step of the reaction is assumed to involve the  $\pi$  cyclization of the 1-rhoda-1,3,5-tetraene intermediates, the reaction was extended to 1-tungsta-1,3,5,7-octatetraene **56**. While this compound did not undergo a  $\pi$  cyclization at 65 °C, it could be smoothly transformed into the vinylcyclopentadiene **57** in the presence of 2.5 mol %  $[(\text{cod})_2\text{RhCl}]_2$  at 20 °C.<sup>29</sup>

To provide additional evidence of the intermediacy of  $\text{Rh}$ –carbene complexes in the catalytic reactions, carbene

Scheme 22



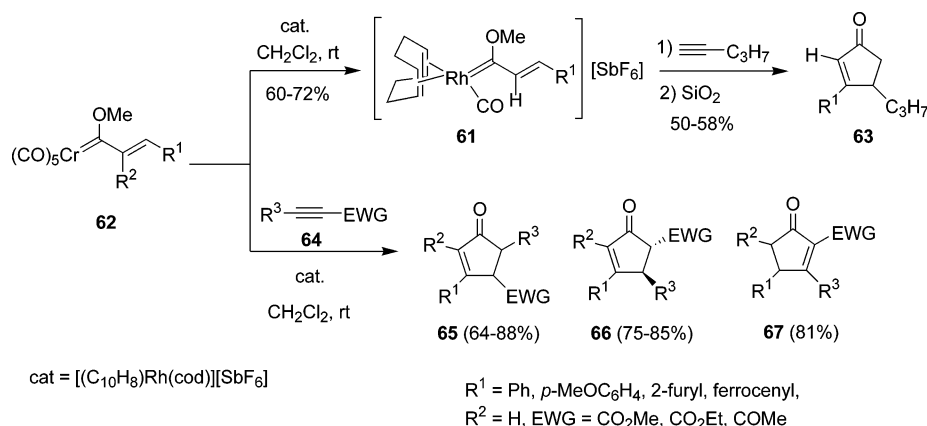
rhodium complex **58a** was obtained as the major isomer by transmetalation of the carbene ligand of the tungsten complex **59** with a stoichiometric amount of  $[(\text{cod})_2\text{RhCl}]_2$  (Scheme 22). The structure of the rhodium carbene complex **58a** was unambiguously established by NMR experiments. This compound was transformed into the vinylcyclopentadiene **60** by heating in toluene at 70 °C. It was shown that rhodaocotetraene **58a** (4 mol %) also catalyzed the smooth transformation of the tungsten compound **59** into the cyclopentadiene **60** within 10 h according to NMR spectra in  $[\text{D}_8]$ toluene at 79 °C.

The chromium–rhodium transmetalation has also been employed by Barluenga's group to obtain cyclopentenones.<sup>30</sup> Thus, carbene complexes of rhodium(I) **61** were easily prepared from chromium methoxycarbene complexes **62**. The simultaneous transfer of two ligands (carbene and CO) observed in this case represents a rare process.<sup>10a,b</sup> Treatment of complexes **61** with 1-pentyne in  $\text{CH}_2\text{Cl}_2$  at room temperature for 16 h resulted in the regioselective formation of cyclopentenones **63** in reasonable yield (Scheme 23).

The reaction of carbene complexes **62** and electrophilic alkynes **64** in the presence of a catalytic amount of  $[(\text{naphthalene})\text{Rh}(\text{cod})][\text{SbF}_6]$  (10 mol %) yields the expected cyclopentenone derivatives with complete selectivity and good yields (Scheme 23). The reaction is a [3+2] cyclization, and the regiochemistry of the products depends on the alkyne nature. Thus, terminal alkynes **64** ( $\text{R}^3 = \text{H}$ ) yield exclusively cyclopentenones **65**, whereas electron-poor internal alkynes **64** ( $\text{R}^3 = \text{Ph}, 1\text{-cyclohexenyl}, \text{Me}$ ) afford cyclopentenones with reversal of regiochemistry (**66** and **67**).

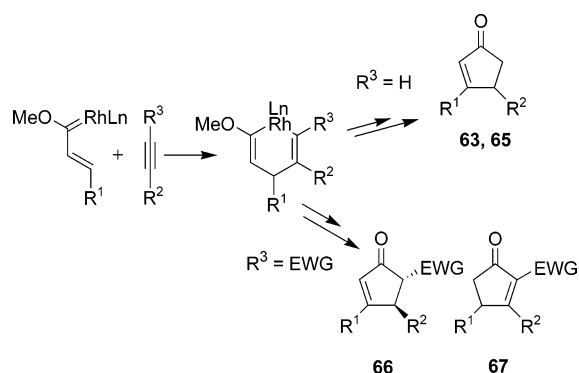
The course of the reaction could be explained by chromium–rhodium initial transmetalation and formation of a rhodium metalladiene followed by a metalla Diels–Alder reaction with the alkyne. The regiochemistry observed in the case of the terminal alkynes would be dictated simply by steric discrimination, with the larger alkyne substituent being placed away from rhodium. In

Scheme 23



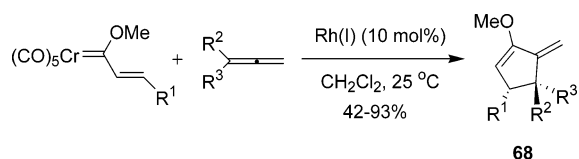
the case of internal electron-poor alkynes, the steric differentiation is not so large and the electronic factors, which favor the interaction between the electrophilic metal center and the nucleophilic C $\alpha$  alkyne, would dominate, leading to cycloadducts with the opposite regiochemistry (Scheme 24).

Scheme 24



A similar mechanism has been considered to explain the reaction between alkenyl chromium carbene complexes and allenes in the presence of 10 mol % [(naphthalene)(cod)Rh][SbF<sub>6</sub>] to give cyclopentene derivatives **68** in good yields (Scheme 25).<sup>31</sup> The reaction resulted to be completely chemo-, regio-, and stereoselective. Only the more substituted C=C bond of the allene is involved in the reaction, and monosubstituted allenes afforded exclusively the *trans*-cyclopentene derivatives.

Scheme 25



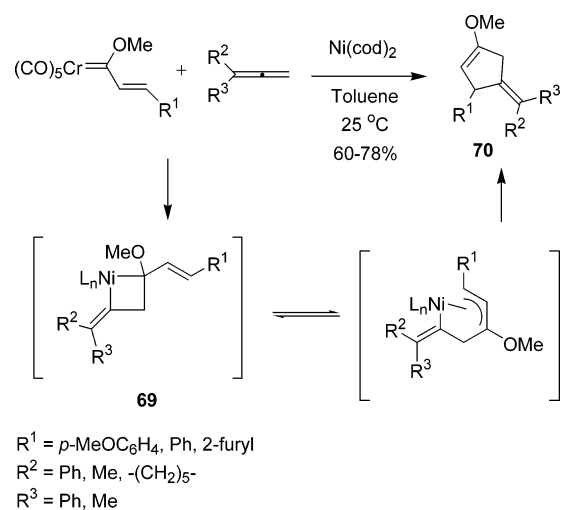
R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ph, 2-furyl, ferrocenyl, 1-cyclohexenyl  
R<sup>2</sup> = Ph, Me, CH<sub>2</sub>CH<sub>2</sub>OH, -(CH<sub>2</sub>)<sub>5</sub>-  
R<sup>3</sup> = Ph, Me, H  
Rh(I) = [(naphthalene)(cod)Rh][SbF<sub>6</sub>]

## Ni-Catalyzed Transmetalation Reactions

The reaction of chromium carbene complexes and allenes to give cyclopentenes has been also carried out in the

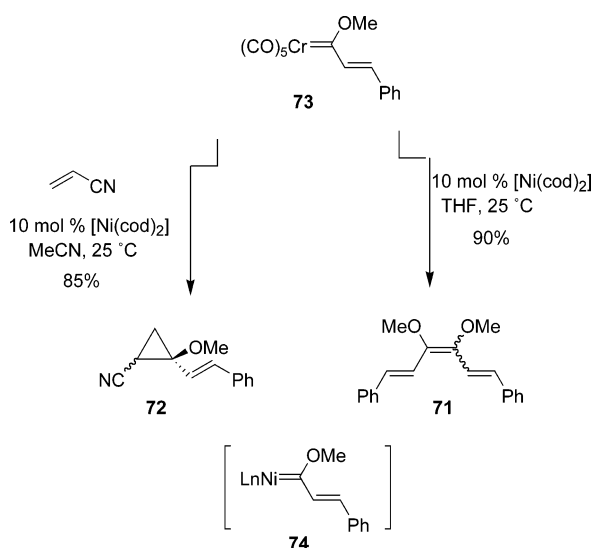
presence of Ni(cod)<sub>2</sub> by Barluenga's group. Like other catalytic reactions discussed in this Account, the reaction mechanism requires an initial transmetalation step (Cr–Ni), but in this case, 1 equiv of Ni<sup>0</sup> is employed.<sup>31</sup> The process is a [3+2] cyclization that takes place through a rather unusual metathesis reaction involving metallacyclobutane species **69** as an intermediate. Ring opening of **69** followed by reductive elimination of Ni<sup>0</sup> yields 4-alkylidenecyclopentenes **70** in 60–78% isolated yields (Scheme 26). The regioselectivity of the reaction is exactly the opposite to that reported above for the rhodium-catalyzed [3+2] cyclization of alkenyl chromium carbene complexes and allenes, which may be regarded as an interesting complementary synthetic approach to functionalized cyclopentene derivatives.

Scheme 26



The reactivity of Fischer carbene complexes toward alkynes in the presence of Ni<sup>0</sup> complexes as catalysts was tested by the same research group.<sup>32</sup> The active role of Ni was seen in the formation of either dimer **71** or cyclopropane **72** from complex **73** in the presence of 10 mol % [Ni(cod)<sub>2</sub>] (Scheme 27). Neither reaction occurs in the absence of the nickel catalyst. In both cases, the active nickel intermediate species is supposed to be nickel carbene complex **74**.

Scheme 27

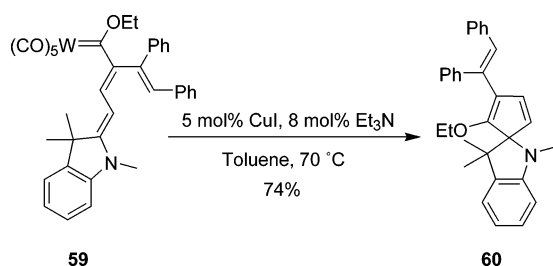


In this context, we have carried out a systematic study of the transfer of the carbene ligand transfer in alkoxy Fischer carbene complexes in the presence of different nickel and copper catalysts.<sup>33</sup> The efficiency of a series of Ni and Cu catalysts in self-dimerization processes and cyclopropanations in the presence of electron-poor alkenes has been established. Our results indicate that compared with palladium, Ni catalysts are the least efficient in these reactions, while Cu catalysts have an intermediate reactivity.

## Cu-Catalyzed Transmetalation Reactions

The possibility that Fischer carbene complexes could efficiently transfer the carbene ligand to a copper(I) center was first reported by Aumann et al.<sup>29</sup> when describing the enhanced formation of vinylcyclopentadiene **60** from tungstaoctatetraene **59** in the presence of a catalytic amount of CuI/Et<sub>3</sub>N (Scheme 28).

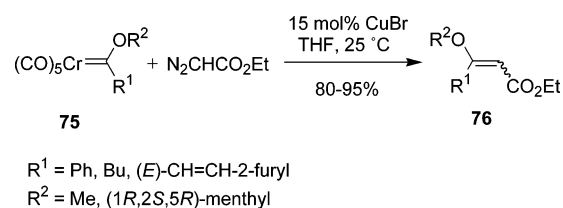
Scheme 28



Afterward, Barluenga et al.<sup>34</sup> reported the CuBr-catalyzed cross-coupling reaction of alkoxychromium carbene complexes **75** with ethyl diazoacetate allowing the preparation of functionalized alkenes, dienes, and trienes **76** (Scheme 29).

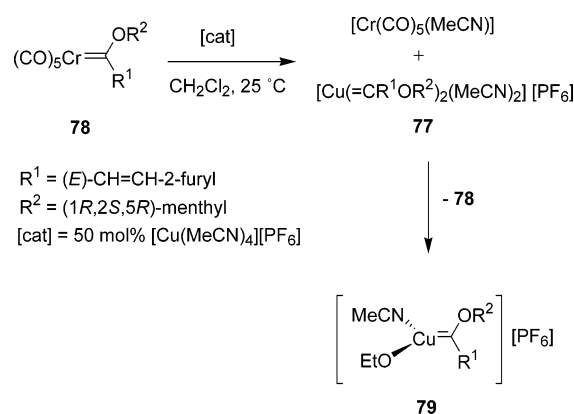
The intermediacy of a copper biscarbene species such as **77** was confirmed in the reaction of homochiral (menthoxy)carbene complex **78** and 0.5 equiv of  $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ . The reaction yielded a clean mixture of  $[\text{Cr}(\text{CO})_5(\text{MeCN})]$  and copper carbene complex **77** that

Scheme 29



evolved to a new complex **79** (Scheme 30). The structure of **79** was confirmed by a single-crystal X-ray analysis, and it shows an uncommon tricoordinate pattern together with the presence of two ligands with fair (MeCN) and very low (Et<sub>2</sub>O) coordination capability. This is one of the rare cases in which a copper(I) carbene complex has been isolated and characterized.<sup>34</sup>

Scheme 30



The carbene ligands of both complexes **77** and **79** dimerized stereoselectively in the presence of tributylphosphine, affording the expected triene in **75** and 82% yields, respectively.

## Conclusions and Outlook

Despite the enormous development of the chemistry of metal carbene complexes and even though transmetalation reactions are essential processes in organometallic chemistry, the catalytic metal–metal transfer from a carbene ligand in metal–carbene complexes is still a young and promising field of research. We and others have demonstrated that the reactivity of metal–carbene complexes can be enhanced in the presence of catalytic amounts of a transition metal. In this Account, we have pointed out that the transfer of the carbene ligand in the presence of Pd, Rh, Ni, and Cu catalysts can be done under mild conditions, leading to different reaction products depending on the structure of the starting carbene complex and the catalyst. Thus, metal-catalyzed self-dimerization reactions, C–H insertions, tandem cyclizations, cyclopropanations, and cycloadditions have been described in detail. Many of the reaction products cannot be obtained by conventional routes. The reactions are always clearly advantageous over the noncatalyzed process. Now our challenge is to explore the limits of this new research area, establishing the patterns of reactivity



of known compounds under catalytic conditions and trying to understand the mechanisms of these processes in depth.

We are indebted to all our co-workers who have contributed to the research on catalytic transmetalation for their enthusiasm, effort, ideas, and friendship. We wish to especially remember Dr. Juan C. del Amo who started this project as an undergraduate student and was killed in the terrorist act in Madrid, March 11th, 2004. We also thank the financial support from the Ministerios de Ciencia y Tecnología, Educación y Cultura y la Comunidad Autónoma de Madrid (Spain). The continuous support from Johnson Matthey PLC providing us with Pd catalysts is also gratefully acknowledged.

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AR040005R