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Catalytic Transmetalation of Alkoxychromium(0) Carbenes to Late Transition Metals: Self-Dimerization and Cyclopropanation Reactions

Juan C. del Amo,[#] María J. Mancheño, Mar Gómez-Gallego, and Miguel A. Sierra*

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040-Madrid, Spain

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A systematic study of the transfer of the carbene ligand from [pentacarbonylalkoxychromium-(0)]carbene complexes catalyzed by Ni and Cu catalysts is reported. The results obtained indicate that Ni and Cu catalysts are not as effective as palladium to promote the carbene self-dimerization process. Ni catalysts are the less efficient in these reactions, while Cu catalysts are of intermediate reactivity. In the presence of electron-deficient olefins, cyclopropanation products or γ-ketoesters can be selectively formed by choosing the adequate Ni or Cu catalyst, while Pd catalysts are ineffective in these processes. Cyclopropanes are better formed with $Ni(PPh_3)_4$, $Ni(COD)_2$, or Cu(0) and electron-poor olefins at room temperature, whereas γ-ketoesters are the exclusive products with Ni-Raney or Zn(0)/CuCl in stoichiometric reactions. The transmetalation from Cr to the late transition metal to form a new metal-carbene complex is the key step of these reactions and is strongly dependent on the nucleophilicity of the catalyst used.

Introduction

Today Fischer carbene complexes are standard synthetic tools in organic synthesis.[1] Although the chemistry of these complexes has been widely explored, the catalytic transfer of the carbene ligand from a Fischer-type group 6 carbene complex to another metal center is still a rare process.[2] In fact, until our original report[3] on the room-temperature self-dimerization of alkoxychromium(0) carbene complexes in the presence of catalytic amounts of Pd catalysts, the catalytic transmetalation of group 6 metal carbene complexes was unknown. Since this report, the number of processes involving group 6 Fischer carbene complexes as the stoichiometric reagent and a transition metal as the catalyst has steadily grown. Later on, we and others have explored this chemistry, and now Cr→Pd,[4] Cr→Rh,[5] Cr→Ni,[6] and Cr→Cu[5d,7] catalytic exchange processes have been reported, and their usefulness in organic synthesis has been demonstrated. Furthermore, recently, Barluenga and co-workers[7] have isolated and characterized a copper carbene (**1**) obtained by Cr→Cu transmetalation. This report was followed by the isolation and characterization of a Fischer-Pd carbene complex (**2**) obtained by W→Pd transmetalation by Spinet's group (Scheme 1).[8]

The growing interest in this type of chemistry emanates from the great potential and tremendous versatility of these reactions in organic synthesis. Most of the results reported until now on truly catalytic processes from group 6 metal carbene complexes can be under-

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* To whom correspondence should be addressed. E-mail: sierraor@quim.ucm.es.

[#] Deceased. Dr. del Amo was a victim of the March 11, 2004, tragedy in Madrid.

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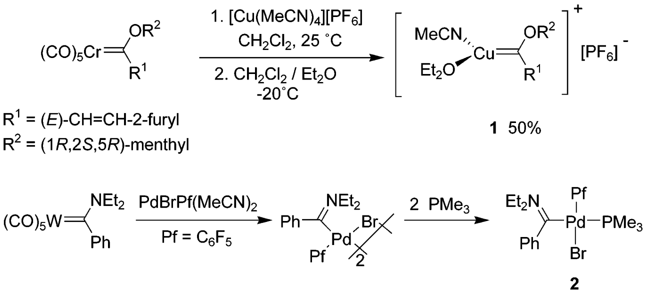
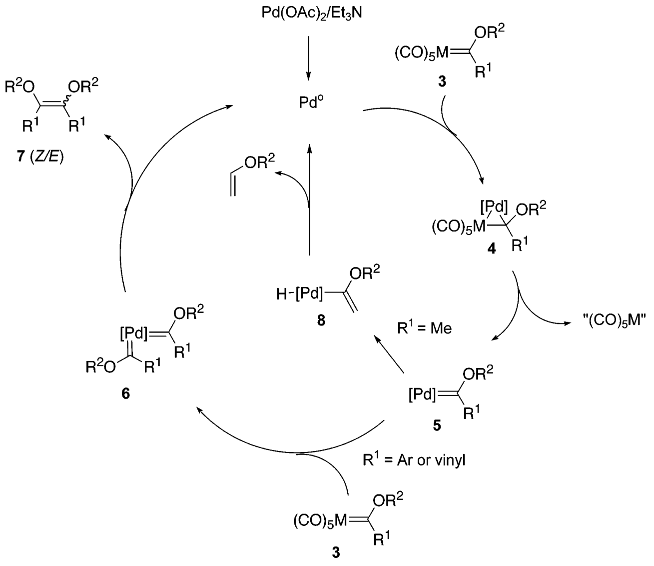
10.1021/om049455d CCC: $27.50

Scheme 1



stood by the catalytic cycle depicted in Scheme 2 for a Pd-catalyzed process.[4a] The key step is the transmetalation from the stoichiometric reagent (the metal(0) carbene complex) to the catalytic metal to form a new metal-carbene complex (**5**) that determines the outcome of the reaction. In the catalytic cycle represented in Scheme 2, a new transmetalation step forms the bis-palladacarbene complex **6**, which regenerates the catalyst by extrusion of olefin **7**. β-Elimination of hydride can favorably compete with the self-dimerization process through intermediates **8** depending on the structure of the starting complex **3**. Clearly, in according with the proposal in Scheme 2 the nature of the catalyst plays a key role in determining the nature of the reaction products.

Scheme 2



The mechanism and synthetic projection of these processes may be better understood by studying the catalyst dependence on the distribution of reaction products in competitive processes such as self-dimerization, cyclopropanation, and related reactions. This dependence is a good probe to understand the essence of the catalytic transmetalation reaction from group 6 carbene complexes. Reported herein is a systematic study of the effect of the nature of the metal catalyst in the reaction of chromium(0) carbene complexes and different Ni and Cu catalysts.

Results and Discussion

Initially we focused our study on the behavior of alkoxy Fischer carbene complexes toward Ni and Cu species. Since the self-dimerization of pentacarbonyl[(methoxy)(phenyl)carbene]chromium(0), **9**, is highly efficient using Pd catalysts,[3,4a] this reaction was chosen to establish the relative reactivity of Ni catalysts in the transmetalation process. Table 1 compiles the catalysts studied as well as the results obtained. In all cases compound **10**, isolated as a mixture of *E*/*Z* isomers, and methyl benzoate **11**, arising from the oxidation of complex **9**, were the only products detected (Scheme 3).

Scheme 3

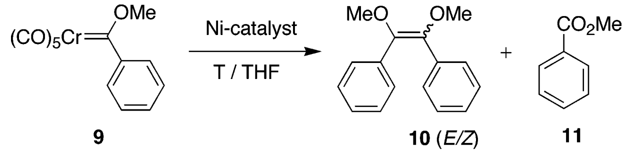


Table 1. Reactivity of Complex 9 with Ni Catalysts

entry	catalyst	*T* (°C)	time (h)	yield **10** (*E*/*Z*)[b] (%)	yield **11** (%)
1	10% Ni(acac)$_2$	rt	60	traces	69
2	10% Ni(acac)$_2$	50	14	94 (6:1)	0
3	10% Ni(OAc)$_2$× 4H$_2$O	50	14	84 (4.2:1)	0
4	2% Ni(OAc)$_2$× 4H$_2$O	50	21	78 (4.3:1)	0
5	10% Ni/C,[a] *n*BuLi, PPh$_3$	rt	88	0	78
6	10% Ni/C[a]	rt	88	no reaction[c]	
7	10% NiCl$_2$, *n*BuLi, PPh$_3$	rt	192	(1:1)[d]	(5)[d]
8	10% NiCl$_2$, PPh$_3$	rt	336	0	81
9	100% NiCl$_2$(PPh$_3$)$_2$/ 2PPh$_3$/Zn(0)	rt	16	89 (1:1.3)	

[a] Concentration: 0.24 mmol of Ni/g of C.[9] [b] The ratio of *E*/*Z* isomers was measured by integration of the signals attributable to the methoxy groups in the ^{1}H NMR spectrum of the reaction mixture. The given yields are for isolated products. [c] 75% of the starting carbene complex **9** was recovered. [d] Ratio between the dimerization product **10** (mixture of isomers) and the ester **11** obtained by integration of the signals attributable to the methoxy groups in the ^{1}H NMR spectrum of the reaction mixture.

The results compiled in Table 1 show that the self-dimerization of carbene complex **9** is inefficient at room temperature (22−23 °C), yielding high amounts of methyl benzoate **11** probably derived from the oxidation of **9** during either the workup or the long reaction times. However, both Ni(OAc)$_2$ and Ni(acac)$_2$ lead to dimer **10** in good yields but at temperatures of 50 °C (Table 1, entries 2−4). A reduction of the catalyst load from 10% (Table 1, entry 3) to 2% of Ni(OAc)$_2$ (Table 1, entry 4) has only a slight effect on the yields and reaction times. Neither Ni(C)[9] (Table 1, entries 5 and 6) nor catalysts derived from NiCl$_2$[10] (Table 1, entries 7 and 8) are able to perform the self-dimerization of carbene complex **9**. Only the system NiCl$_2$(PPh$_3$)/2PPh$_3$/Zn(0) afforded dimer **10** in 89% yield at room temperature (entry 9), but it has to be used in stoichiometric amounts.[11] When

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(9) Prepared following the literature methods, see: (a) Lipshutz, B. H.; Blomgren, P. A. *J. Am. Chem. Soc.* **1999**, *121*, 5819. (b) Lipshutz, B. H.; Tasler, S.; Chrisman, W.; Spliethoff, B.; Tesche, B. *J. Org. Chem.* **2003**, *68*, 1177. (c) Tasler, S.; Lipshutz, B. H. *J. Org. Chem.* **2003**, *68*, 1190.

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(11) Under these conditions the active catalyst is Ni(PPh$_3$)$_3$. For the use of these conditions in catalytic reactions, see: (a) Zembayashi, M.; Tamao, K.; Yoshida, J.-I.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089. For the use of these conditions in stoichiometric reactions, see: (b) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375.

comparing the results for the different Ni catalysts with those obtained previously by us[4a] using Pd catalysts, it can be concluded that Ni(II) derivatives are able to catalyze the self-dimerization of complex **9** but in a less efficient manner than Pd(II) catalysts. In fact, longer reaction times and higher temperatures are required with Ni catalysts (compare 14 h at 50 °C for the self-dimerization of complex **9** in the presence of $Ni(acac)_2$ with 1 h at room temperature for $Pd(OAc)_2/Et_3N$).[4a] However, the presence of high amounts of $Ni(PPh_3)_3$ in the reaction medium (Table 1, entry 9) promotes the self-dimerization at room temperature in nearly quantitative yields. Since it is known that $Ni(PR_3)_3$ complexes are good electron transfer reagents,[12] probably a different mechanism from that proposed in Scheme 2 has to be considered in this case (see below). Accordingly to it, the key step for the transmetalation is the formation of a heterodimetallacyclopropane species such as **4**, derived from the nucleophilic attack of the catalyst to the carbene complex. The differences in reactivity observed between nickel and palladium catalysts may be a consequence of their differences in nucleophilicity.[13] It is necessary to point out that Ni(C) is not able to promote the self-dimerization process, while Pd(C) gives good yields (49%) of the dimeric product **10**.[4a]

Scheme 4

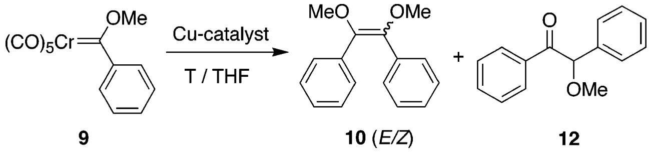

Table 2. Reactivity of Complex 9 with Cu Catalysts

entry	catalyst	*T* (°C)	time (h)	**10** (*E*/*Z*):**12**	yield **10**[c] (%)	yield **12**[c] (%)
1	10% CuI	rt	168			*d*
2	10% CuOTf·C_6H_6	rt	168			*d*
3	10% CuCN	rt	21	7:1	88	n.i.
4	10 $Cu(OTf)_2$	rt	94			*d*
5	10% $Cu(acac)_2$	rt	72	1.8:1[a]	n.i.[b]	n.i
6	10% $Cu(acac)_2$	50	14	100:0	88	*e*
7	10% $Cu(acac)_2PPh_3$	rt	48	1:4.3	12	51
8	10% Cu(0)	rt	96	0:100		43[f]
9	10% Cu(0)	40	21	100:0	88	
10	10% Cu(2-ThCOO)[g]	rt	29	5.8:1[a]	n.i.[e]	n.i.
11	10% Cu(2-ThCOO)[g]	50	5	100:0	68	
12		50	21			

[a] Ratio between compounds **10** and **12** obtained by integration of the signals attributable to the methoxy groups in the ^1H NMR spectrum of the reaction mixture. [b] Not isolated. [c] In pure, isolated compound as a mixture of *E*/*Z* isomers. [d] The main reaction product was methyl benzoate **11**. [e] Methyl benzoate **11** was identified in the reaction mixture. [f] Methyl benzoate **11** was isolated in 26% yield. [g] 2-Thienyl carboxylate.

The self-dimerization of complex **9** catalyzed by Cu species was studied next. Table 2 compiles the results obtained in these reactions. Dimer **10** was obtained together with α-methoxyketone **12** and methyl benzoate **11**. As expected, the relative amounts of products strongly depend on the catalyst employed (Scheme 4).

Only two Cu(I) catalysts formed the self-dimerization product **10** in good yields: CuCN at room temperature (Table 2, entry 3) and Cu(2-ThCOO) at 50 °C (Table 2, entry 11).[14] Other Cu(I) species such as CuI, or Cu(I) and Cu(II) triflates (Table 2, entries 1, 2 and 4), produced only traces of compound **10** together with high amounts of methyl benzoate **11** in sluggish reactions. On the other hand, while $Cu(acac)_2$ gives compound **10** in good yield at 50 °C (Table 2, entry 6), the use of $Cu(acac)_2$ and PPh_3 leads to a mixture of dimer **10** and α-methoxyketone **12** at room temperature (Table 2, entry 7). Cu(0) dust is very efficient at 40 °C (Table 2, entry 9), but at room temperature, ketone **12** was the single reaction product (Table 2, entry 8). Finally, in the absence of Cu catalyst, methyl benzoate **11** was the only observed product together with the starting material unaltered, even after prolonged reaction times. The results obtained with Cu(0) suggest that α-methoxyketone **12** is formed at the expense of dimer **10** by hydrolysis. In fact, **12** is obtained after 72−96 h at room temperature (Table 2, entries 7 and 8), while at 40 °C the reaction requires only 21 h and dimer **10** is exclusively formed.

The reactivity observed for the Cu catalysts is intermediate between the most reactive Pd catalysts and the less reactive Ni catalysts. In fact, CuCN is able to promote the self-dimerization reaction at room temperature, but the reaction requires longer reaction times than in the case of Pd catalysts.[4a] Again, the nucleophilicity of the catalyst seems to be crucial to determine the success of the key transmetalation step. Catalysts having strong electron-withdrawing substituents such as CuI or Cu(I) triflates inhibit the transmetalation step and thence the self-dimerization reaction. Furthermore, higher temperatures or the addition of PPh_3 is required to obtain clean reactions and good yields in products **10** and **12** when $Cu(acac)_2$ is used as the catalyst.

Once the order of reactivity of the metal catalysts in the self-dimerization of alkoxychromium(0) carbene complexes was established ($Pd \gg Cu > Ni$), the reaction of cyclopropanation of olefins by chromium(0) Fischer carbene complexes was next studied. The goal pursued was to effect this reaction under mild conditions (rt).[15,16] The initial attempts were carried out with $Pd(OAc)_2/Et_3N$ in the reaction of pentacarbonyl[(*p*-bromophenyl)-(methoxy)carbene]chromium(0) (**13**) with methyl acry-

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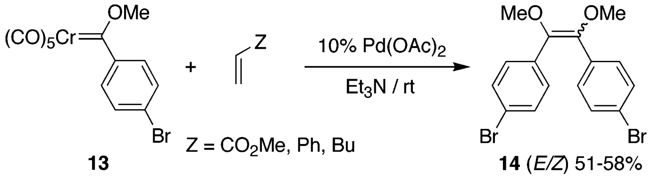
(15) For reviews about cyclopropanation reactions using Fischer carbene complexes see: (a) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Able, E. W., Stone, F. G. A., Wilkinson, G.. Eds.; Pergamon: Oxford, 1995; Vol. 12, p 387. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. Selected examples: (c) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (d) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. (e) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966. (f) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Yeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574. (g) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (h) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736. (i) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908. (j) Södeberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113. (k) Barluenga, J.; Montserrat, J. M.; Flórez, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1068. (l) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73. (m) Ullman, A.; Gruner, M.; Reissig, H.-U. *Chem. Eur. J.* **1999**, *5*, 187. (n) Barluenga, J.; Fernández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591. (o) Barluenga, J.; Aznar, F.; Gutiérrez, I.; Martín, J. A. *Org. Lett.* **2002**, *4*, 2719.

Scheme 5



late, styrene, and 1-hexene, to cover a range of alkenes with different electronic requirements (Scheme 5). No cyclopropanation products were observed, and only dimer **14** was isolated with good yield in all cases. It is clear from these results that although $Pd(OAc)_2/Et_3N$ is very efficient in promoting the self-dimerization of alkoxychromium(0) carbene complexes, it is not a suitable reagent for the cyclopropanation of olefins. Assuming that the sequence Pd $\gg$ Cu > Ni reflects the reactivity of the metal also in the second transmetalation step of the reaction, to generate the metallabiscarbene **6**, we can affirm that the cyclopropanation competes unfavorably with this transmetalation step in the presence of a palladium catalyst.

Ni catalysts are the less reactive in the self-dimerization reaction as discussed above. Therefore, five Ni(0) compounds were studied as cyclopropanating catalysts, covering a wide range of metal nucleophilicity. The results obtained in the catalytic cyclopropanation of methyl acrylate and acrylonitrile by complexes **9** and **15**–**17** using $Ni(PPh_3)_4$, $Ni(PCl_3)_4$, $Ni(P(O\textit{i}\text{-}Pr)_3)_4$,[17] Ni-Raney, and $Ni(COD)_2$ are compiled in Table 3 (Scheme 6).

The data collected in Table 3 indicate that the efficiency of $Ni(PPh_3)_4$ strongly depends on the structure of the Fischer carbene complex employed. Thus, aryl complex **9** renders cyclopropanes **18a** with good yields, at room temperature, with methyl acrylate and acrylonitrile (Table 3, entries 1 and 4). On the opposite side are methyl carbene complexes **15** and **16,** which are unreactive under the same reaction conditions, even after prolonged reaction times (entries 2 and 3). Other Ni catalysts such as $Ni(PCl_3)_4$ or $Ni(P(O\textit{i}\text{-}Pr)_3)_4$ are less effective in promoting the reaction between complex **9** and methyl acrylate (entries 5 and 6), and considerable amounts of methyl benzoate are recovered in theses cases.

The cyclopropanation reaction proceeds in good yields with $Ni(COD)_2$ as the catalyst regardless of the carbene complex used (Table 3, entries 7 and 8). While this work was in progress Barluenga et al.[6] have reported the self-dimerization of the methoxycarbene complex analogue to **17** as well as the cyclopropanation of acrylonitrile by this complex catalyzed by $Ni(COD)_2$. Therefore, $Ni(COD)_2$ combines the necessary reactivity to promote the initial transmetalation process and the necessary stability of the intermediate Ni-carbene complex to effect the cyclopropanation of electron-deficient olefins at room temperature.

Together with the cyclopropanes **18**, ketones **19** are obtained in the presence of $NiCl_2(PPh_3)_2/2PPh_3/Zn$ or Ni-Raney. Now, the amount of compound **19** depends on the load of catalyst for $NiCl_2(PPh_3)_2/2PPh_3/Zn$ (Table 3, entries 9 and 10) but is the sole product when Ni-Raney is employed (Table 3, entries 11 and 14).

Considering the results in Table 3, both $Ni(COD)_2$ and $Ni(PPh_3)_4$ could be the catalysts of choice to perform cyclopropanation reactions using Fischer carbene complexes and electron-deficient olefins. $Ni(COD)_2$ is more general, as $Ni(PPh_3)_4$ is only effective for aryl Fischer carbene complexes. The ability of both catalysts to transfer the carbene ligand to neutral alkenes was tested next. Complex **9** was reacted with 1-hexene under different conditions, as illustrated in Table 4. In no case were cyclopropanation products formed, and only dimer **10** could be isolated in these reactions, regardless of the temperature. From these results it may be concluded that although the transmetalation of Cr–Ni occurs, the intermediate Ni-carbenes formed are not electrophilic enough to react with neutral olefins, yielding exclusively dimers derived from an intermolecular ligand transfer process.

The ability of Cu(0) as cyclopropanation catalyst was subsequently studied. The results are compiled in Table 4 (entries 6–9) (Scheme 7). The reaction of carbene complexes **9**, **15**, **17**, and **20** with methyl acrylate in the presence of Cu(0) yielded the expected cyclopropanes **18** only for aryl complex **9** and alkenyl complex **17**, although in the latter case in very low yield.

Finally, taking into account the well-known ability of Zn(0)/CuCl to perform cyclopropanation processes this was the last system explored (Scheme 8).[18] The results are collected in Table 4 (entries 10–13). The use of Zn(0)/CuCl leads to the formation of ketoesters **19** with good yields[19] for aryl complex **9** and styryl complex **17**. However, alkyl and alkynyl carbene complexes **15** and **20** were recovered unaltered even after prolonged (1 week) reaction times (Scheme 8). Formation of compounds **19** may be explained by metal-induced cyclopropane ring opening followed by hydrolysis of the enol-ether thus formed.[19a]

Some general trends can be extracted from the results collected in Tables 1–4. First, the results obtained can be systematized by means of a catalytic cycle represented in Scheme 9, analogous to that proposed by us to explain the Pd-catalyzed carbene transfer processes in Scheme 2.[4a] As discussed above, the efficiency of the catalytic transmetalation step increases with the catalyst nucleophilicity. Therefore, the nucleophilic attack of the catalyst to the carbene carbon in complexes **21** to form the new metal carbene species **22** (through the dimetallacyclopropane **23**)[20] determines the easiness of the catalytic process. The competence between self-

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[16] Examples of cyclopropanation reactions using Fischer carbene complexes under mild conditions: Photochemical: (a) Sierra, M. A.; Del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *Tetrahedron Lett.* **2001**, *42*, 5435. Thermal: (b) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653.

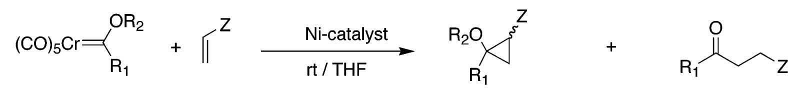
[17] Leadbeater, N. E. *J. Org. Chem.* **2001**, *66*, 7539.

[18] (a) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323. (b) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256. (c) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057. For an extensive review, see ref 15a.

[19] The formation of 4-oxo esters has been reported in diverse thermal reactions of alkoxy, acyloxy, and amino carbene chromium(0) complexes and electron-deficient olefins. See, among others: (a) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133. (b) Sierra, M. A.; Soderbeg, B. C.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769. (c) Soderberg, B. C.; York, D. C.; Harriston, E. A.; Caprara, K. J.; Flurry, A. H. *Organometallics* **1995**, *14*, 3712.

[20] Heptacoordinated Cr-carbene complexes have been previously reported: (a) Stumpf, R.; Jaeger, M.; Fischer, H. *Organometallics* **2000**, *19*, 4040. (b) Jaeger, M.; Stumpf, T.; Carsten, T.; Fischer, H. *Chem. Commun.* **2000**, 931, and the pertinent references therein.

Scheme 6



18 (*cis/trans*) **19**

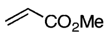
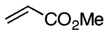
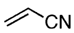
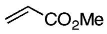
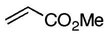
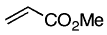
9 R^1 = Ph, R^2 = Me
15 R^1 = Me, R^2 = Bn
16 R^1 = Me, R^2 = Et
17 R^1 = (*E*)-CH=CH-Ph, R^2 = Et

Z = CO_2Me, CN

18a R^1 = Ph, R^2 = Me, Z = CO_2Me
18b R^1 = Me, R^2 = Bn, Z = CO_2Me
18c R^1 = Ph, R^2 = Me, Z = CN

19a R^1 = Ph, Z = CO_2Me
19b R^1 = Me, Z = CO_2Me
19c R^1 = (*E*)-CH=CH-Ph, Z = CO_2Me

Table 3. Ni-Catalyzed Cyclopropanation of Electron-Deficient Olefins

Entry	Complex	Alkene[a]	Catalytic System	Time (h)	Yield **18**(*cis/trans*)	Yield **19**
1	**9**		5% $Ni(PPh_3)_4$	24	92% (1.5:1)	traces
2	**15**		5% $Ni(PPh_3)_4$	96	—[c]	—
3	**16**		5% $Ni(PPh_3)_4$	96	no reaction[b]	—
4	**9**		5% $Ni(PPh_3)_4$	96	76% (1.5:1)	—
5	**9**		20% $Ni(PCl_3)_4$	72	76% (1:1)[e]	0
6	**9**		10% Ni(P(O*i*-Pr)$_3$)$_4$	48	21% (1:1)[e]	0
7	**9**		15% $Ni(COD)_2$	6	95% (1.7:1)	0
8	**15**		15% $Ni(COD)_2$	45	75% (6:4)	(1)[d]
9	**9**		5% $NiCl_2(PPh_3)_2$/ 2 PPh_3/Zn(0)	20	58% (1:1)	(1)[d]
10	**9**		100% $NiCl_2(PPh_3)_2$/ 2 PPh_3/Zn(0)	16	(1:1)	(21)[d]
11	**9**		Ni-Raney	18	0	56%
12	**15**		Ni-Raney	96	no reaction[b]	0
13	**17**		Ni-Raney	24	0	49%

[a] An excess of 5 equiv of olefin was used for all reactions. [b]Starting carbene complex was recovered unaltered together with a complex mixture of unidentified products. [c]Benzyl acetate was isolated in 93% yield. [d]Ratio of compounds **18** and **19** obtained by integration of the signals corresponding to the methoxy groups in ^1H NMR. [e]Benzyl acetate was obtained as the main reaction product.

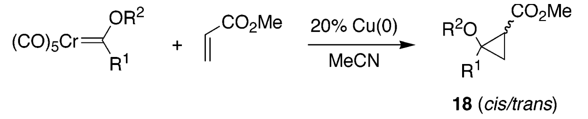
dimerization and other processes such as cyclopropanation depends also on the nucleophilicity of the catalyst. Pd catalysts produce strongly nucleophilic carbenes **22** and a second transmetalation occurs. This process forms biscarbene **24**, which yields dimers **10**. It is worth noting that the transmetalation from Pd-carbene **22** to form biscarbene **24** is so favored that it occurs even in the presence of electron-deficient alkenes. This is not the case of less nucleophilic Ni-carbenes (**22**, M = Ni), which in the presence of electron-deficient olefins form metallacyclobutanes **25**, precursors of cyclopropanes **18**. However, these Ni-carbenes **22** are not electrophilic enough to react with neutral olefins, and dimerization products are obtained in these conditions. The behavior of Cu catalysts toward cyclopropanation is intermediate between Pd and Ni catalysts. In these cases, the

Table 4. Entries 1−5: Reactivity with 1-Hexene in the Presence of Ni Catalysts. Entries 6−9: Reactivity with Methyl Acrylate Catalyzed by 20% Cu(0). Entries 10−13: Reactivity with Methyl Acrylate in the Presence of Zn(0)/CuCl[a]

entry	complex	catalyst[b]	temp (°C)	time (h)	product	yield (%)
1	**9**	5% $Ni(PPh_3)_4$	rt	120	**10**[b]/**11**	(4.6:27)
2	**9**	10% $Ni(PPh_3)_4$	50	24	**10**[b]/**11**	(4.5:7)
3	**9**	100% $NiCl_2(PPh_3)_2 \cdot 2PPh_3/Zn(0)$	rt	20	**10**[b]/**11**	(2:1)
4	**9**	15% $Ni(COD)_2$	rt	24	**10**[b]	96
5	**9**	20% $Ni(COD)_2$	68	6	**10**[b]	97
6	**9**	20% Cu(0)	rt	48	**18**[c]	58
7	**9**	20% Cu(0)	rt	24	**18**[c]	76
8	**17**	20% Cu(0)	rt	96	traces[d]	
9	**15**	20% Cu(0)	rt	24		
10	**9**	Zn(0)/CuCl	rt	24	**19a**	80
11	**17**	Zn(0)/CuCl	rt	24	**19c**	63
12	**15**	Zn(0)/CuCl	rt	168	*e*	
13	**20**	Zn(0)/CuCl	rt	192	no reaction[f]	

[a] Olefin in excess (5 equiv) was used for all reactions. [b]A mixture of *E*/*Z* isomers. See Experimental Section. [c]A mixture of *cis*/*trans* isomers. See Experimental Section. [d]The ester derived from oxidation of the starting carbene complex was the major product formed.[e]The starting Fischer carbene complex oxidized after long reaction times. [f]Complex **20** was recovered unaltered.

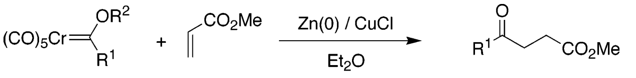
Scheme 7



9 R^1 = Ph, R^2 = Me
15 R^1 = Me, R^2 = Bn
17 R^1 = (*E*)-CH=CH-Ph, R^2 = Et
20 R^1 = C≡C−Ph, R^2 = Et

18a R^1 = Ph, R^2 = Me
18d R^1 = (*E*)-CH=CH-Ph, R^2 = Et

Scheme 8

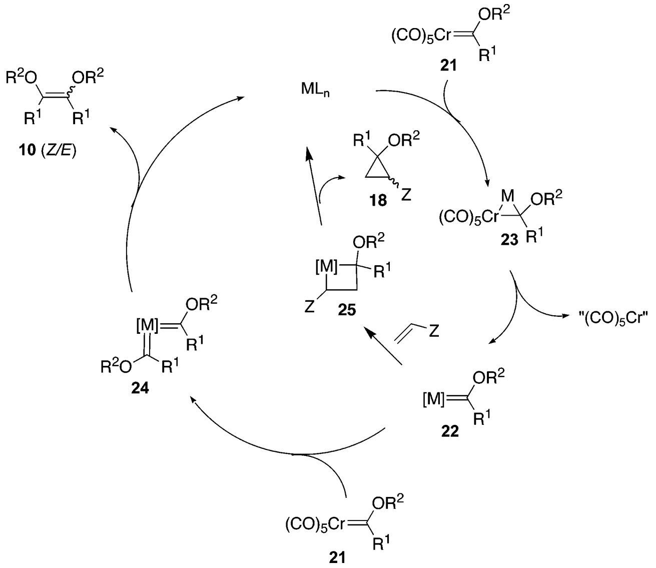


9 R^1 = Ph, R^2 = Me
15 R^1 = Me, R^2 = Bn
17 R^1 = (*E*)-CH=CH-Ph, R^2 = Et
20 R^1 = −C≡C−Ph, R^2 = Et

19a R^1 = Ph
19c R^1 = (*E*)-CH=CH-Ph

intermediate carbene complex **22** (M = Cu) forms only the corresponding metalacyclobutane **25** in the presence of electron-deficient olefins, provided that arylchromium(0) Fischer carbene complexes are used. For alkyl-substituted chromium(0) carbenes the dimerization products are obtained (Scheme 9).

Scheme 9



In conclusion, carbene ligand transfer processes can be performed under mild conditions in alkoxy Fischer carbene complexes in the presence of different metal catalysts: palladium, nickel, and copper. Palladium seems to be the most effective to catalyze the self-dimerization process in group 6 Fischer carbene complexes.[4a] Ni catalysts are the less efficient in these reaction, while Cu catalysts have an intermediate reactivity. Cyclopropanes or γ-ketoesters can be selectively formed by choosing the adequate Ni or Cu catalyst, while Pd catalysts are inefficient in these processes using alkoxychromium(0) carbene complexes. Cyclopropanes are better formed with $Ni(PPh_3)_4$, $Ni(COD)_2$, or Cu(0) and electron-poor olefins at room temperature, whereas γ-ketoesters are the exclusive products with Ni-Raney or Zn(0)/CuCl. The formation of ketoesters is not catalytic under these conditions. Additional work pursuing the full understanding of these and related processes is already in progress in our laboratories.

Experimental Section

General Procedures. ^1H NMR and ^{13}C NMR spectra were recorded at 22 °C in $CDCl_3$, on Varian XL-300S (300.1 and 75.4 MHz), Bruker Avance-300 (300.1 and 75.4 MHz), and Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer. Mass spectra were carried out on a GC-MS HP-5989 (60 eV) mass spectrometer using methanol as solvent. All solvents used in this work were purified by distillation and were freshly distilled immediately before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone; CH_2Cl_2 and *N*,*N*-dimethyformamide (DMF), from CaH_2. Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Merck silica gel (230−400 mesh) was used as the stationary phase for purification of crude reaction mixtures by flash column chromatography. Identification of products was made by TLC (Kiesegel 60F-254). UV light ($\lambda = 254$ nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. All commercially available compounds were used without further purification. The following products were prepared according to literature methods: pentacarbonyl[(methoxy)(phenyl)carbene]chromium(0), **9**,[21] pentacarbonyl[(ethoxy)(methyl)carbene]chromium(0), **16**,[22] pentacarbonyl[(*p*-bromophenyl)(methoxy)carbene]chromium(0), **13**,[4a] pentacarbonyl[(benzyloxy)(methyl)carbene]chromium(0), **15**,[23] pentacarbonyl[(ethoxy)(2-phenylethenyl)carbene]chromium(0), **17**,[24]

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(21) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 963.
(22) Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *12*, P15.

pentacarbonyl[(ethoxy)(2-phenylethynyl)carbene]chromium(0), **20**.[25]

General Procedure for the Ni-Catalyzed Carbene Ligand Dimerization of Complex 9. An anhydrous and degassed THF solution of the carbene complex **9** and the Ni catalyst was placed in a 10 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times). The mixture was stirred under argon atmosphere at the temperature specified in each case until the disappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate and filtered through Celite. After removal of the solvent in vacuo, the composition of the crude was checked by ^{1}H NMR. The pure compounds were isolated by flash column chromatography on silica gel.

$Ni(acac)_2$. From a mixture of carbene complex **9** (50 mg, 0.16 mmol) and 10% $Ni(acac)_2$ (4 mg, 0.016 mmol) in 1 mL of THF after 60 h at room temperature was obtained 15 mg (69%) of methyl benzoate **11**. The same reaction was carried out at 50 °C, affording after 14 h 18 mg (94%) of compound **10**[4a] as a mixture of isomers (*E*/*Z* 6:1).

$Ni(OAc)_2 \times 4H_2O$. From a mixture of carbene complex **9** (50 mg, 0.16 mmol) and 10% $Ni(OAc)_2 \times 4H_2O$ (4 mg, 0.016 mmol) in 1 mL of THF after 14 h at 50 °C was obtained 16 mg (84%) of compound **10** as a mixture of isomers (*E*/*Z* 4.2:1). The reaction was also carried out using 2% $Ni(OAc)_2 \times 4H_2O$, affording after 21 h at 50 °C 15 mg (78%) of compound **10** as a mixture of isomers (*E*/*Z* 4.3:1).

Ni/C.[9] From a mixture of carbene complex **9** (100 mg, 0.32 mmol), 10% Ni/C (133 mg, 0.032 mmol), *n*BuLi (40 μL, 1.6 M), and PPh_3 (34 mg, 0.13 mmol) in 2 mL of THF after 88 h at room temperature was obtained 54 mg (78%) of methyl benzoate **11**. In a similar experiment starting from carbene complex **9** (100 mg, 0.32 mmol) and 10% Ni/C (133 mg, 0.032 mmol) in 2 mL of THF, the starting material **9** (75 mg, 75%) was recovered unaltered after 88 h at room temperature.

$NiCl_2$, *n*-BuLi, and PPh_3. From a mixture of carbene complex **9** (312 mg, 1.0 mmol), 10% $NiCl_2$ (13 mg, 0.1 mmol), *n*BuLi (120 μL, 1.6 M), and PPh_3 (52 mg, 0.2 mmol) in 6 mL of THF after 192 h at room temperature was obtained 120 mg of a 2:5 mixture of *E*/*Z* isomers **10** (ratio 1:1) and methyl benzoate **11**. The ratios were determined by ^{1}H NMR.

$NiCl_2$ and PPh_3. From a mixture of carbene complex **9** (312 mg, 1.0 mmol), 10% $NiCl_2$ (13 mg, 0.1 mmol), and PPh_3 (52 mg, 0.2 mmol) in 6 mL of THF after 336 h at room temperature was obtained 110 mg (81%) of methyl benzoate **11**.

General Procedure for $Ni[PPh_3]_3$[11]-Catalyzed Carbene Ligand Dimerization of Complex 9. $NiCl_2(PPh_3)_2$ (419 mg, 0.64 mmol), PPh_3 (336 mg, 1.28 mmol), and Zn(0) powder (42 mg, 0.64 mmol) were placed in a 25 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times). Then anhydrous DMF (5 mL) was added, and the mixture was stirred for 30 min under argon atmosphere at room temperature (the color of the solution changes from light blue to deep red). Then, carbene complex **9** was added (200 mg, 0.64 mmol) in 2 mL of anhydrous DMF, and the mixture was stirred under argon atmosphere until the disappearance of starting material (16 h, checked by TLC). EtOAc was added to the resulting suspension, and the organic layer was washed with water, extracted with EtOAc, dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure, the crude reaction was purified by flash column chromatography on silica gel to yield dimer **10** (68 mg, 89%) as a mixture of isomers (*E*/*Z* 1:1.3).

General Procedure for the Cu-Catalyzed Carbene Ligand Dimerization of Complex 9. An anhydrous and degassed THF solution of the carbene complex **9** and the copper catalyst was placed in a 10 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times). The mixture was stirred under argon atmosphere at the temperature specified in each case until the disappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and filtered through a short pad of Celite. After removal of the solvent under reduced pressure the composition of the crude reaction was checked by ^{1}H NMR. The pure products were isolated by flash column chromatography on silica gel.

CuI. From a mixture of carbene complex **9** (50 mg, 0.16 mmol) and 10% CuI (3 mg, 0.016 mmol) in 1 mL of THF after 168 h at room temperature was obtained 20 mg of methyl benzoate **11** accompanied by trace amounts of dimer **10** and 2-methoxy-1,2-diphenylethanone, **12**.[26] The same reaction was carried out for 40 h at 50 °C affording 19 mg of the ester **11** and only trace amounts of compound **10**.

CuCN. From a mixture of carbene complex **9** (50 mg, 0.16 mmol) and 10% CuCN (2 mg, 0.016 mmol) in 1 mL of MeCN after 21 h at room temperature was obtained a (7:1) mixture of compounds **10** (17 mg, 88%, *E*/*Z* isomers 4:1 ratio) and **12** (checked by ^{1}H NMR).

$CuOTf\cdot(C_6H_6)$. From a mixture of carbene complex **9** (100 mg, 0.32 mmol) and 10% $CuOTf\cdot(C_6H_6)$ (8 mg, 0.032 mmol) in 2 mL of THF after 168 h at room temperature was obtained 18 mg of methyl benzoate **11** accompanied by trace amounts of compounds **10** and **12**.

$Cu(OTf)_2$. From a mixture of carbene complex **9** (150 mg, 0.48 mmol) and 10% $Cu(OTf)_2$ (17 mg, 0.048 mmol) in 3 mL of THF after 94 h at room temperature was obtained 60 mg of methyl benzoate **11** together with trace amounts of compounds **10** and **12**.

$Cu(acac)_2$. From a mixture of carbene complex **9** (50 mg, 0.16 mmol) and 10% $Cu(acac)_2$ (4 mg, 0.016 mmol) in 1 mL of THF after 72 h at room temperature was obtained 16 mg of a (1.8:1) mixture of compounds **10** (*E*/*Z* isomers in the ratio 1:1.2) and **11**. The same reaction was carried out for 14 h at 50 °C affording 17 mg (88%) of compound **10** (*E*/*Z* isomers in the ratio 1:1.4) and trace amounts of methyl benzoate **11**.

$Cu(acac)_2$ and PPh_3. From a mixture of carbene complex **9** (50 mg, 0.16 mmol), 10% $Cu(acac)_2$ (4 mg, 0.016 mmol), and PPh_3 (13 mg, 0.048 mmol) in 1 mL of THF after 72 h at room temperature was obtained 2 mg (12%) of compound **10** as a mixture of isomers (*E*/*Z* 1:1) and 9 mg (51%) of α-methoxyketone **12**.

Cu(0). From a mixture of carbene complex **9** (156 mg, 0.5 mmol) and 10% Cu(0) powder (3 mg, 0.05 mmol) in 3 mL of MeCN at rt after 96 h was obtained 24 mg (43%) of α-methoxyketone **12** together with 18 mg (26%) of methyl benzoate **11**. In a similar experiment, from carbene complex **9** (50 mg, 0.16 mmol) and 10% Cu(0) powder (1 mg, 0.016 mmol) in 1 mL MeCN after 21 h at 40 °C was obtained 17 mg (88%) of compound **10** as a mixture of isomers (*E*/*Z* 1:1.2).

Cu(2-ThCOO). From a mixture of carbene complex **9** (50 mg, 0.16 mmol) and 10% copper(I) 2-thienylcarboxylate (3 mg, 0.016 mmol) in 1 mL of THF after 29 h at room temperature was obtained 16 mg of a (1:4.8:1:1.4) mixture of compounds **10**, **12**, and **11**, respectively. The same reaction was carried out for 5 h at 50 °C, affording 13 mg (68%) of compound **10** as a mixture of isomers (*E*/*Z* 1:2.9).

General Procedure for the Cyclopropanation of Carbene Complexes Catalyzed by $Ni(PPh_3)_4$, $Ni(PCl_3)_4$, or $Ni(P(O\textit{i}-Pr)_3)_4$.[12] Nickelocene and 4 equiv of PPh_3 or P(O*i*-

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[23] Hafner, A.; Hegedus, L. S.; de Weck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

[24] Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

[25] (a) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229. (b) Duetsch, M.; Stein, F.; Lackman, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. (c) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421.

[26] 2-Methoxy-1,2-diphenylethanone **12** was identified by comparison of its NMR data with those obtained from a commercial sample (Aldrich).

Pr)$_3$ were placed in a 10 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times). The mixture was heated at 80 °C under argon atmosphere for 15 min. When using PCl_3 the mixture was dissolved in degassed pentane and heated at 30 °C for 15 min. After that, in all cases, the reaction mixture was cooled to room temperature, and then was added a solution of the corresponding carbene complex and 5 equiv of methyl acrylate in anhydrous THF. The reaction was stirred until the disappearance of the starting carbene complex (checked by TLC). The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and filtered through a short pad of Celite. After removal of the solvent in vacuo, the composition of the crude reaction was checked by ^{1}H NMR. The pure compounds were isolated by flash column chromatography on silica gel.

Ni(PPh$_3$)$_4$. (a) From a mixture of carbene complex **9** (312 mg, 1.0 mmol), methyl acrylate (430 mg, 5.0 mmol), 5% nickelocene (10 mg, 0.05 mmol), and PPh_3 (52 mg, 0.2 mmol) in 5 mL of THF after 24 h at room temperature was obtained 188 mg (92%) of **18a**[16a,19a] as a *cis*−*trans* (58:40) mixture and trace amounts of compound **19a**.[27] (b) From a mixture of carbene complex **15** (163 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), 5% nickelocene (5 mg, 0.025 mmol), and PPh_3 (26 mg, 0.1 mmol) in 3 mL of THF after 96 h at room temperature was obtained 70 mg (93%) of benzyl acetate. (c) From a mixture of carbene complex **16** (264 mg, 1 mmol), methyl acrylate (430 mg, 5.0 mmol), 5% nickelocene (10 mg, 0.05 mmol), and PPh_3 (52 mg, 0.2 mmol) in 5 mL of THF after 96 h at room temperature the starting carbene complex **15** (200 mg, 76%) was recovered unaltered. (d) From a mixture of carbene complex **9** (312 mg, 1.0 mmol), acrylonitrile (265 mg, 5.0 mmol), 5% nickelocene (10 mg, 0.05 mmol), and PPh_3 (52 mg, 0.2 mmol) in 5 mL of THF after 96 h at room temperature was obtained 132 mg (76%) of **18c**[28] as a *cis*−*trans* (1.5:1) mixture.

Ni(PCl$_3$)$_4$. From a mixture of carbene complex **9** (156 mg, 0.5 mmol), methyl acrylate (215 mg, 5.0 mmol), 5% nickelocene (5 mg, 0.03 mmol), and PCl_3 (14 mg, 0.1 mmol) in 3 mL of THF after 72 h at room temperature was obtained 70 mg of a (2:2.6) mixture of cyclopropanes **18a** (70 mg, 76%, *cis*−*trans* 1:1 ratio) and methyl benzoate **11**.

Ni(P(O*i*-Pr)$_3$)$_4$. From a mixture of carbene complex **9** (156 mg, 0.5 mmol), methyl acrylate (215 mg, 5.0 mmol), 10% nickelocene (10 mg, 0.05 mmol), and P(O*i*-Pr)$_3$ (44 mg, 0.2 mmol) in 3 mL of THF after 48 h at room temperature was obtained 80 mg of a (2:2.4) mixture of cyclopropanes **18a** (29 mg, 22%, *cis*−*trans* 1:1 ratio) and methyl benzoate **11**.

General Procedure for the Cyclopropanation of Carbene Complexes Catalyzed by Ni(COD)$_2$. Ni(COD)$_2$ was placed in a Schlenk flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times). Then, a THF a solution of the carbene complex and the olefin was transferred via cannula. The resulting mixture was stirred under argon atmosphere at the temperature specified in each case until the disappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure, and the residue was dissolved in ETOAc and filtered through a short pad of Celite. After removal of the solvent in vacuo, the composition of the crude reaction was checked by ^{1}H NMR. The pure compounds were isolated by flash column chromatography on silica gel.

(a) From a mixture of carbene complex **9** (175 mg, 0.56 mmol), methyl acrylate (240 mg, 2.8 mmol), and 15% Ni(COD)$_2$ (14 mg, 0.08 mmol) in 2 mL of THF after 6 h at room temperature was obtained 110 mg (95%) of **18a** as a *cis*−*trans* (1.7:1) mixture (colorless oil). (b) From a mixture of carbene complex **15** (215 mg, 0.66 mmol), methyl acrylate (284 mg, 3.3 mmol), and 15% Ni(COD)$_2$ (17 mg, 0.10 mmol) in 3 mL of THF after 45 h at room temperature was obtained a (10:1) mixture of compounds **18b**[16a] (109 mg, 75%, *cis*−*trans* 1.4:1 ratio) and **19b**.

General Procedure for the Cyclopropanation of Carbene Complexes Catalyzed by Ni[PPh$_3$]$_3$.[12] (a) In a 25 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times), were placed 33 mg (0.05 mmol) of $NiCl_2(PPh_3)_2$, 105 mg (0.4 mmol) of PPh_3, and 65 mg (1.0 mmol) of Zn(0) powder. Then, anhydrous DMF (2 mL) was added, and the reaction mixture was stirred under argon atmosphere at room temperature for 30 min (the color of the solution changes from light blue to deep red). A solution of carbene complex **9** (312 mg, 1.0 mmol) and methyl acrylate (430 mg, 5.0 mmol) in 3 mL of anhydrous DMF was transferred via cannula, and the mixture was stirred for 20 h at room temperature. EtOAc was added to the resulting suspension and washed several times with water. The organic layer was separated, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, affording a (2:1) mixture of **18a** (120 mg, 58%, *cis*−*trans* 1:1 ratio) and compound **19a**. The same procedure was followed for 330 mg (0.5 mmol) of $NiCl_2(PPh_3)_2$, 840 mg (4 mmol) of PPh_3, 650 mg (10 mmol) of Zn(0) powder, carbene complex **9** (156 mg, 0.5 mmol), and methyl acrylate (215 mg, 2.5 mmol). After 16 h at room temperature a (2:21) mixture of **18a** (*cis*−*trans* 1:1 ratio) and compound **19a** was obtained.

General Procedure for the Cyclopropanation of Carbene Complexes Catalyzed by Ni-Raney. To a solution of the carbene complex and methyl acrylate (5 equiv) in EtOH contained in a 10 mL flame-dried airless flask provided with a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times), was added 1 mL of aqueous suspension of Ni-Raney. The reaction mixture was stirred under argon atmosphere at room temperature until the disappearance of starting carbene complex (checked by TLC). Then, the mixture was filtered and the residue washed with EtOH. The solvent was removed under reduced pressure, and the crude reaction was suspended in EtOAc and filtered through a short pad of Celite. After removal of the solvent in vacuo the residue was purified by flash column chromatography on silica gel.

(a) From a mixture of carbene complex **9** (100 mg, 0.32 mmol), methyl acrylate (140 mg, 1.6 mmol), and Ni-Raney (1 mL) after 18 h of reaction was obtained 34 mg (56%) of **19a** as a colorless oil. (b) From a mixture of carbene complex **15** (163 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), and Ni-Raney (1 mL) after 4 days of reaction was obtained 190 mg of a mixture of the starting carbene complex unaltered and unidentified products. (c) From a mixture of carbene complex **17** (175 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), and Ni-Raney (1 mL) after 24 h of reaction was obtained 53 mg (49%) of **19c** as a white solid.

Methyl 4-Oxo-6-phenyl-5-hexenoate, 19c. ^{1}H NMR (200 MHz): δ 7.53 (d, $J = 16.3$ Hz, 1H, $=$CH), 7.49 (m, 2H, ArH) 7.33 (m, 3H, ArH), 6.70 (d, $J = 16.3$ Hz, 1H, $=$CH), 3.64 (s, 3H, OCH_3), 2.96 (t, $J = 6.6$ Hz, 2H, CH_2), 2.64 (t, $J = 6.6$ Hz, 2H, CH_2). ^{13}C NMR (50 MHz): δ 197.9 (CO), 173.3 (COO), 142.9, 134.4, 130.5, 128.9, 128.3, 125.8 (aromatics C and CH), 51.8 (OCH_3), 35.2 (CH_2), 27.9 (CH_2). IR (CCl_4): ν 1742, 1695, 1672, 1614, 1165 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_3$: C 71.54, H 6.47. Found: C 71.78, H 6.75.

Pd-Catalyzed Dimerization of Carbene Complex 13 in the Presence of Olefins. To a THF solution of the carbene complex **13** (392 mg, 1 mmol) and the alkene (5 equiv) in a flame-dried airless flask provided with a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times), $Pd(OAc)_2$ (0.1 mmol, 10%) and Et_3N (1.1 mmol) were added at room temperature, and the mixture was stirred until the disappearance of the starting carbene complex (from 1 h to 1.5 h)

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[28] (a) Reissig, H.-U.; Wienand, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129. (b) Reissig, H.-U.; Buchert, M.; Hoffmann, M. *Chem. Ber.* **1995**, *128*, 605.

(checked by TLC). The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and filtered through Celite. After removal of the solvent in vacuo the residue was purified by flash column chromatography on silica gel (10:1 hexane/EtOAc) to give the dimerization product **14** as a *E*/*Z* mixture of isomers (2:1). Methyl acrylate (56%); styrene (58%); 1-hexene (51%).

Ni-Catalyzed Dimerization of Carbene Complex 9 in the Presence of 1-Hexene. Ni(PPh$_3$)$_4$. (a) Following the experimental procedure described above, from a mixture of carbene complex **9** (312 mg, 1.0 mmol), 1-hexene (420 mg, 5.0 mmol), 5% nickelocene (10 mg, 0.05 mmol), and PPh$_3$ (52 mg, 0.2 mmol) in 5 mL of THF after 120 h at room temperature was obtained 120 mg of a (4.6:27) mixture of compounds **10** (*E*/*Z* isomers in the ratio 3.6:1) and methyl benzoate **11**. (b) Following the experimental procedure described above, from a mixture of carbene complex **9** (312 mg, 1.0 mmol), 1-hexene (420 mg, 5.0 mmol), 10% nickelocene (19 mg, 0.1 mmol), and PPh$_3$ (105 mg, 0.4 mmol) in 5 mL of THF after 24 h at 50 °C was obtained 235 mg of a (4.5:7) mixture of compounds **10** (*E*/*Z* isomers in the ratio 3.5:1) and methyl benzoate **11**. (c) Following the experimental procedure described above, from 330 mg (0.5 mmol) of NiCl$_2$(PPh$_3$)$_2$, 840 mg (4 mmol) of PPh$_3$, 650 mg (10 mmol) of Zn(0) powder, carbene complex **9** (156 mg, 0.5 mmol), and 1-hexene (210 mg, 2.5 mmol), after 20 h at room temperature was obtained a (2:1) mixture of compounds **10** (*E*/*Z* isomers in the ratio 1:1) and methyl benzoate **11**.

Ni(COD)$_2$. (a) Following the experimental procedure described above, from a mixture of carbene complex **9** (152 mg, 0.52 mmol), 1-hexene (218 mg, 2.6 mmol), and 15% Ni(COD)$_2$ (13 mg, 0.08 mmol) in 2 mL of THF after 24 h at room temperature was isolated 60 mg (96%) of compound **10** as a white solid and as a mixture of isomers (*E*/*Z* 4.6:1). (b) Following the experimental procedure described above, from a mixture of carbene complex **9** (187 mg, 0.6 mmol), 1-hexene (252 mg, 3 mmol), and 20% Ni(COD)$_2$ (20 mg, 0.12 mmol) in boiling THF (3 mL) after 6 h of reaction was obtained 70 mg (97%) of compound **10** as a mixture of isomers (*E*/*Z* 5:1).

General Procedure for the Cyclopropanation of Carbene Complexes Catalyzed by Cu(0). In a 10 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times), were place the carbene complex and Cu(0) powder. Then, a solution of methyl acrylate in anhydrous and degassed MeCN was added, and the reaction mixture was stirred under argon atmosphere at the temperature indicated in each case until the disappearance of starting carbene complex (checked by TLC). The solvent was removed under reduced pressure, and the crude reaction was suspended in EtOAc and filtered through a short pad of Celite. After removal of the solvent in vacuo the composition of the crude reaction was checked by ^{1}H NMR. The pure compounds were isolated by flash column chromatography on silica gel.

(a) From a mixture of carbene complex **9** (156 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), and 20% Cu(0) powder (6 mg, 0.1 mmol) after 48 h at room temperature was obtained a (2.6:1) mixture of cyclopropanes **18a** (60 mg, 58%, *cis*−*trans* 1:1.6 ratio) and methyl benzoate **11**. (b) From a mixture of carbene complex **9** (156 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), and 20% Cu(0) powder (6 mg, 0.1 mmol) after 24 h at 40 °C was obtained a (3.9:1) mixture of cyclopropanes **18a** (78 mg, 76%, *cis*−*trans* 1:2 ratio) and methyl benzoate **11**. (c) From a mixture of carbene complex **17** (50 mg, 0.14 mmol), methyl acrylate (61 mg, 0.71 mmol), and 20% Cu(0) powder (2 mg, 0.03 mmol) after 96 h at room temperature was obtained 20 mg (81%) of methyl benzoate **11** together with trace amounts of the cyclopropanation product **18d**. (d) From a mixture of carbene complex **15** (100 mg, 0.31 mmol), methyl acrylate (132 mg, 1.5 mmol), and 20% Cu(0) powder (4 mg, 0.06 mmol) after 24 h at room temperature was obtained 40 mg (80%) of 2,3-dibenzyloxy-2-butene as a mixture of isomers (*E*/*Z* 1:2).[4a]

General Procedure for Zn(0)/CuCl-Catalyzed Carbene Ligand Transfer of Chromium(0) Carbene Complexes with Methyl Acrylate. In a 10 mL flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3 times) and equipped with a microcondenser, were placed Zn(0) powder and CuCl. Then, Et$_2$O was added and the mixture was heated until reflux under argon atmosphere for 1 h. Once the reaction mixture has reached rt, the carbene complex and methyl acrylate were added and the mixture was stirred until the disappearance of starting carbene complex (checked by TLC). The solvent was removed under reduced pressure, and the crude reaction was dissolved in ethyl acetate and filtered through a short pad of Celite. After removal of the solvent in vacuo the composition of the crude reaction was checked by ^{1}H NMR. The pure compounds were isolated by flash column chromatography on silica gel.

(a) From a mixture of carbene complex **9** (156 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), Zn(0) powder (65 mg, 1.0 mmol), and CuCl (99 mg, 1.0 mmol) after 24 h of reaction was obtained 77 mg (80%) of compound **19a** as a white solid. (b) From a mixture of carbene complex **17** (176 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), Zn(0) powder (65 mg, 1.0 mmol), and CuCl (99 mg, 1.0 mmol) after 24 h of reaction was obtained 69 mg (63%) of compound **19c** together with trace amounts of a *cis*−*trans* mixture of cyclopropanes **18d**. (c) From a mixture of carbene complex **15** (163 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), Zn(0) powder (65 mg, 1.0 mmol), and CuCl (99 mg, 1.0 mmol) after 168 h of reaction was obtained 100 mg of a mixture of methyl benzoate **11** and unreacted starting carbene **15**. (d) From a mixture of carbene complex **20** (175 mg, 0.5 mmol), methyl acrylate (215 mg, 2.5 mmol), Zn(0) powder (65 mg, 1.0 mmol), and CuCl (99 mg, 1.0 mmol), after 192 h of reaction, was recovered 170 mg of the starting carbene complex **20** unaltered.

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