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Control over the *E*/*Z* Selectivity of the Catalytic Dimerization of Group 6 (Fischer) Metal Carbene Complexes

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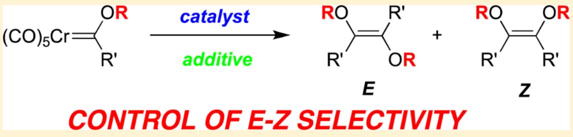
Ⓢ *Supporting Information*

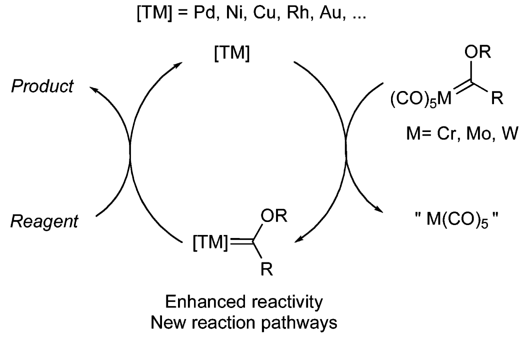
ABSTRACT: The systematic investigation of the effect of different catalysts and additives in the reaction of self-dimerization of alkoxychromium(0) (Fischer) carbene complexes resulted in the selection of $Pd(P^tBu_3)_2$ to effect this transformation with good to excellent *E* selectivities and acceptable to excellent chemical yields. This catalyst will allow the control of the geometry in the synthesis of polyconjugated olefins, one emerging application of these catalytic reactions.



INTRODUCTION

Transmetalation processes from group 6 Fischer metal carbene complexes to late transition metals (Pd, Pt, Cu, Ni, Rh, Au, etc.) lead to new carbene complexes, exhibiting exceedingly different chemical behavior with respect to the starting metal complex.[1] Thus, the new carbene complexes may show an enhanced reactivity compared to the precursor complex[2] or they may undergo different reaction pathways, opening doors to the synthesis of new classes of compounds (Scheme 1). This fascinating process has been profusely exploited since our original report on the self-dimerization of chromium(0) and tungsten(0) carbene complexes promoted by Pd catalysts.[3]

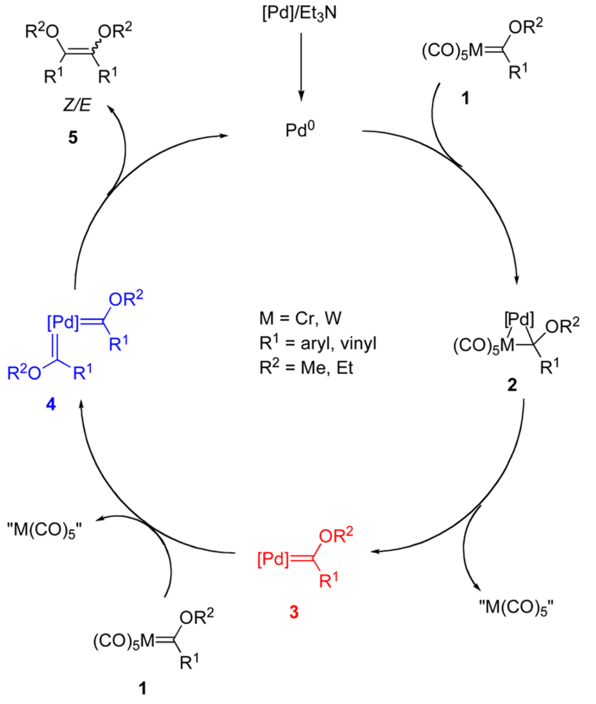
Scheme 1. Effect of Transmetalation in the Reactivity of Group 6 Metal Carbene Complexes



The reaction mechanism for this transformation, which has been proposed on the basis of experimental and theoretical studies,[3,4] is summarized in Scheme 2. Accordingly, a transmetalation reaction of the carbene ligand from complex **1** to the palladium(0) catalyst leads to a new Pd−carbene complex such as **3**, through a heterobimetallic intermediate **2** that evolves to **3** by extrusion of the $[M(CO)_5]$ (M = Cr, W) fragment, mediated by coordination of the solvent. Subsequent transmetalation from a new molecule of the carbene complex **1** leads to the Pd(0) bis-carbene complex **4**, which produces a mixture of the *Z*/*E* olefins **5** with concomitant regeneration of the catalyst.

The key intermediates in this catalytic cycle are the mono-carbene complexes **3** and bis-carbene complexes **4**. Very recently,[5] Albéniz and Espinet isolated the first Pd alkoxycarbene **7** from the reaction of the W(0) Fischer carbene complex **6** and $[PdCl_2(NCMe)_2]$.[6] In addition, related Cu(I)[7]

Scheme 2. Catalytic Cycle for the Self-Dimerization of Group 6 Carbene (Fischer) Complexes in the Presence of Pd Catalysts



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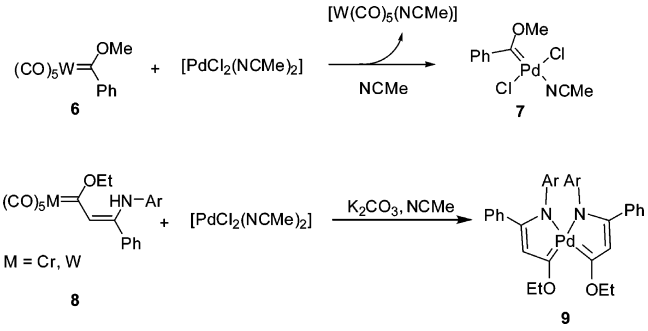
or Au(I)[8] mono-carbene complexes have been isolated and fully characterized in similar transformations. Moreover, the reaction of β-arylamino-substituted chromium(0) and tungsten(0) carbene complexes **8** with Pd reagents leads to the mononuclear Pd bis-carbene complexes **9**,[9] the putative second key intermediates shown in Scheme 2 (Scheme 3).

Scheme 3. Examples of Isolation of Mono- and Bis-Carbene Pd Complexes by Transmetalation of Group 6 Fischer Carbene Complexes



The main shortcoming of the catalytic self-dimerization of group 6 metal carbene complexes is the lack of E/Z selectivity. This is highly important due to the emerging applications of this process toward the synthesis of polyconjugated olefins,[10] some of which have been patented as conjugated polymers and devices.[11] Therefore, the control of the E/Z selectivity is required for this method to become of full utility in synthesis. Reported herein is a study to accomplish this challenging goal.

■ RESULTS AND DISCUSSION

According to the previously reported experimental and computational studies of the transmetalation process (see above) and to the plethora of literature on the influence of ligands in the outcome of Pd-catalyzed reactions,[12] we hypothesized that the ligand directly attached to the catalyst may play a fundamental role in the E/Z selectivity of the self-dimerization reactions of group 6 metal (Fischer) carbenes. Thus, series of phosphines differing in their steric volume were initially tested against the self-dimerization of complex **10** (Scheme 4, Table 1) using $PdCl_2(MeCN)_2$ as the catalyst. The E/Z ratio of olefins **11** in the absence of an external added phosphine was 1/1.3 in THF and was nearly independent of the reaction solvent (1/1.2 in MeCN, entries 1 and 2 in Table 1). Addition of the bulky P^tBu_3 results in a small decrease of the selectivity (1/1.1, entry 3), while the best selectivities were observed for PPh_3 (1/4.4) and PMe_3 (1/2.4), both showing a moderate selectivity. It is noteworthy that in all cases the reaction was Z selective. Other sources of Pd were tested against the addition of P^tBu_3. The use of $Pd(OAc)_2$ proportionates a selectivity of 1/3.5, slightly increased from that obtained without additive (1/2),[3,4] while $[Pd(allyl)Cl]_2$ gave essentially the same selectivity as $PdCl_2(MeCN)_2$.

Scheme 4. Self-Dimerization of Carbene Complex 10

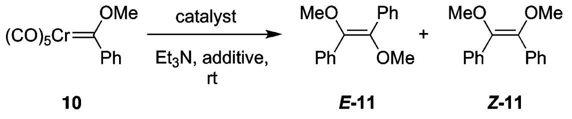


Table 1. Self-Dimerization Reactions of Complex 10 in the Presence of Phosphines and Phosphites

entry	cat.[a]	solvent	additive[b]	E/Z[c]
1	$PdCl_2(MeCN)_2$	THF	none	1/1.3
2	$PdCl_2(MeCN)_2$	MeCN	none	1/1.2
3	$PdCl_2(MeCN)_2$	MeCN	P^tBu_3	1/1.1
4	$PdCl_2(MeCN)_2$	MeCN	PPh_3	1/4.4
5	$PdCl_2(MeCN)_2$	MeCN	PMe_3	1/2.4
6	$Pd(OAc)_2$	MeCN	none	1/2[3b]
7	$Pd(OAc)_2$	MeCN	P^tBu_3	1/3.5
8	$[Pd(allyl)Cl]_2$	MeCN	none	1/1.5
9	$[Pd(allyl)Cl]_2$	MeCN	P^tBu_3	1/1
10	$PdCl_2(MeCN)_2$	MeCN	$P(OMe)_3$	1/1.5
11	$PdCl_2(MeCN)_2$	MeCN	$P(OEt)_3$	1/1.3
12	$Pd(OAc)_2$	MeCN	$P(OMe)_3$	1/3.2

[a] 5% of catalyst was used in all cases. [b] Et_3N (1 mmol/mmol of carbene was used in all cases as coadditive). [c] Determined by integration of the ^1H NMR signals corresponding to MeO groups in the reaction mixtures: 3.61 ppm for the Z isomer and 3.42 ppm for the E isomer.[13a]

The use of phosphites follows the same pattern as that observed for phosphines. Thus, while no changes were observed in the selectivity of the reactions using $PdCl_2(MeCN)_2$ (entries 10 and 11), increased Z selectivity was observed when $Pd(OAc)_2$ was the catalyst (entry 12, Table 1).

N-heterocyclic carbene (NHC) species **12**−**15** (Figure 1) were also tested as additives in the reaction of self-dimerization of carbene complex **10**. However, additives **12**−**14** did not produce changes in the E/Z selectivities of the reaction that were equal to those obtained in the absence of additive (E/Z = 1/1.3), while NHC **15** proportionates a slight increase in selectivity (E/Z = 1/1.5).

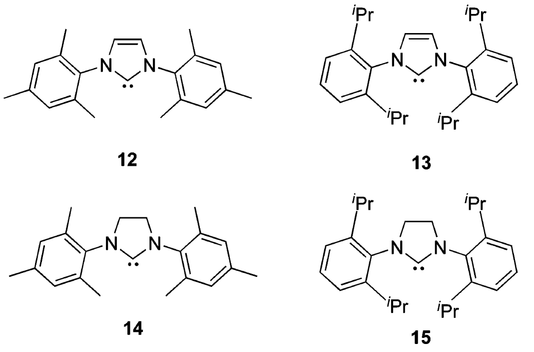


Figure 1. NHC additives used in this work.

The self-dimerization reactions of pentacarbonyl[ethoxyphenylcarbene]chromium(0) **16** were examined next (Scheme 5) to determine the effect of the substituent at the oxygen atom attached to the carbene carbon atom on the E/Z selectivity of the corresponding olefins **17**. The results are collected in Table 2.

Scheme 5. Self-Dimerization of Ethoxycarbene Complex 16

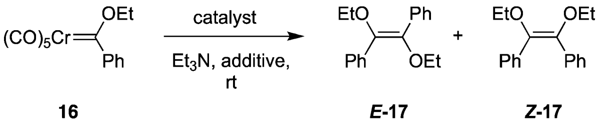


Table 2. Self-Dimerization Reactions of Complex 16 in the Presence of Phosphines and Phosphites

entry	cat.[a]	solvent	additive[b]	*E*/*Z*[c]
1	$PdCl_2(MeCN)_2$	MeCN	none	1.2/1
2	$PdCl_2(MeCN)_2$	MeCN	P^tBu_3	9.4/1
3	$PdCl_2(MeCN)_2$	MeCN	PMe_3	1/1.4
4	$Pd(OAc)_2$	MeCN	none	1/1.7
5	$Pd(OAc)_2$	MeCN	P^tBu_3	7/1
6	$[Pd(allyl)Cl]_2$	MeCN	none	1/1.3
7	$[Pd(allyl)Cl]_2$	MeCN	P^tBu_3	2.7/1
8	$Pd_2(dba)_3$	MeCN	none	1/2.4
9	$Pd_2(dba)_3$	MeCN	P^tBu_3	1.7/1
10	$Pd(dba)_2$	MeCN	none	1/2.8
11	$Pd(dba)_2$	MeCN	P^tBu_3	1/1.7
12	$Pd(OAc)_2$	MeCN	$P(OMe)_3$	1/1.8
13	$PdCl_2(MeCN)_2$	MeCN	$P(OEt)_3$	1/1.1
14	$PdCl_2(Me_3CN)_2$	MeCN	$P(OMe)_3$	1/1.3
15	$[Pd(allyl)Cl]_2$	MeCN	PPh_3	1/1.1
16	$[Pd(allyl)Cl]_2$	MeCN	$AsPh_3$	1/1.7
17	$[Pd(allyl)Cl]_2$	MeCN	$BiPh_3$	1/1.1

[a] 5% of catalyst was used in all cases. [b] Et_3N (1 mmol/mmol of carbene was used in all cases as coadditive). [c] Determined by integration of the ^1H NMR signals corresponding to CH_2O groups in the reaction mixtures: 3.80 ppm for the *Z* isomer and 3.57 ppm for the *E* isomer.[13b]

Table 3. Self-Dimerization Reactions of Complexes 10 and 16 in the Presence of Catalysts Incorporating Phosphine Ligands

entry	cat.[a]	complex	additive[b]	*E*/*Z*[c]
1	$Pd(PPh_3)_4$	**10**	none	1/4.1
2	$PdCl_2(PPh_3)_2$	**10**	none	1/1.8
3	$Pd(P^tBu_3)_2$	**10**	none	9.4/1
4	$Pd(dppe)_2$	**10**	none	5.7/1
5	$Pd(PPh_3)_4$	**16**	none	1/2.6
6	$PdCl_2(PPh_3)_2$	**16**	none	1/1.2
7	$PdCl_2(PPh_3)_2$	**16**	P^tBu_3	2.4/1
8	$Pd(P^tBu_3)_2$	**16**	none	15.7/1
9	$Pd(dppe)_2$	**16**	none	1/2.2

[a] 5% of catalyst was used in all cases. [b] Et_3N (1 mmol/mmol of carbene was used in all cases as coadditive, except for Pd(0) catalysts). [c] Determined by integration of the ^1H NMR signals in the reaction mixtures.

The results in Table 2 show a different trend than that obtained for complex **10**. In the absence of additives, the use of $PdCl_2(MeCN)_2$ as the catalyst affords the *E* isomer as the major isomer (although still close to an equimolar ratio). Strikingly, addition of P^tBu_3 resulted in an excellent increase in the *E* selectivity for $Pd(OAc)_2$ and $PdCl_2(MeCN)_2$ catalysts (up to 9.4/1 when the latter catalyst was used). The use $[Pd(allyl)Cl]_2$ leads to poorer but still noticeable *E* selectivities (*E*/*Z* = 2.7/1). Other additives (phosphites, PPh_3, $AsPh_3$, $BiPh_3$)[3] give selectivities close to 1/1. In contrast to complex **10**, the use of NHCs carbenes **12**−**15** (Figure 1) in the self-dimerization reaction proportionates low, albeit noticeable, changes in selectivities. Thus, NHC **12** was nearly unselective (*E*/*Z* = 1/1.1), NHCs **14** and **15** were slightly *Z* selective (*E*/*Z* = 1/1.4 and 1/1.3, respectively), and NHC **13** was slightly *E* selective (*E*/*Z* 1.3/1).

The use of Pd(0) catalysts having monodentate phosphine ($PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, and $Pd(P^tBu_3)_2$) and bidentate diphosphine ligands ($Pd(dppe)_2$) was studied next (the combination of $PdCl_2(PPh_3)_2/P^tBu_3$ as the additive was also tested for comparison reasons). The results of these reactions with complexes **10** and **16** are collected in Table 3. For both complexes, the best results were obtained with $Pd(P^tBu_3)_2$ (which affords a remarkable 15.7/1 *E*/*Z* selectivity for carbene complex **16**). The use of $Pd(PPh_3)_4$ led also to an increased selectivity, but now favoring the *Z* isomer. $Pd(dppe)_2$ catalyst produces good *E* selectivities (5.7/1) with carbene complex **10** while the selectivity decreases and inverts for complex **16** (1/2.2). The use of $PdCl_2(PPh_3)_2$ with added P^tBu_3 reversed the selectivity observed in the absence of the additive (1/1.2 vs 2.4/1), but the *E* selectivity is considerably lower than that obtained with $Pd(P^tBu_3)_2$.

Results in Tables 1−3 pointed to P^tBu_3 (as additive or directly as $Pd(P^tBu_3)_2$) and the use of an ethoxy carbene instead of a methoxy carbene complex as the optimum combination for obtaining high *E* selectivities. The influence of the amount of the $Pd(P^tBu_3)_2$ catalyst in the *E*/*Z* selectivity was tested next in the self-dimerization of complex **16** (Table 4). The selectivity is maintained using higher loads of catalyst (up to 20%), while it steadily decreases with lower catalyst loads (reaching 1/1 ratio for catalyst loads of 1%). Therefore, the optimum balance of catalyst load/selectivity was 5% mol of catalyst/mol of carbene complex.

Table 4. Self-Dimerization Reactions of Complex 16 in the Presence of Different Amounts of $Pd(P^tBu_3)_2$

entry	cat. load (%)[a]	*E*/*Z*[b]
1	20	13.6/1
2	10	14.0/1
3	5	15.7/1
4	2.5	4.6/1
5	1	1.6/1
6	0.5	1/1

[a] Referenced to carbene complex. [b] Determined by integration of the ^1H NMR signals in the reaction mixtures.

To test these conclusions, different ethoxychromium(0) complexes **18**−**25** were reacted with $PdCl_2(MeCN)_2$ in the absence of additives or in the presence of 5% of P^tBu_3 (Table 5). From the data in Table 4, it becomes obvious that the trend observed in Tables 2 and 3 also holds in complexes **18**−**22**, with the *E* isomer formation being the main reaction product in the presence of P^tBu_3 (the exception is complex **23**, forming a 1/2.2 *E*/*Z* mixture). To demonstrate the ability of $Pd(P^tBu_3)_2$ as catalyst for the selective preparation of *E* olefins, the self-dimerization reaction was conducted in a preparative scale using $Pd(P^tBu_3)_2$ as the catalyst (Scheme 6). While yields were usually acceptable (complexes **16**, **19**−**21**, and **23**−**25**) in some cases (complexes **18** and **22**) the corresponding olefins were obtained together with variable amounts of the corresponding esters due to oxidation of the starting materials[14] (probably as a consequence of the instability of the intermediate Pd mono- or bis-carbene complexes having bulky phosphine ligands). Despite that, it is clear in all cases that the use of $Pd(P^tBu_3)_2$ leads to the favored formation of the corresponding *E* olefin.

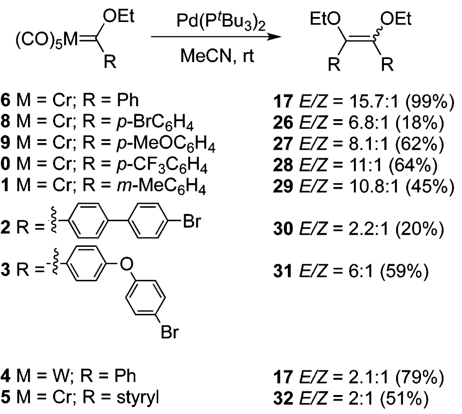
Finally, pentacarbonyl[(benzyloxy)(methyl)carbene]-chromium(0) (**33**) was reacted in the presence of $Pd(P^tBu_3)_2$ (5%) under the usual reaction conditions. The self-dimerization product **34** was obtained in a 70% yield as a 1/1.6 *E*/*Z* mixture (Scheme 7). Although the selectivity of the reaction was low, it

Table 5. Catalytic Self-Dimerization Reactions of Fischer Carbene Complexes 18−25

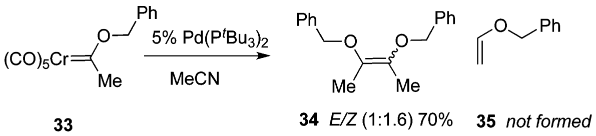
entry	cat.[a]	complex	additive[b]	E/Z[c]
1	$PdCl_2(MeCN)_2$	**18**	none	1/1
2	$PdCl_2(MeCN)_2$	**18**	P^tBu_3	5.8/1
3	$Pd(P^tBu_3)_2$	**18**	none	6.8/1
4	$PdCl_2(MeCN)_2$	**19**	none	1/1.1
5	$PdCl_2(MeCN)_2$	**19**	P^tBu_3	6/1
6	$Pd(P^tBu_3)_2$	**19**	none	8.1/1
7	$PdCl_2(MeCN)_2$	**20**	none	1.5/1
8	$PdCl_2(MeCN)_2$	**20**	P^tBu_3	1.5/1
9	$Pd(P^tBu_3)_2$	**20**	none	11/1
10	$PdCl_2(MeCN)_2$	**21**	none	1/1.5
11	$PdCl_2(MeCN)_2$	**21**	P^tBu_3	7.6:1
12	$Pd(P^tBu_3)_2$	**21**	none	10.8/1
13	$PdCl_2(MeCN)_2$	**22**	none	1/1.4
14	$PdCl_2(MeCN)_2$	**22**	P^tBu_3	1.7/1
15	$Pd(P^tBu_3)_2$	**22**	none	2.2/1
16	$PdCl_2(CH_3CN)_2$	**23**	none	1/2.5
17	$PdCl_2(CH_3CN)_2$	**23**	P^tBu_3	1/2.2
18	$Pd(P^tBu_3)_2$	**23**	none	6/1
19	$Pd(P^tBu_3)_2$	**24**	none	2.1/1
20	$Pd(P^tBu_3)_2$	**25**	none	2.0/1

[a] 5% of catalyst was used in all cases. [b] Et_3N (1 mmol/mmol of carbene was used in all cases as coadditive, except for $Pd(P^tBu_3)_2$ catalyst). [c] Determined by integration of the ^1H NMR signals corresponding to CH_2O groups in the reaction mixtures.

Scheme 6. Self-Dimerization of Complexes 16 and 18−25 Catalyzed by $Pd(P^tBu_3)_2$



Scheme 7. Self-Dimerization of the Aliphatic Carbene Complex 33



is worthy noting that while complex **33** is prone to experience β-elimination processes to yield enol ether **35** in the presence of several Pd(0) catalysts,[3b] $Pd(P^tBu_3)_2$ behaves in this case as $Pd(PPh_3)_4$, which gave **34** as a 1/1.1 E/Z mixture in 87% yield.[3b]

CONCLUSIONS

From the systematic investigation of the effects of different catalysts and additives in the reaction of self-dimerization of alkoxychromium(0) (Fischer) carbene complexes, it can be concluded that the E/Z selectivity of the process can be indeed controlled with the proper selection of these variables. Thus, the use of $Pd(P^tBu_3)_2$ and chromium(0) ethoxycarbene complexes is recommended in order to obtain good to excellent E selectivities and acceptable to excellent chemical yields in most cases. This catalyst will allow the control of the geometry in the synthesis of polyconjugated olefins, one of the main emerging applications of these reactions.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere. All solvents used in this work were purified by distillation and were freshly distilled immediately before use. Acetonitrile (MeCN) and triethylamine (Et_3N) were distilled from calcium hydride, whereas tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified using a Pure Solv PS-MD-5 system. Flame-dried glassware was used for moisture-sensitive reactions. Silica gel (Merck: 230−400 mesh) was used as stationary phase for purification of crude reaction mixtures by flash column chromatography. Identification of products was made by thin-layer chromatography (Kieselgel 60F-254). UV light (λ 254 nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. NMR spectra were recorded at 25 °C in $CDCl_3$, at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts are given in ppm relative to $CDCl_3$ (^1H, 7.27 ppm; ^{13}C, 77.0 ppm). IR spectra were taken on a MIR (8000−400 cm^{-1}) spectrometer as solid films by slow evaporation of the solvent using the ATR (attenuated total reflectance) technique. MS spectra (HRMS) were acquired on a QTOF mass spectrometer. All commercially available products were used without further purification. The following metal carbenes were prepared according to previously described methods: pentacarbonyl[(methoxy)(phenyl)carbene]chromium(0),[15] pentacarbonyl[(ethoxy)(phenyl)carbene]chromium(0),[16] pentacarbonyl[(p-bromophenyl)(ethoxy)carbene]chromium(0),[17] pentacarbonyl[(p-methoxyphenyl)(ethoxy)carbene]chromium(0),[18] pentacarbonyl[(m-tolyl)(ethoxy)carbene]chromium(0),[19] pentacarbonyl[(ethoxy)(phenyl)carbene]tungsten(0),[20] pentacarbonyl[(2E)-1-ethoxy-3-phenyl-2-propen-1-ylidene]chromium(0),[21] pentacarbonyl[(benzyloxy)(methyl)carbene]chromium(0).[22]

Pentacarbonyl[(p-trifluoromethylphenyl)(ethoxy)carbene]chromium(0) (20). To a solution of 1-bromo-4-(trifluoromethyl)benzene (0.77 g, 3.42 mmol) in 4 mL of dry Et_2O was added 2.1 mL (3.42 mmol) of n-BuLi (1.6 M in hexanes) at −78 °C. After it was stirred for 30 min, the solution was transferred via cannula at 0 °C to a suspension of $Cr(CO)_6$ (0.75 g, 3.42 mmol) in 8 mL of Et_2O at room temperature. The mixture was refluxed for 3 h, the solvent was removed under reduced pressure, and the residue was dissolved in 6.3 mL of degassed water. Et_3OBF_4 (1.13 g, 5.95 mmol) was added slowly to the solution at 0 °C and stirred for 10 min. The mixture was extracted with EtOAc and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was purified by flash chromatography (hexane) to yield 0.8 g (59%) of a dark red solid; mp 46−48 °C. ^1H NMR (300 MHz, ppm): δ 7.69 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 4.98 (br s, 2H), 1.69 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, ppm): δ 348.4, 223.8, 215.7, 156.3, 131.2, 130.0, 125.4, 122.1, 77.5, 15.1. IR (ATR): ν 2064, 1928 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_9CrF_3O_6$ $[M + H]^+$ 394.9840, found 394.9850.

Pentacarbonyl[(p-(p-bromophenyl)phenyl)(ethoxy)carbene]chromium(0) (22). To a solution of 4,4′-dibromobiphenyl (1.42 g, 4.54 mmol) in 5.4 mL of dry Et_2O was added 2.8 mL (4.54 mmol) of n-BuLi (1.6 M in hexanes) at −78 °C. After it was stirred for 30 min, the solution was transferred via cannula at 0 °C to a suspension of $Cr(CO)_6$ (1 g, 4.54 mmol) in 2.7 mL of Et_2O at room temperature. The mixture was refluxed for 3 h, the solvent was removed under reduced pressure, and the residue was dissolved in 5.4 mL of degassed water. Et_3OBF_4 (1.47 g, 7.72 mmol) was added slowly to the solution at 0 °C and stirred for 10 min. The mixture was extracted with EtOAc and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was purified by flash chromatography (hexane) to yield 570 mg (26%) of a dark red solid; mp 108−110 °C. ^{1}H NMR (300 MHz, ppm): δ 7.68−7.41 (m, 8H), 5.07 (q, J = 7.1 Hz, 2H), 1.72 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, ppm): δ 346.5, 224.0, 216.3, 152.5, 141.9, 138.6, 132.0, 128.6, 126.5, 124.5, 122.4, 77.2, 15.2. IR (ATR): ν 2064, 1928 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{13}BrCrO_6$ [M + H]$^+$ 480.9386, found 480.9392.

Pentacarbonyl[(*p*-bromophenoxyphenyl)(ethoxy)carbene]-chromium(0) (23). To a solution of bis(4-bromophenyl) ether (1.49 g, 4.54 mmol) in 5.4 mL of dry Et_2O was added 2.8 mL (4.54 mmol) of *n*-BuLi (1.6 M in hexanes) at −78 °C. After it was stirred for 30 min, the solution was transferred via cannula at 0 °C to a suspension of $Cr(CO)_6$ (1 g, 4.54 mmol) in 2.7 mL of Et_2O at room temperature. The mixture was refluxed for 3 h, the solvent was removed under reduced pressure, and the residue was dissolved in 5.4 mL of degassed water. Et_3OBF_4 (1.47 g, 7.72 mmol) was added slowly to the solution at 0 °C and stirred for 10 min. The mixture was extracted with EtOAc and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was purified by flash chromatography (hexane) to yield 1.1 g (47%) of a dark red solid; mp 84−86 °C. ^{1}H NMR (300 MHz, ppm): δ 7.59 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.00−6.95 (m, 4H) 5.14 (q, J = 7.1 Hz, 2H), 1.72 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, ppm): δ 342.0, 223.8, 216.5, 160.1, 154.8, 148.4, 133.0, 128.0, 121.7, 117.2, 117.0, 77.2, 17.9. IR (ATR): ν 2059, 1926 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{13}BrCrO_7$ [M + H]$^+$ 496.9335, found 496.9357.

General Procedure for Carbene Ligand Dimerization. *Method A.* To a solution of the corresponding alkoxycarbene complex (1 mmol) in MeCN (6 mL/mmol carbene complex) were added the $PdCl_2(MeCN)_2$ catalyst (5%) and the corresponding additive (0.1 mmol) and Et_3N (1 mmol/mmol of carbene complex). The reaction mixture was stirred at room temperature until total disappearance of the starting material (checked by TLC). The solvent was then removed under reduced pressure. The residue was dissolved in EtOAc, the solution was filtered through a short pad of Celite, and finally the solvent was removed again under reduced pressure. An *E*/*Z* isomer mixture was obtained. The crude product was then purified by flash column chromatography (hexane/EtOAc 100/1). This method was used for characterizing both *E* and *Z* isomers.

Method B. To a solution of the corresponding alkoxycarbene complex (1 mmol) in MeCN (6 mL/mmol of carbene complex) was added $Pd(P^tBu_3)_2$ (5%). The reaction mixture was stirred at room temperature until total disappearance of the starting material (checked by TLC). The solvent was then removed under reduced pressure. The residue was dissolved in EtOAc, the solution was filtered through a short pad of Celite, and finally the solvent was removed again under reduced pressure. A mixture of *E* and *Z* isomers was obtained, together with variable amounts of the corresponding ester formed either by oxidation of the starting carbene complex or by oxidation of Pd carbene intermediates.[14] The crude product was then purified by flash column chromatography (hexane/EtOAc 100/1).[23]

(*Z*)-, and (*E*)-α,β-Diethoxystilbene (17).[13b] *Method A.* Carbene complex **16** (200 mg, 0.61 mmol), Pd catalyst (0.031 mmol) and Et_3N (91 μL, 0.61 mmol) were reacted for 3 h, to yield compound **17** as a white solid (70 mg, 82%, *E*/*Z* = 1.2/1). *Z* isomer: ^{1}H NMR (300 MHz) δ 8.1−7.1 (m, 10H), 3.80 (q, J = 7.2 Hz, 4H), 1.15 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz) δ 144.1, 135.4, 129.8, 127.9, 127.5, 66.4, 15.2; IR (ATR): 1599, 1259 cm^{-1}. *E* isomer: ^{1}H NMR (300 MHz) δ 8.1−7.1 (m, 10H), 3.57 (q, J = 7.1 Hz, 4H), 1.15 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz) δ 142.6, 134.7, 128.3, 127.8, 127.3, 65.9, 15.2. IR (ATR) 1665, 1351 cm^{-1}.

Method B. Carbene complex **16** (200 mg, 0.61 mmol) and $Pd(P^tBu_3)_2$ (16 mg, 0.008 mmol) were reacted for 7 h, to yield compound **17** as a white solid (80 mg, 99%, *E*/*Z* = 15.7/1).

Method B. Carbene complex **24** (50 mg, 0.11 mmol) and $Pd(P^tBu_3)_2$ (0.006 mmol) were reacted for 28 h, to yield compound **17** as a white solid (12 mg, 79%, *E*/*Z* = 2.1/1).

(*Z*)- and (*E*)-1,2-Bis(*p*-bromophenyl)-1,2-diethoxyethylene (26). *Method A.* Carbene complex **18** (200 mg, 0.49 mmol), Pd catalyst (0.025 mmol), and Et_3N (70 μL, 0.49 mmol) were reacted for 6 h, to yield compound **26** as a white solid (100 mg, 96%, *E*/*Z* = 1/1); mp 77−79 °C. *Z* isomer: ^{1}H NMR (300 MHz) δ 7.32 (d, J = 8.7 Hz, 4H), 7.05 (d, J = 8.7 Hz, 4H), 3.77 (q, J = 7.0 Hz, 4H), 1.32 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz) δ 142.1, 134.1, 131.6, 131.1, 121.5, 66.1, 15.5; IR (ATR): ν 1274, 1107, 1013, 820. *E* isomer: ^{1}H NMR (300 MHz) δ 7.65 (d, J = 8.7 Hz, 4H), 7.53 (d, J = 8.7 Hz, 4H), 3.52 (q, J = 7.1 Hz, 4H), 1.13 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz) δ 143.8, 133.5, 131.2, 130.0, 121.5, 66.6, 15.3. IR (ATR): ν 1150, 1105, 1014, 834 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{19}Br_2O_2$ [M + H]$^+$ 425.9780, found 425.9776.

Method B. Carbene complex **18** (200 mg, 0.49 mmol) and $Pd(P^tBu_3)_2$ (13 mg, 0.025 mmol) were reacted for 18 h, to yield compound **26** as a white solid (18 mg, 18%, *E*/*Z* = 6.8/1).

(*Z*)- and (*E*)-1,2-Diethoxy-1,2-bis(*p*-methoxyphenyl)ethylene (27). *Method A.* Carbene complex **19** (50 mg, 0.14 mmol), Pd catalyst (0.007 mmol), and Et_3N (20 μL, 0.14 mmol) were reacted for 4 h, to yield compound **27** as a pale yellow solid (20 mg, 89%, *E*/*Z* = 1/1.1); mp 78−80 °C. *Z* isomer: ^{1}H NMR (300 MHz) δ 7.12 (d, J = 8.7 Hz, 4H), 6.71 (d, J = 8.7 Hz, 4H), 3.77 (s, 6H), 3.76 (q, J = 7.0 Hz, 4H), 1.31 (t, J = 7.0 Hz, 6H). *E* isomer: ^{1}H NMR (300 MHz) δ 7.69 (d, J = 8.7 Hz, 4H), 6.93 (d, J = 8.7 Hz, 4H), 3.85 (s, 6H), 3.54 (q, J = 7.0 Hz, 4H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz) δ 159.0, 143.6, 142.0, 132.0, 131.3, 129.9, 128.3, 113.9, 113.7, 110.0, 66.6, 66.1, 55.6, 55.5, 16.0, 15.7. IR (ATR) ν 1271, 1106, 1073, 815, 759 cm^{-1}. Exact mass data could not be collected for this compound under any of the conditions tested. The reasons for this anomalous result are not known.

Method B. Carbene complex **19** (200 mg, 0.56 mmol) and $Pd(P^tBu_3)_2$ (7 mg, 0.014 mmol) were reacted for 18 h, to yield compound **27** as a pale yellow solid (57 mg, 62%, *E*/*Z* = 8.1/1).

(*Z*)- and (*E*)-1,2-Diethoxy-1,2-bis(*p*-trifluoromethylphenyl)-ethylene (28). *Method A.* Carbene complex **20** (50 mg, 0.17 mmol), Pd catalyst (0.085 mmol), and Et_3N (24 μL, 0.17 mmol) were reacted for 2 h, to yield compound **28** as a pale yellow solid (11 mg, 33%, *E*/*Z* = 1.5/1); mp 112−114 °C. *Z* isomer: ^{1}H NMR (300 MHz) δ 7.54 (d, J = 8.1 Hz, 4H), 7.29 (d, J = 8.1 Hz, 4H), 3.80 (q, J = 7.0 Hz, 4H), 1.35 (t, J = 7.0 Hz, 6H; ^{13}C NMR (75 MHz) δ 142.8, 138.8, 130.0, 129.9, 128.7, 125.1 (q, J = 3.9 Hz), 66.5, 15.6. *E* isomer: ^{1}H NMR (300 MHz) δ 7.90 (d, J = 8.1 Hz, 4H), 7.67 (d, J = 8.1 Hz, 4H), 3.54 (q, J = 7.0 Hz, 4H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz) δ 144.3, 137.9, 129.6 (q, J = 32.2 Hz), 129.5, 126.0, 125.0 (q, J = 3.8 Hz), 66.9, 15.2. IR (ATR): ν 1327, 1116 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{19}F_6O_2$ [M + H]$^+$ 405.1284, found 405.1301.

Method B. Carbene complex **20** (200 mg, 0.51 mmol) and $Pd(P^tBu_3)_2$ (13 mg, 0.026 mmol) were reacted for 24 h, to yield compound **28** as a pale yellow solid (66 mg, 64%, *E*/*Z* = 11/1).

(*Z*)- and (*E*)-1,2-Diethoxy-1,2-bis(*m*-tolyl)ethylene (29). *Method A.* Carbene complex **21** (100 mg, 0.29 mmol), Pd catalyst (0.014 mmol), and Et_3N (40 μL, 0.29 mmol) were reacted for 16 h, to yield compound **29** as a yellow oil (40 mg, 94%, *E*/*Z* = 1/1.5). *Z* isomer: ^{1}H NMR (300 MHz) δ 7.57−6.93 (m, 16H, *Z* + *E*), 3.79 (q, J = 7.0 Hz, 4H), 2.23 (s, 6H), 1.33 (t, J = 7.0 Hz, 6H). *E* isomer: ^{1}H NMR (300 MHz) δ 7.56 (s, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.29 (dd, J = 7.8, 7.4 Hz, 2H), 7.11 (d, J = 7.4 Hz, 2H), 3.57 (q, J = 7.0 Hz, 4H), 2.40 (s, 6H), 1.16 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz) δ 142.6, 137.3, 137.2, 135.3, 130.1, 130.0, 128.9, 128.2, 128.0, 127.8, 127.6, 127.0, 126.6, 125.4, 66.4, 65.8, 21.6, 21.3, 15.6, 15.2. IR (ATR): ν 1280, 1105 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{25}O_2$ [M + H]$^+$ 297.1849, found 297.1860.

Method B. Carbene complex **21** (200 mg, 0.59 mmol) and $Pd(P^tBu_3)_2$ (15 mg, 0.03 mmol) were reacted for 5 h, to yield compound **29** as a pale yellow oil (39 mg, 45%, *E*/*Z* = 10.8/1).

(*Z*)- and (*E*)-1,2-Bis[(*p*-bromophenyl)-*p*-phenyl]-1,2-diethoxyethylene (30). *Method A.* Carbene complex **22** (100 mg, 0.21 mmol), Pd catalyst (0.011 mmol), and Et_3N (29 μL, 0.21 mmol) were reacted for 16 h, to yield compound **30** as a pale yellow solid (19 mg, 32%, *E*/*Z* = 1/1.4); mp 63−65 °C. *Z* + *E* isomers: ^{1}H NMR (300 MHz) δ 7.89−7.30 (m, 32H, *Z* + *E*) 3.88 (q, J = 7.0 Hz, 4H, *Z*), 3.66 (q, J = 7.0 Hz, 4H, *E*), 1.39 (t, J = 7.0 Hz, 6H, *Z*), 1.23 (t, J = 7.0 Hz, 6H, *E*); ^{13}C NMR (75 MHz) δ 144.4, 139.7, 138.9, 134.2, 132.1, 132.0, 131.9, 130.3, 130.0, 129.0, 128.9, 128.7, 128.6, 128.5, 126.9, 126.5, 126.4, 121.6, 66.7, 66.2, 15.7, 15.4; IR (ATR) ν 1480, 1263, 1115, 1073, 816 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{27}Br_2O_2$ [M + H]$^+$ 579.0354, found 579.0359.

Method B. Carbene complex **22** (200 mg, 0.42 mmol) and Pd(P^{t}Bu$_3$)$_2$ (11 mg, 0.021 mmol) were reacted for 6 h, to yield compound **30** as a pale yellow solid (36 mg, 30%, *E*/*Z* = 2.2/1).

(*Z*)- and (*E*)-1,2-Bis[(*p*-bromophenyl ether)-*p*-phenyl]-1,2-diethoxyethylene (31). *Method A.* Carbene complex **23** (200 mg, 0.4 mmol), Pd catalyst (0.02 mmol), and Et_3N (56 μL, 0.4 mmol) were reacted for 16 h, to yield compound **31** as a yellow oil (33 mg, 28%, *E*/*Z* = 1/2.5). *Z* isomer: ^{1}H NMR (300 MHz) δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.83 (q, *J* = 7.1 Hz, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). *E* isomer: ^{1}H NMR (300 MHz) δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.59 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz) δ 156.3, 156.1, 143.4, 133.1, 132.8, 131.7, 131.3, 130.1, 129.9, 128.8, 122.0, 120.8, 120.7, 118.9, 118.3, 118.2, 117.2, 115.9, 66.5, 66.1, 15.7, 15.3. IR (ATR): ν 1487, 1240 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $C_{30}H_{27}O_4Br_2$ [M + H]$^+$ 609.0271, found 609.0304.

Method B. Carbene complex **23** (200 mg, 0.4 mmol) and Pd(P^{t}Bu$_3$)$_2$ (2.6 mg, 0.005 mmol) were reacted for 22 h, to yield compound **31** as a white solid (72 mg, 59%, *E*/*Z* = 6/1).

(*E*,*Z*,*E*)- and (*E*,*E*,*E*)-3,4-Diethoxy-1,6-diphenyl-1,3,5-hexatrienes (32).[3b] *Method B.* Carbene complex **25** (100 mg, 0.28 mmol) and Pd(P^{t}Bu$_3$)$_2$ (0.005 mmol) were reacted for 16 h, to yield compound **32** as a dark brown solid (23 mg, 51%, *E*/*Z* = 2/1). *Z* + *E* isomers: ^{1}H NMR (300 MHz) δ 7.42 (d, *J* = 7.6 Hz, 8H), 7.31−7.16 (m, 12H), 7.07 (d, *J* = 16.1 Hz, 2H), 6.99 (d, *J* = 15.5 Hz, 2H), 6.81 (d, *J* = 15.5 Hz, 2H), 6.72 (d, *J* = 16.1 Hz, 2H), 3.97 (q, *J* = 7.0 Hz, 4H), 3.84 (q, *J* = 7.0 Hz, 4H), 1.36 (t, *J* = 7.0 Hz, 6H), 1.34 (t, *J* = 7.0 Hz, 6H).

(*Z*)- and (*E*)-1,2-Dibenzyloxy-1,2-dimethyethene (34).[3b] *Method B.* Carbene complex **33** (50 mg, 0.15 mmol) and Pd(P^{t}Bu$_3$)$_2$ (0.002 mmol) were reacted for 22 h, to yield compound **34** as a mixture of isomers (14 mg, 70%, *E*/*Z* = 1/1.6). Compound **34** was unstable for further purification. *Z* + *E* isomers: ^{1}H NMR (300 MHz) δ 7.40−7.23 (m, 20H), 4.71 (s, 4H), 4.56 (s, 4H), 1.77 (s, 6H), 1.71 (s, 6H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra of the new compounds prepared in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Chem. **1969**, *16*, P29. For ethoxy-derivatives: (b) Hansen, P.-E. *J. Chem. Soc., Perkin Trans. I* **1980**, *8*, 1627.

(14) The proposed mechanism for the oxygen oxidation of group 6 metal carbene complexes involves the stepwise addition of oxygen to the M═C bond, followed by the cycloreversion of the metalladioxetane thus formed, generating the corresponding ester and $(CO)_5Cr{=}O$. See, among others: (a) Gibert, M.; Ferrer, M.; Lluch, A.-M.; Sánchez-Baeza, F.; Messeguer, A. *J. Org. Chem.* **1999**, *64*, 1591. This process is easy, and it is the basis of the oxidative demetalation of group 6 metal-carbene complexes, a standard tool to remove the metal fragment. See the following, for example. (b) DMDO: Lluch, A.-M.; Jordi, L.; Sánchez-Baeza, F.; Ricart, S.; Camps, F.; Messeguer, A.; Moretó, J. M. *Tetrahedron Lett.* **1992**, *33*, 3021. (c) CAN: Luo, N.; Zheng, Z.; Yu, Z. *Org. Lett.* **2011**, *13*, 3384. (d) S/$NaBH_4$: Sandoval-Chavez, C.; López-Cortes, J. G.; Gutiérrez-Hernández, A. I.; Ortega-Alfaro, M. C.; Toscano, A.; Álvarez-Toledano, C. *J. Organomet. Chem.* **2009**, *694*, 3692. (e) SCO or SeCO: Zheng, Z.; Chen, J.; Luo, N.; Yu, Z.; Han, X. *Organometallics* **2006**, *25*, 5301. (f) TFMD: Barluenga, J.; Canteli, R.-M.; Florez, J.; García-Granda, S.; Gutíerrez-Rodríguez, A. *J. Am. Chem. Soc.* **1994**, *116*, 6949. (g) PyNO: Capriati, V.; Florio, S.; Luisi, R.; Perna, F. M.; Barluenga, J. *J. Org. Chem.* **2005**, *70*, 5852. (h) I_2: Soderberg, B. C.; Bowden, B. A. *Organometallics* **1992**, *11*, 2220. (i) Electrochemical oxidation: Lloyd, M. K.; McClever, J. A.; Orchard, D. G.; Connor, J. A.; Hall, M. B.; Hillier, H.; Jones, E. M.; McEven, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 1743 Additionally, the recently reported Pd carbene complexes are extremely sensitive to water and oxygen.[5].

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(23) The reported *E*/*Z* ratios reflected the ratio of olefins obtained during the catalytic self-dimerization process. To discard, as proposed by a reviewer, the possibility of the Pd catalytic species reacting with the originally formed olefins and therefore affecting the final *E*/*Z* ratio, three separate experiments were carried out. Thus, a 1/1 *E*/*Z* mixture of olefins **17** (15 mg) was reacted in the presence of 1.3 mg of $Pd(P^tBu_3)_2$ in 0.4 mL of MeCN for 48 h. The resulting mixture contains a 1/1 *E*/*Z* mixture of olefins **17**. The olefins were recovered quantitatively. Two additional experiments were carried out with olefins (*Z*)-**11** and (*E*)-**26**. Both compounds were recovered unaltered under the reactions conditions used for **17**. These experiments prove that the obtained olefins are configurationally stable under the catalytic conditions used.