Pd-Catalyzed Inter- and Intramolecular Carbene Transfer from Group 6 Metal−Carbene Complexes[1]

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Abstract: The use of group 6 metal−carbene complexes in inter- and intramolecular carbene transfer reactions has been studied. Thus, pentacarbonyl[(aryl)(methoxy)carbene]chromium(0) and tungsten complexes, **10**, efficiently dimerize at room temperature in the presence of diverse Pd(0) and Pd(II)/Et_3N catalysts. The effect of additives (PPh_3, $AsPh_3$, or $SbPh_3$) on the nature and the isomeric ratio of the reaction products is negligible. The nature of the reaction products is more catalyst-dependent for metal carbenes **12** bearing alkyl groups attached to the carbene carbon. In these cases, either carbene ligand dimerization or β-hydrogen elimination reactions are observed, depending on the catalyst. The carbene ligand dimerization reaction can be used to prepare conjugated polyenes, including those having metal moieties at both ends of the polyene system, as well as enediyne derivatives. The intramolecular carbene ligand dimerization of chromium bis-carbene complexes **28** and **30** allows the preparation of mono- and bicyclic derivatives, with ring sizes from six to nine members. For bis-carbene derivatives the β-hydrogen elimination reaction is inhibited, provided that both metal centers are tethered by an *o*-xylylene group. Other alkyl complexes **32** form new mononuclear carbene complexes **37** or decompose to complex reaction mixtures. The results obtained in these reactions may be explained by transmetalation from Cr(0) to Pd(0) and the intermediacy of Pd−carbene complexes. Aminocarbene−chromium(0) complexes **15**, need harsher reaction conditions to transfer the carbene ligand, and this transfer occurs only in the presence of deactivated olefins. The corresponding insertion/hydrolysis products **48** resulted in these cases. A catalytic cycle involving transmetalation from a chromacyclobutane to a palladacyclobutane is proposed to explain these results.

Introduction

The ability of group 6 metal−carbene (Fischer) complexes to act as stable carbene sources was early recognized. In fact the cyclopropanation of olefins was one of the first reactions of these complexes ever reported.[2] Since those early days, many other reactions of this class of organometallic reagents have been discovered, and their applications in organic synthesis are now far beyond that of a "simple" role as carbene-transferring reagents.[3] Nevertheless, the use of group 6 metal−carbene complexes as stable reagents for carbene transfer has not yet encountered its place in modern organic synthesis. Extensive efforts have been done to study the thermal reactivity of these complexes and olefins, the main reactions disclosed being cyclopropanation[4] and C−H insertion.[5] The thermal decomposition of heteroatom-stabilized group 6 carbene complexes occurred at high temperatures (T > 130 °C), leading to carbene dimers.[6] The *E/Z* ratio of the olefinic products is metal-dependent, which excludes the participation of free carbenes at least in some of these processes.[7] Additionally, the absence of cyclobutanone derivatives in the thermolysis of pentacarbonyl-[(2-oxacyclopentyliden)carbene]chromium(0) in boiling Decaline (139 °C), discarded the existence of free carbenes in these processes.[8] The thermal intramolecular dimerization of some group 6 bis-carbene complexes **1**[9] and **2**[10] to yield compounds **3** and **4**, respectively, have also been reported (Scheme 1). In contrast, chelating [(diphenylalkoxy)chromium](0) bis-carbene mononuclear complexes thermally evolve by α-elimination to the corresponding dienes, instead of the expected intermolecular double dimerization products.[11]

On the other hand, it is well-known that the in situ generation of highly reactive metallo−carbene species from an organic precursor and a metal-reagent from groups 8−11 leads to transient metal−carbene complexes. The reaction of these complexes and olefins have been extensively exploited in organic synthesis as a general route to different kind of cyclopropanes.[4a,12] Moreover, the carbene ligand dimerization of these in situ generated reagents is a topic of continued

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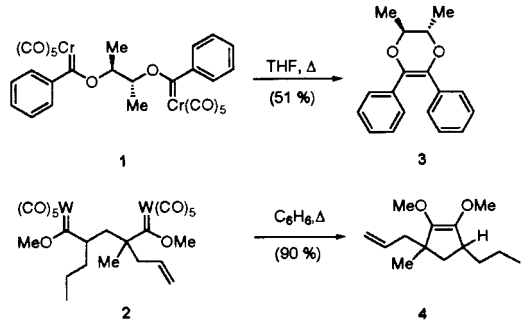
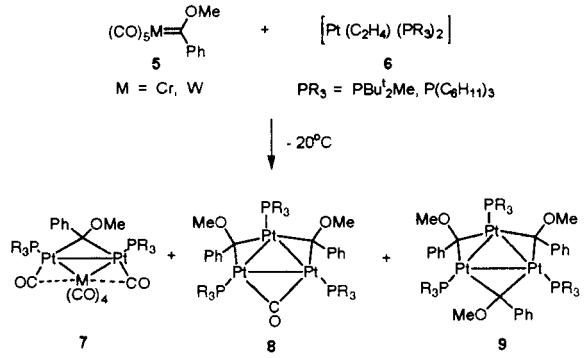
interest.[13] It seemed attractive to study the viability of making an analogous reaction using group 6 metal−carbene complexes as the source of the carbene in a transmetalation reaction. The goal was to generate a new intermediate metal−carbenoid complex more reactive than the original to effect the carbene transfer at temperatures lower than the usual for group 6 carbene complexes.

Scheme 1



The transfer of a carbene ligand from a Fischer-type group 6 carbene complex to another metal center is a rare process. Thus, Cp(CO)(NO)MCYPh (M = Cr, Mo, W; Y = OMe, NMe_2) transfer the carbene ligand to photochemically generated $Fe(CO)_5$ to yield the iron carbenes $(CO)_4FeCYAr$ in acceptable yields.[14] The thermal equilibrium (140 °C) between alkoxychromium−carbene complexes and $W(CO)_6$ to form alkoxytungsten−carbene complexes and $Cr(CO)_6$ has also been reported.[15] The stoichometric transmetalation of group 6 mononuclear alkoxypentacarbonylmetal−carbene complexes **5** to group 10 metal centers **6** was reported by Stone. These reactions yielded trimetallic complexes having μ-carbene ligands **7** together with different triangular clusters **8** and **9** (Scheme 2).[16] Several Au(I)− and Au(III)−carbene complexes have been prepared from the reaction of $(CO)_5MC(NMe_2)Ph$ and $(CO)_5MC(OMe)Ph$ (M = Cr, Mo, W) with chloroauric acid.[17,18] The transition metal-catalyzed carbene transfer from a group 6 alkoxymetal−carbene complex was, to the best of our knowledge, unknown at the beginning of this work. Reported herein is a full account of the use of group 6 metal−carbene complexes both in inter- and intramolecular carbene transfer reactions.[1]

Scheme 2



Results and Discussion

The first assays 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) complexes **10a** and **10b** and catalytic amounts of $Rh_2(OAc)_4$ at different temperatures.[19] We observed that carbene ligand dimerization of complex **10a** occurred at temperatures around 100 °C, high enough to not

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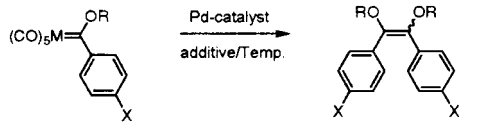
Table 1. Self-dimerization of Complexes **10**

entry	compd	catalyst (load)[a]/additive	solvent	T	reaction time (h)[b]	**11** E/Z[c]	yield (%)
1	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	THF	rt	1.0	2:1	53
2	**10a**	$Pd(OAc)_2$ (2%)/Et_3N	THF	rt	12.0	4:1	58
3	**10a**	$Pd(OAc)_2$ (10%)/Et_3N/PPh_3 (30%)[a]	THF	rt	0.75	2.5:1	65
4	**10a**	$Pd(OAc)_2$ (10%)/Et_3N/$AsPh_3$ (30%)[a]	THF	rt	1.5	3.6:1	72
5	**10a**	$Pd(OAc)_2$ (10%)/Et_3N/$SbPh_3$ (30%)[a]	THF	rt	3.0	2:1	52
6	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	THF	0 °C	2.0	2.5:1	48
7	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	hexane	rt	20.0	2.4:1	50
8	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	C_6H_6	rt	4.0	2.2:1	63
9	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	Et_2O	rt	8.0	2.6:1	57
10	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	MeCN	rt	0.25	2:1	94
11	**10a**	$Pd(OAc)_2$ (10%)/Et_3N	CH_2Cl_2	rt	1.5	2.2:1	68
12	**10a**	Pd(C) (5%)	THF	rt	21.0	5.1:1	49
13	**10a**	$Pd_2(dba)_3$·$CHCl_3$ (5%)	THF	rt	5.0	2.1:1	80
14	**10a**	$PdCl_2(PPh_3)_2$ (5%)/Et_3N	THF	rt	1.25	2.7:1	64
15	**10a**	$PdCl_2(MeCN)_2$ (5%)/Et_3N	THF	rt	0.75	2:1	72
16	**10b**	$Pd(OAc)_2$ (10%)/Et_3N	THF	rt	1.0	2:1	62
17	**10b**	$Pd(PPh_3)_4$ (3%)	THF	rt	2.5	2:1	55
18	**10b**	$Pd(PPh_3)_4$ (0.6%)	THF	rt	18.0	2:1	40
19	**10c**	$Pd(OAc)_2$ (10%)/Et_3N	THF	rt	5.0	1:1	46

[a] Referred to the carbene complex. [b] The reactions were followed by TLC until complete disappearance of the spot corresponding to the starting carbene complex. [c] Determined by integration of the signals corresponding to the MeO-groups in the ^1H NMR spectra of the crude reaction mixtures. Each experiment was repeated at least twice and the value given is the average of both experiments.

Scheme 3



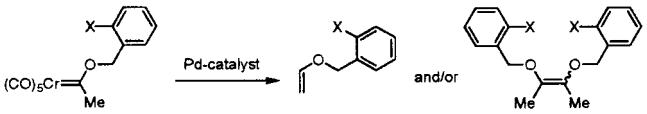
10a M = Cr, X = H, R = Me
10b M = Cr, X = Br, R = Me
10c M = W, X = H, R = Et

11a X = H, R = Me
11b X = Br, R = Me
11c X = H, R = Et

clearly be advantageous over the uncatalyzed process. Thus, we turned our attention to Pd catalysts. The viability of the dimerization of the carbene ligand of a group 6 alkoxycarbene complex promoted by a Pd-catalyst was first studied using complex **10a** as the substrate. Reaction of this compound with $Pd(OAc)_2$ in the presence of Et_3N using THF as solvent led to a 2:1 *E/Z* mixture of 1,2-dimethoxydiphenylethene **11a** (Scheme 3, Table 1). Lower loads of catalyst (2%) resulted in longer reaction times and in an increase of the *E*-selectivity (entry 2, Table 1). Addition of additives such as PPh_3, $AsPh_3$, or $SbPh_3$ had little effect in the overall result of the reaction (entries 3−5, Table 1). No appreciable variation on the *E/Z* isomer ratio of the reaction products was found by changing the nature of the solvent (entries 7−11, Table 1). Decreasing the temperature from room temperature (rt) to 0 °C resulted in longer reaction times, but it has no effect either in the nature of the products or in the ratio of isomers. The use of $(Ph_3P)_4Pd$ instead of $Pd(OAc)_2$ in the reaction of complex **10b** also resulted in a 2:1 mixture of compounds **11b**. Again, a decrease of the catalyst load brought about longer reaction times to consume the starting carbene complex (entries 16−18, Table 1). Other Pd(II) and Pd(0) catalysts, including Pd on charcoal, were equally efficient in promoting the carbene ligand dimerization of complex **10a** (entries 12−15, Table 1).

The catalyst used has a stronger influence on the nature of the reaction products when the substituents on the carbene carbon are methyl groups. Thus, alkyl carbene complexes **12a** and **12b** gave exclusively vinyl ethers **13a** and **13b**, respectively, in the presence of $Pd(OAc)_2/Et_3N$. Clearly, for alkyl-substituted carbene complexes a process of hydrogen β-elimination competes favorably in these conditions with the carbene ligand dimerization. However, other Pd-catalysts gave the carbene ligand dimerization products **14** in a process that is analogous to that experienced by aryl-substituted complexes (Scheme 4, Table 2). For those reactions forming compounds **14**, the influence of the Pd-catalyst in the reaction selectivity was negligible, but the reactions were considerably faster for Pd(II)/Et_3N catalysts (entries 5 and 6 in Table 2) than for Pd(0) catalysts (entries 2, 3 and 4 in Table 2). Due to the fact that in group 6 alkyl−carbene complexes the hydrogen β-elimination induced by bases to form vinyl ethers is a known reaction, it can be though that enol-ethers **13** are formed without participation of the Pd-catalyst when Et_3N is present. To exclude this possibility complex **12b** was stirred in a THF solution in the presence of Et_3N for 3 h but in the absence of Pd-catalyst. The complex was recovered unchanged. It is clear that the elimination reaction has to occur in the presence of the Pd-catalyst. Phenyltungsten−carbene **10c** was also reactive in this kind of reactions, forming the corresponding dimer **11c** in 46% yield when submitted to treatment with $Pd(OAc)_2$ in the presence

Scheme 4



12a X = H
12b X = Me

13a X = H
13b X = Me 65%

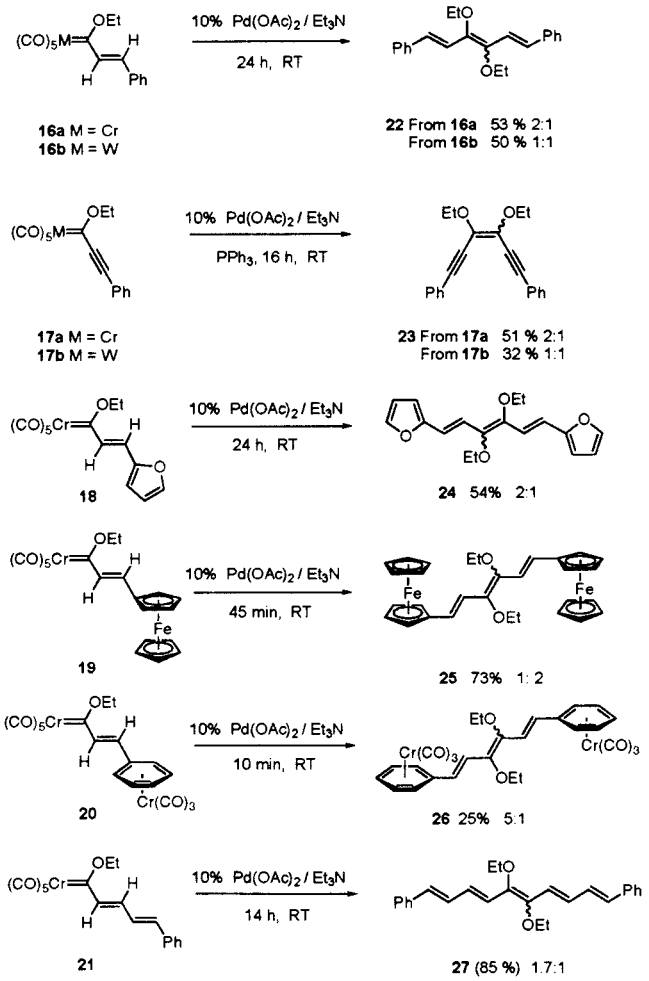
14a X = H 70 %

Table 2. Reaction of Alkyl-Substituted Carbene Complexes **12** with Different Pd-Catalysts

entry	compound	catalyst (10%)[a] /additive	reaction time (h)[b]	**13**/**14**[c]	**14** *E/Z*[d]	yield (%)
1	**12a**	$Pd(OAc)_2/Et_3N$	1	100:0	−	−[e]
2	**12a**	$Pd(PPh_3)_4$	20	0:100	1.1:1	87
3	**12a**	Pd(C)	20	0:100	1.3:1	70
4	**12a**	$Pd_2(dba)_3$·$CHCl_3$	5	0:100	1.9:1	76
5	**12a**	$PdCl_2(PPh_3)_2/Et_3N$	3	5:95	1.3:1	72
6	**12a**	$PdCl_2(MeCN)_2/Et_3N$	1	8:92	1.1:1	78
7	**12b**	$Pd(OAc)_2/Et_3N$	1	100:0	−	65

[a] Referred to the carbene complex. [b] The reaction were followed by TLC until complete disappearance of the spot corresponding to the carbene complex. [c] Determined by ^1H NMR analysis of the crude reaction mixture. [d] Determined by integration of the signals corresponding to the Me groups. Each experiment was repeated at least twice and the value given is the average of both experiments. [e] Compound **13a** was unstable. See Experimental Section.

Scheme 5

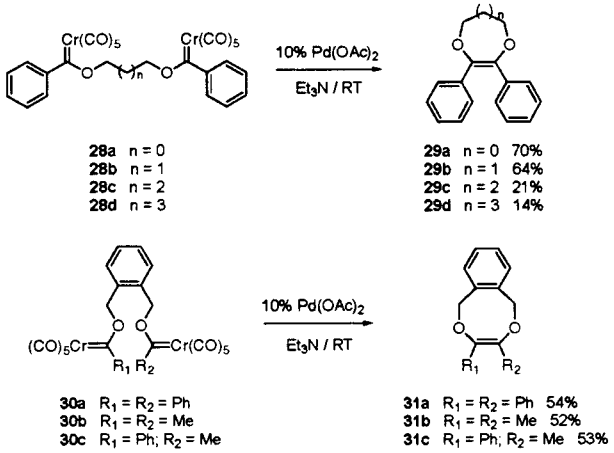


of Et_3N. In clear contrast, pentacarbonyl[(dimethylamino)-(phenyl)carbene)]chromium(0), **15a**, and pentacarbonyl[(dimethyl-amino)(*p*-bromophenyl)carbene)]chromium(0), **15b**, complexes were unreactive in the conditions used for alkoxycarbene complexes **10**. Their reactivity under harsher reaction conditions and in the presence of deactivated olefins is discussed below.

The possibility to obtain polyene-conjugated systems using this methodology was attractive due to increasing interest of these compounds in material chemistry, especially those compounds incorporating metal ends.[20] Complexes **16**−**21** were submitted to $Pd(OAc)_2/Et_3N$, and the corresponding polyene derivatives **22**−**27** were obtained in fair to good yields (Scheme 5). Small amounts of the oxidation products were sometimes obtained together with the mixture of enol ethers. It is noteworthy that the presence of additional metallic centers in the starting material is fully compatible with the dimerization reaction, allowing the preparation of conjugated polyene systems with metal moieties at both ends of the conjugated system. Compound **25** was obtained in 73% yield and easily isomerizes from a starting isomer ratio of 12:1 to a final 1:2 ratio after column chromatography. Triene **26** was formed in essentially quantitative yield but decomposed during purification, leading to an isolated yield of 25%. The method was also applicable to the synthesis of higher conjugated polyenes such as **27** that was obtained in 85% yield from chromium−carbene complex **21**, and enediyne **23** obtained from carbene complex **17a** in 51% yield. In this case PPh_3 was added to the reaction as it was found that better yields were obtained in this way. α,β-Unsaturated tungsten−carbene complexes **16b** and **17b** were again reactive, leading to triene **22** and enediyne **23**, respectively, as in the case of their chromium counterparts (Scheme 5).

The possibility to effect intramolecular carbene ligand dimerizations to obtain cyclic compounds was next addressed. Thus, bis[pentacarbonyl(alkoxy)(phenyl)carbene]chromium(0) complexes **28**, differing exclusively in the length of the tether separating both carbene ligands, were submitted to reaction with $Pd(OAc)_2$ under the usual conditions. Bicyclic enol ethers **29** were obtained in good to low yields depending on the size of the ring formed. In fact, yields decreased steadily as the ring size increased, being maximum for six- and minimum for nine-membered rings. An equal improvement in the formation of polymeric materials of unknown structure was also observed while the ring size increased. Complexes **30** having both metal nuclei joined by an *o*-xylylene group formed also the corresponding bicyclic derivatives. It should be noted that complexes **30b** and **30c**, bear methyl groups but exclusively gave the dimerization products **31b** and **31c**. Although $Pd(OAc)_2/Et_3N$ was used as the catalyst, none of the expected vinyl ethers arising from β-elimination processes were formed (Scheme 6).

Scheme 6

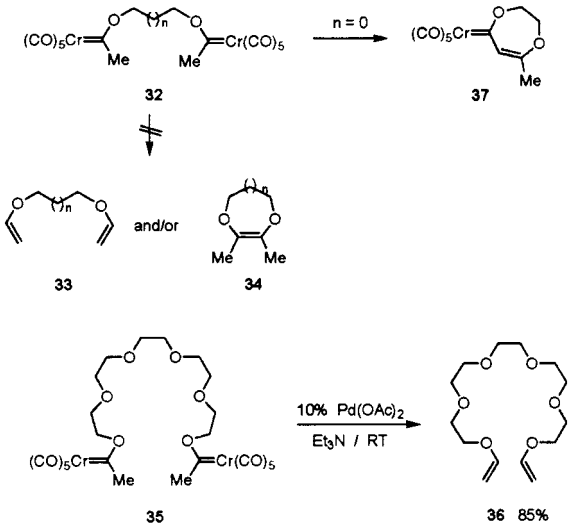


A different process may still occur in these intramolecular reactions. According to the results obtained at the moment, bis-carbene complexes **32** should evolve in the presence of $Pd(OAc)_2/Et_3N$, either by β-elimination to yield the corresponding bis-enolethers **33** or by carbene ligand dimerization to form dioxacycles **34**. The β-elimination product was observed for complex **35** which would have led to a large ring had the dimerization process occurred. Complex **32** ($n = 0$) formed a new carbene complex **37** almost instantaneously. Other complexes **32** ($n = 1, 2, 3$) reacted with $Pd(OAc)_2/Et_3N$ or $Pd(PPh_3)_4$ forming transient, unidentified, highly colored intermediates to yield finally complex reaction mixtures, from which we were unable to separate any identifiable product (Scheme 7).

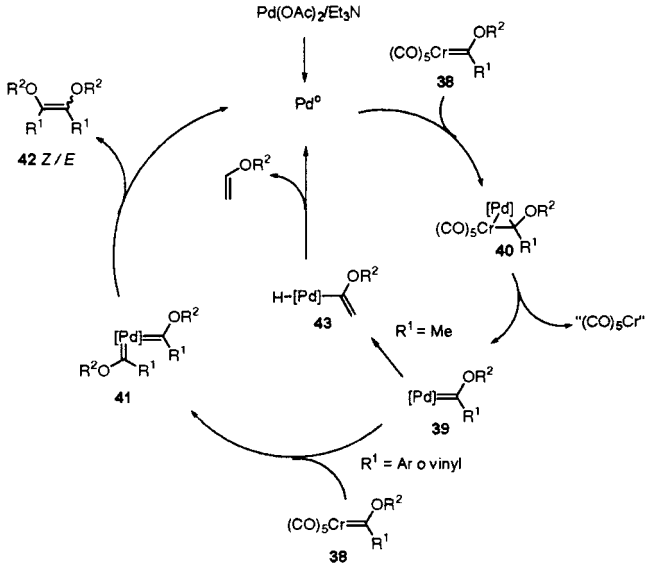
To explain the results obtained in these reactions it is necessary to propose the transmetalation of the carbene ligand from complex **38** to the Pd-catalyst to form a new Pd−carbene complex like **39**, probably through a heterobimetallic cyclopropane intermediate **40** that evolves to **39** by extrusion of the $M(CO)_5$ (M = Cr, W) moiety. Evidence of formation of transient Pd−carbene complexes was initially shown by Busacca[21] to explain the anomalous Stille reactions of methyl

(20) (a) Müller, T. J. J.; Netz, A.; Ansorge, M.; Schmälzlin, E.; Bräuchle, C.; Meerholz, K. *Organometallics* **1999**, *18*, 5066 and pertinent references therein. For a review, see: (b) Long, N. J. *Angew. Chem, Int. Ed. Engl.* **1995**, *34*, 6.

Scheme 7



Scheme 8



α-(tributylstannyl)acrylate, and the likeliness of the intermediacy of Pd−carbenes in processes involving cine-substitution during Stille reactions is now recognized.[22] Assuming the initial formation of a Pd−carbene complex **39**, the subsequent transmetalation from a new molecule of the carbene complex would form the Pd−bis-carbene complexes **41**. The nature of the reaction products is defined from the evolution of these Pd−carbene intermediates **39** and **41** (Scheme 8). Thus, for aryl- or vinyl-carbene complexes lacking α-hydrogens the evolution of complex **39** to Pd−bis-carbene **41** occurred. Elimination of Pd led to the observed products **42**. The evolution of Pd−carbene complexes having α-hydrogens follows a different pathway by hydride transfer to the metal center to form a new Pd−hydrido complex **43**. This process competes favorably with the incorporation of a second carbene ligand, depending on the nature of the catalyst. The Pd−hydrido intermediate **43** evolves by reductive elimination forming the observed vinyl ethers, and regenerating the catalyst (Scheme 8).

An analogous process should occur with bis-carbene complexes **44**. In these cases, the second transmetalation to form the Pd−bis-carbene complex is intramolecular, forming complexes **46** having both carbene ligands tethered by a methylene or an *o*-xylylene chain. Complex **32** ($n = 0$) form first heterobimetallic Cr−Pd−bis-carbene complexes **45**, but instead of evolving through a second intramolecular transmetalation from Cr to Pd, complex **45** ($R^1 = R^2 = Me$, $n = 0$) experiments an intermolecular C−H insertion, to form complex **37** by Pd reductive elimination. The reasons why complexes **32** ($n = 1$, 2, 3) yield complex reaction mixtures are not yet fully understood. The clear bias of complexes **30b−c** by the intramolecular dimerization reaction in detriment of the hydrogen β-elimination and the intermolecular dimerization reactions, may be conformational in origin. In these cases the double transmetalation to form bimetallic Pd−carbene **46** should be favored by the chelating effect of the *o*-xylylene moiety.[23] The resulting complex has both carbene ligands attached to the Pd-center, and the metalla-ring may be unable to adopt the required *syn*-disposition to experiment the β-elimination process. Evidently, the double metalation should be disfavored for larger rings and the β-elimination is competing favorably with the intramolecular carbene ligand dimerization. This hypothesis is supported by the behavior of complex **35** that formed exclusively the double β-elimination product **36** in high yield. The macrocycle resulting from a dimerization has not been detected in the reaction mixtures. The simultaneous presence of the two carbene ligands in the Pd-center should be entropically disfavored in this case. Hence, the double elimination product should arise from elimination in different Pd-centers (Scheme 9).

As stated earlier amino-substituted chromium−carbene complexes did not react at rt in the presence of $Pd(OAc)_2$ in the conditions used to dimerize alkoxychromium(0)−carbenes. Thus, pentacarbonyl[(*N*,*N*-dimethylamino)(*p*-bromophenyl)carbene]chromium(0), **15b**, remained unaltered after 78 h of reaction at rt. Increasing the temperature resulted in the formation of *N*,*N*-dimethyl-*p*-bromobenzamide and *p*-bromobenzaldehyde after prolonged reaction times. We thought that in these cases the carbene ligand dimerization should be precluded, and thence, the possibility to effect the carbene transfer to olefins in the presence of Pd-catalysts would be opened using aminocarbene complexes. Thus, complex **15b** was then reacted with methyl acrylate and acrylonitrile in the presence of $Pd(OAc)_2$ (10% and 2% molar ratio)/Et_3N in boiling THF. γ-Keto-ester **48b** (75%) and γ-ketonitrile **48c** (40%) were respectively obtained, together with small amounts of *N*,*N*-dimethyl-*p*-bromobenzamide and *p*-bromobenzaldehyde. The analogous reaction of complex **15a** with methyl acrylate and $Pd(OAc)_2$ (2%)/ Et_3N or $Pd(PPh_3)_4$ (10% molar ratio) as the catalyst gave γ-ketoester **48a** (80%). It is known that compounds analogous to **48** are formed by heating pentacarbonyl[(*N*,*N*-dimethylamino)methylene]chromium(0) and different olefins.[24] This fact raises the question of whether the reaction products are formed without transmetalation to the catalyst or if this transmetalation really occurs. Complex **15b** was reacted with methyl acrylate in boiling THF and in the absence of catalyst. A mixture of *N*,*N*-dimethyl-*p*-bromobenzamide, formed by oxidation of the complex during the prolonged heating, and γ-ketoester **48b** (4:1 ratio) was obtained after 48 h of reaction. The distribution of products is clearly different from the catalyzed process as the reaction time is considerably shorter

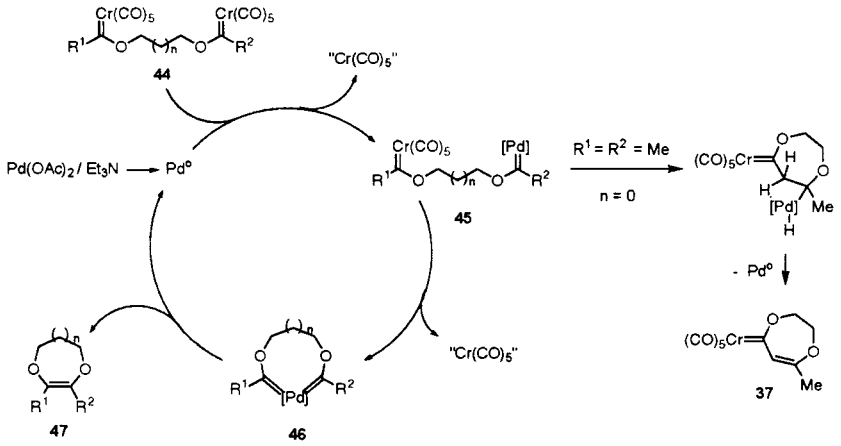
(21) Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553.

(22) (a) Farina, V.; Hossain, M. A. *Tetrahedron Lett.* **1996**, *37*, 6997. (b) Quayle, P.; Wang, J.; Xu, J.; Urch, C. J. *Tetrahedron Lett.* **1998**, *39*, 489.

(23) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, California, 1987.

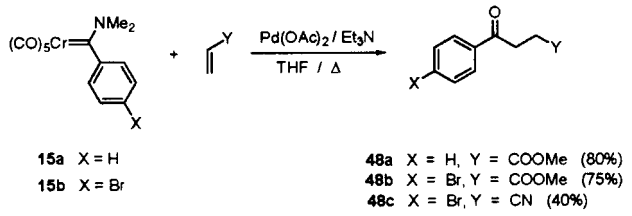
(24) Sierra, M. A.; Soderberg, B.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769.

Scheme 9



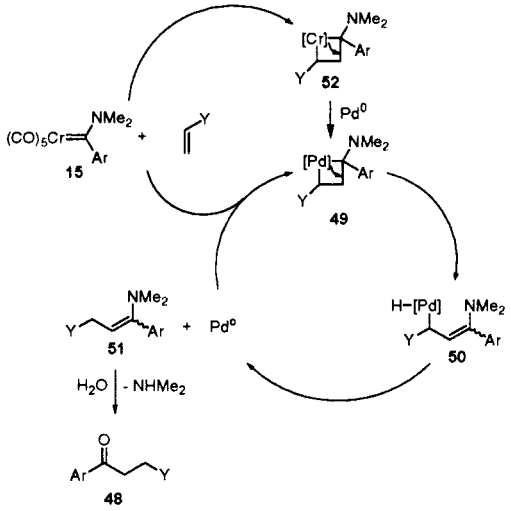
(8 h) for the catalytic reaction. These results point to the participation of Pd intermediates in the reactions of aminocarbene complexes and deactivated olefins (Scheme 10). It should be noted that products derived from the Heck's coupling on the aryl bromide were not observed, although it has been described that organic substrates related to complexes **15** produced high yields of coupling products[25] under reaction conditions analogous to those employed by us.[26]

Scheme 10



It is intriguing that for aminocarbenes the transmetalation to Pd seems to be productive only when a carbene acceptor is present. The observed products **48** would result from cyclization of the Pd carbene and the carbene acceptor followed by transfer of a β-hydrogen to the metal center of intermediate **49** and reductive elimination on **50** to form enamine **51**. Hydrolysis of **51** during workup would account for the obtained β-ketoderivatives **48**.[27,28] However, this reaction pathway does not explain the absence of transmetalation when the carbene acceptor is not present. A more likely reaction pathway may involve transmetalation to Pd from the chroma-cyclobutane **52** initially formed by cyclization of the chromium−carbene and the carbene acceptor. Chroma-cyclobutanes are the accepted first intermediates in the thermal reaction of group 6 metal−carbene complexes and olefins.[4a−b] This pathway may account for the observed inertia of aminochromium(0)−carbenes in the absence of a carbene acceptor (Scheme 11).

Scheme 11



To conclude, group 6 metal−carbene complexes can be used as carbene sources in the presence of Pd-catalysts. Inter- and intramolecular carbene ligand dimerization processes of the metal−carbene complexes lead to linear or cyclic derivatives, in reactions that in most cases are effected with low catalyst loads and that occurred without the formation of side products. In fact, although the isolated yields listed throughout this paper are in some cases low, this is not due to byproduct formation but to the unstability of the final products. For complexes having acidic hydrogens in groups attached to the carbene carbon, elimination competes favorably with carbene ligand dimerization in some cases, and enol ethers are thus formed. Nevertheless, the process of β-elimination may be almost inhibited by changing the catalyst. In clear contrast bis-carbene complexes, having the metal nuclei tethered by an aliphatic chain and alkyl groups in both carbene carbons, either decompose to mixtures of unknown products or evolve to new mononuclear carbene complexes through an intramolecular C−H insertion. To explain the observed results the transmetalation of Cr(0) to Pd(0) and the intermediacy of Pd−carbene complexes in the catalytic cycle is proposed. The structure of these intermediate complexes and hence the structure of the starting group 6 metal−carbene complex define the fate of the reaction, especially the possibility

(25) Heck, R. F. *Org. React.* **1982**, *27*, 345.

(26) The Stille's coupling of diverse ethynyl chromium(0)− and tungsten(0)−carbene complexes and organometallic iodides, has been reported by Fischer: (a) Hartbaum, C.; Roth, G.; Fischer, H. *Chem. Ber.* **1997**, *130*, 479. (b) Hartbaum, C.; Mauz, E.; Roth, G.; Weissenbach, K.; Fischer, H. *Organometallics* **1999**, *18*, 2619.

(27) Compounds **51** have been detected sometimes as minor products in the ^{1}H NMR of crude reaction mixtures.

(28) An alternative to the mechanism written in Scheme 11 would be to consider that the formation of an intermediate Pd−aminocarbene occurs, followed by cyclopropanation of the olefin. Thus, compounds **51** would be then formed by cyclopropane ring opening. The formation in low yields of products analogous to **51** in the reaction of pentacarbonyl[(pyrrolydinyl)(phenyl)carbene]chromium(0) and acrylonitrile in boiling cyclooctane (140 °C) have been explained by Reissig by the ring opening of a transient aminocyclopropane (see ref 4h). However, taking into account that the aminocarbene complexes tested are stable in boiling THF for hours and that there is complete absence of dimerization products in these reactions makes this alternative mechanism, albeit attractive, little believable in our case.

of hydrogen β-elimination. Finally, aminocarbene complexes need harsher reaction conditions to effect the transfer of the carbene ligand, and even then this only occurs in the presence of electron-poor olefins. The corresponding insertion/hydrolysis products resulted in these cases. Efforts to effect the transfer of the carbene ligand to double bonds to form cyclopropanes in very mild conditions by employing catalysts based on metals other than Pd, as well as to elucidate the nature of the Pd-intermediates, are ongoing in our group.

Experimental Section

General Procedure. ^{1}H NMR and ^{13}C NMR spectra were recorded at 22 °C in $CDCl_3$, on a Varian XL-300S (300 and 75.4 MHz), Bruker 250-AM (250 and 63 MHz) and Bruker 200-AC (200 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^{1}H, 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. Melting points were measured on an Electrothermal digital melting point apparatus (Gallenkamp) and are uncorrected. 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 Et_3N from CaH_2. Flame-dried glassware and standard Schlenck 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 (λ = 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[(ethoxy)(methyl)carbene]chromium(0),[29] pentacarbonyl[(methoxy)(methyl)carbene]chromium(0),[30] pentacarbonyl[(methoxy)-(phenyl)carbene]chromium(0),[30] pentacarbonyl[(ethoxy) (phenyl)carbene]tungsten(0),[31] pentacarbonyl[(benzyloxy)(methyl)carbene]chromium-(0),[32] pentacarbonyl[(ethoxy)(2-phenylethenyl)carbene]chromium(0),[33] pentacarbonyl[(ethoxy)(2-phenylethenyl)carbene]tungsten(0),[33] pentacarbonyl[(ethoxy)(2-furylethenyl)carbene]chromium(0),[33] pentacarbonyl[(ethoxy)(4-phenylbutadienyl)carbene]chromium(0),[33] pentacarbonyl-[(ethoxy)(2-phenylethynyl)carbene]chromium(0),[34] pentacarbonyl[(ethoxy)-(2-phenylethynyl)carbene]tungsten(0),[34] pentacarbonyl[(methyl)(tetramethylammonio)oxycarbene]chromium(0),[35] pentacarbonyl[(phenyl)-(tetramethylammonio)oxycarbene]chromium(0),[35] decacarbonyl[μ-(ethylen-1,2-dioxy)bis(phenyl)carbene]dichromium(0),[9] decacarbonyl[μ-(ethylen-1,2-dioxy)bis(methyl) carbene]dichromium(0),[36] pentacarbonyl-[(dimethylamino)(phenyl)carbene)]chromium(0),[37] tricarbonylchromium-(0)benzaldehyde.[38]

Synthesis of Carbene Complexes. Pentacarbonyl[(*p*-bromophenyl)(methoxy)carbene]chromium(0), 10b. To a solution of dibromobenzene (2 g, 8.5 mmol) in 10 mL of dry Et_2O was added 3.4 mL (8.5 mmol) of *n*-BuLi (2.5 M in hexane) at −78 °C. After stirring for 30 min, the solution was transferred via cannula at 0 °C to a suspension of $Cr(CO)_6$ (1.86 g, 8.5 mmol) in 20 mL of Et_2O at rt. The mixture was refluxed for 3 h, the solvent was removed under reduced pressure, and the residue was dissolved in 10 mL of degassed water. Me_3OBF_4 (2.20 g, 14.8 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 to yield 2.6 g (79%) of a red solid identified as **10b**. ^{1}H NMR (300 MHz): δ 7.34 (d, J = 8.3 Hz, 2H, ArH), 7.19 (d, J = 8.3 Hz, 2H, ArH), 4.64 (s, 3H, OCH_3). ^{13}C NMR (75 MHz): δ 348.3 (Cr═C), 223.7 (CO *trans*), 215.9 (CO *cis*), 152.0 (C *ipso*), 136.9 (C *ipso*), 131.4, 125.3 (aromatic CH), 67.4 (OCH_3). IR (KBr): ν 2100, 1960, 1925 cm^{-1}. $C_{13}H_7BrCrO_6$: Calcd C 39.92, H 1.80, Br 20.43. Found C 40.12, H 1.97, Br 20.65.

Pentacarbonyl[(methyl)(*o*-methylbenzyloxy)carbene]chromium-(0), 12b. Following the general procedure described by Hegedus[32] using 2 g (6.5 mmol) of pentacarbonyl[(methyl)[(tetramethylammonio)oxy]-carbene]chromium(0), 0.48 mL (6.5 mmol) of acetyl bromide and 0.79 g (6.5 mmol) of *o*-methylbenzyl alcohol was obtained **12b** (1.22 g, 56%) as an orange solid.^{1}H NMR (300 MHz): δ 7.33−7.17 (m, 4H, ArH), 5.83 (br s, 2H, OCH_2), 2.91 (s, 3H, CH_3), 2.32 (s, 3H, CH_3).^{13}C NMR (75 MHz): δ 358.8 (Cr═C), 223.3 (CO *trans*), 216.5 (CO *cis*), 137.5 (C *ipso*), 132.3 (C *ipso*), 130.9, 130.5, 126.5 (aromatic CH), 81.8 (OCH_2), 49.7 (CH_3), 19.1 (CH_3). IR (KBr): ν 2080, 1990, 1950, 1900, 1240 cm^{-1}. $C_{15}H_{12}CrO_6$: Calcd C 52.95, H 3.55. Found C 53.17, H 3.72.

Pentacarbonyl[(*p*-bromophenyl)(dimethylamino)carbene]chromium(0), 15b. To a solution of the carbene complex **10b** (200 mg, 0.5 mmol) in 10 mL of CH_2Cl_2 was added dimethylamine (liberated in situ from a slurry of 125 mg (1.5 mmol) of dimethylamine chlorhydrate and 0.2 mL (1.5 mmol) of Et_3N in CH_2Cl_2) at rt. The red solution became yellow after 10 min. Then, the mixture was stirred for an additional 20 min, and the solvent was removed in vacuo to give 195 mg (96%) of a yellow solid identified as **15b**. Complex **15b** was used without further purification. ^{1}H NMR (200 MHz): δ 7.48 (d, J = 8.4 Hz, 2H, ArH), 6.58 (d, J = 8.4 Hz, 2H, ArH), 3.97 (s, 3H, CH_3), 3.00 (s, 3H, CH_3). ^{13}C NMR (75 MHz): δ 275.6 (Cr═C), 223.4 (CO *trans*), 217.0 (CO *cis*), 151.1 (C *ipso*), 131.8, 120.7 (aromatic CH), 119.5 (C *ipso*), 51.4 (CH_3), 46.1 (CH_3). IR (KBr): ν 2052, 1971, 1897 cm^{-1}. $C_{14}H_{10}BrCrNO_5$: Calcd C 41.61, H 2.49, N 3.47, Br 19.77. Found C 41.85, H 2.65, N 3.61, Br 20.03.

Synthesis of α,β-Unsaturated Alkoxychromium(0)−Carbenes, 19−20. All of these compounds were synthesized by the method described by Aumann.[33] To an equimolecular solution of pentacarbonyl-[(ethoxy)(methyl)carbene]chromium(0) (1 mmol) and the corresponding aldehyde (1 mmol) in anhydrous Et_2O (5 mL) was added Et_3N (4 mmol) at rt. Then, TMSCl (3 mmol) was added dropwise at the same temperature, and the mixture was stirred until the disappearance of the starting material (checked by TLC). The solvent was removed in vacuo and the product purified by flash column chromatography under argon pressure (SiO_2, 9:1 hexane/Et_2O).

Pentacarbonyl[(ethoxy)(2-ferrocenylethenyl)carbene]chromium-(0), 19. The general procedure was followed, using 1.21 g (4.58 mmol) of pentacarbonyl [(ethoxy)(methyl)carbene]chromium(0), 1.00 g (4.58 mmol) of ferrocenecarbaldehyde, 2.55 mL (18.32 mmol) of Et_3N, and 1.78 mL (13.74 mmol) of TMSCl. After 3 days of reaction and further flash column chromatography, 1.14 g (54%) of **19** as a black crystalline solid was obtained. ^{1}H NMR (200 MHz): δ 7.39 (d, J = 15.0 Hz, 1H, C*H*═CH−Fc), 7.09 (d, J = 15.0 Hz, 1H, CH═C*H*-Fc), 4.90 (q, J = 7.1 Hz, 2H, OCH_2), 4.53 (m, 4H, Cp), 4.13 (s, 5H, Cp), 1.58 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (75 MHz): δ 324.1 (Cr═C), 224.3 (CO *trans*), 217.3 (CO *cis*), 138.4 (*C*H═CH−Fc), 137.4 (CH═*C*H−Fc), 78.4 (Cp), 75.1 (OCH_2), 72.5 (Cp), 70.2 (Cp), 69.8 (Cp), 15.1 (CH_3). IR (KBr): ν 2052, 1924, 1591, 1576, 1215, 1138 cm^{-1}. $C_{20}H_{16}$-$CrFeO_6$: Calcd C 52.20, H 3.50. Found C 52.44, H 3.68.

Pentacarbonyl[(ethoxy)(2-(tricarbonylchromiumphenyl)ethenyl)-carbene]chromium(0), 20. The general procedure was followed, using 0.56 g (2.11 mmol) of pentacarbonyl[(ethoxy)(methyl)carbene]chromium-(0), 0.51 g (2.11 mmol) of tricarbonylchromium(0)benzaldehyde, 1.17 mL (8.45 mmol) of Et_3N, and 0.82 mL (6.33 mmol) of TMSCl. After 4 days and flash column chromatography, 140 mg (16%) of **20** as an unstable deep purple crystalline solid was obtained. ^{1}H NMR (300 MHz): δ 7.62 (d, J = 15.2 Hz, 1H, C*H*═CH−Ar), 6.31 (d, J = 15.2 Hz, 1H, CH═C*H*−Ar), 5.56 (d, J = 6.0 Hz, 2H, ArH), 5.45 (t, J = 6.2 Hz, 1H, ArH), 5.27 (t, J = 6.4 Hz, 2H, ArH), 5.06 (q, J = 7.1 Hz,

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2H, OCH_2), 1.63 (t, $J = 7.1$ Hz, 3H, CH_3). IR (CCl_4): ν 2058, 1981, 1946, 1915, 1583, 1549, 1254 cm^{-1}.

General Procedure for the Synthesis of Bis-carbene Complexes, 28. All of these compounds were synthesized following the general method described by Wulff.[9] To a solution of the corresponding ammonium salt (1 mmol) in anhydrous CH_2Cl_2 (10 mL/mmol) at −30 °C was added dropwise (1 mmol) of pivaloyl chloride or acetyl bromide (as stated in each case). The mixture was stirred for 1 h, and then, the diol (0.5 mmol) was added at the same temperature. Afterward, the reaction was allowed to proceed for an additional 16 h at −30 °C, and slowly allowed to reach rt. The crude reaction was extracted with CH_2Cl_2 and washed with a saturated solution of $NaHCO_3$; the solvent was removed in vacuo and submitted to flash column chromatography under argon pressure (SiO_2, 9:1 hexane/EtOAc) to yield pure compounds **28**.

Decacarbonyl[μ-(propylene-1,3-dioxy)bis(phenylcarbene)]dichromium(0), 28b. The general procedure was followed, using 0.94 g (2.45 mmol) of pentacarbonyl[(phenyl)(tetramethylammonio) oxycarbene]-chromium(0), 0.30 mL (2.45 mmol) of pivaloyl chloride, and 90 μL (1.22 mmol) of freshly distilled propanediol. **28b** (0.28 g, 36%) was obtained as a red solid. ^{1}H NMR (200 MHz): δ 7.32 (br s, 6H, ArH), 7.09 (br s, 4H, ArH), 4.94 (m, 4H, OCH_2), 2.64 (qt, $J = 5.9$ Hz, 2H, CH_2).^{13}C NMR (75 MHz): δ 351.2 (Cr═C), 224.1 (CO *trans*), 215.9 (CO *cis*), 153.9 (C *ipso*), 130.1, 128.3, 122.2 (aromatic CH), 75.9 (OCH_2), 29.2 (CH_2). IR (CCl_4): ν 2062, 1982, 1950, 1109 cm^{-1}. $C_{27}H_{16}Cr_2O_{12}$: Calcd C 50.96, H 2.53. Found C 51.14, H 2.76.

Decacarbonyl[μ-(butylene-1,4-dioxy)bis(phenylcarbene)]dichromium(0), 28c. The general procedure was followed, using 1.25 g (3.37 mmol) of pentacarbonyl[(phenyl)(tetramethylammonio) oxycarbene]-chromium(0), 0.41 mL (3.37 mmol) of pivaloyl chloride, and 0.15 mL (1.68 mmol) of freshly distilled 1,4-butanediol. **28c** (0.48 g, 44%) was obtained as a dark red solid. ^{1}H NMR (200 MHz): δ 7.32 (m, 6H, ArH), 7.16 (m, 4H, ArH), 4.83 (br s, 4H, OCH_2), 2.22 (br s, 4H, CH_2).^{13}C NMR (75 MHz): δ 350.1 (Cr═C), 224.1 (CO *trans*), 216.1 (CO *cis*), 153.5 (C *ipso*), 130.1, 128.3, 122.5 (aromatic CH), 79.7 (OCH_2), 27.1 (CH_2). IR (CCl_4): ν 2062, 1982, 1946, 1215 cm^{-1}. $C_{28}H_{18}Cr_2O_{12}$: Calcd C 51.70, H 2.79. Found C 51.95, H 2.97.

Decacarbonyl[μ-(pentylene-1,5-dioxy)bis(phenylcarbene)]dichromium(0), 28d. The general procedure was followed, using 1.27 g (3.43 mmol) of pentacarbonyl[(phenyl)(tetramethylammonio) oxycarbene]-chromium(0), 0.42 mL (3.43 mmol) of pivaloyl chloride, and 0.18 mL (1.71 mmol) of 1,5-pentanediol. **28d** (0.62 g, 55%) was obtained as a dark red oil. ^{1}H NMR (300 MHz): δ 7.32 (m, 6H, ArH), 7.15 (m, 4H, ArH), 4.79 (br s, 4H, OCH_2), 2.06 (qt, $J = 6.7$ Hz, 4H, CH_2), 1.75 (qt, $J = 6.9$ Hz, 2H, CH_2).^{13}C NMR (75 MHz): δ 349.8 (Cr═C), 224.1 (CO *trans*), 216.0 (CO *cis*), 153.6 (C *ipso*), 130.1, 128.2, 122.5 (aromatic CH), 80.4 (OCH_2), 29.2 (CH_2), 22.7 (CH_2). IR (CCl_4): ν 2062, 1982, 1948, 1215 cm^{-1}. $C_{29}H_{20}Cr_2O_{12}$: Calcd C 52.42, H 3.03. Found C 52.68, H 2.90.

Decacarbonyl[μ-(*o*-xylylenedioxy)bis(phenylcarbene)]dichromium(0), 30a. The general procedure was followed, using 1.38 g (3.7 mmol) of pentacarbonyl [(phenyl)(tetramethylammonio) oxycarbene]chromium(0), 0.45 mL (3.7 mmol) of pivaloyl chloride, and 265 mg (1.85 mmol) of *o*-hydroxymethylbenzyl alcohol. **30a** (0.47 g, 36%) was obtained as a dark-red oil.^{1}H NMR (200 MHz): δ 7.46 (br s, 4H, ArH), 7.29 (m, 6H, ArH), 7.04 (m, 4H, ArH), 5.78 (s, 4H, OCH_2).^{13}C NMR (75 MHz): δ 350.8 (Cr═C), 224.1 (CO *trans*), 215.9 (CO *cis*), 153.3 (C *ipso*), 133.3 (C *ipso*), 130.2, 130.0, 128.3, 122.3 (aromatic CH), 79.3 (OCH_2). IR (CCl_4): ν 2064, 1982, 1952, 1195 cm^{-1}. $C_{32}H_{18}Cr_2O_{12}$: Calcd C 55.03, H 2.60. Found C 55.25, H 2.78.

Decacarbonyl[μ-(*o*-xylylenedioxy)bis(methylcarbene)]dichromium(0), 30b. The general procedure was followed, using 3.0 g (9.71 mmol) of pentacarbonyl [(methyl)(tetramethylammonio) oxycarbene]chromium(0), 0.72 mL (9.71 mmol) of acetyl bromide, and 0.69 g (4.85 mmol) of *o*-hydroxymethylbenzyl alcohol. **30b** (850 mg, 31%) as an orange solid and pentacarbonyl[(*o*-hydroxymethylbenzyloxy)(methyl)-carbene]chromium(0) as an orange oil (0.74 g, 42%) were obtained. ^{1}H NMR (200 MHz): δ 7.52 (br s, 4H, ArH), 5.98 (br s, 4H, OCH_2), 2.93 (s, 6H, CH_3). ^{13}C NMR (50 MHz): δ 360.2 (Cr═C), 222.9 (CO *trans*), 216.3 (CO *cis*), 133.2 (C *ipso*), 130.5, 130.2 (aromatic CH), 80.0 (OCH_2), 50.2 (CH_3). IR (KBr): ν 2064, 1988, 1909, 1252 cm^{-1}. $C_{22}H_{14}Cr_2O_{12}$: Calcd C 46.01, H 2.46. Found C 46.27, H 2.58.

Pentacarbonyl[(*o*-hydroxymethylbenzyloxy) (methyl)carbene]chromium(0): ^{1}H NMR (200 MHz): δ 7.41−7.34 (m, 4H, ArH), 5.98 (br s, 2H, OCH_2), 4.75 (s, 2H, CH_2OH), 2.95 (s, 3H, CH_3). ^{13}C NMR (75 MHz): δ 358.6 (Cr═C), 223.1 (CO *trans*), 216.2 (CO *cis*), 139.0 (C *ipso*), 132.1(C *ipso*), 129.4, 128.6, 128.2 (aromatic CH), 62.7 (OCH_2). The signals corresponding to carbons CH_3 and OCH_2 could not be detected. IR (CCl_4): ν 2064, 1983, 1942, 1246 cm^{-1}. $C_{15}H_{12}CrO_7$: Calcd C 50.57, H 3.40. Found C 50.80, H 3.56.

Decacarbonyl[μ-(*o*-xylylenedioxy)(methyl)(phenyl)biscarbene]-dichromium(0), 30c. The general procedure was followed, using 0.31 g (0.84 mmol) of pentacarbonyl[(phenyl)(tetramethylammonio)-oxycarbene]chromium(0), 100 μL (0.84 mmol) of pivaloyl chloride, and 0.30 g (0.84 mmol) of pentacarbonyl[(*o*-hydroxymethyl- benzyl-oxy)(methyl)carbene]chromium. **30c** (270 mg, 51%) was obtained as a dark red solid. ^{1}H NMR (300 MHz): δ 7.49 (br s, 4H, ArH), 7.33 (br s, 3H, ArH), 7.15 (br s, 2H, ArH), 5.92 (s, 2H, OCH_2), 5.88 (s, 2H, OCH_2), 2.80 (s, 3H, CH_3). ^{13}C NMR (75 MHz): δ 359.8 and 350.6 (Cr═C), 223.9 and 223.0 (CO *trans*), 216.2 and 216.0 (CO *cis*), 153.5 (C *ipso*), 133.6 (C *ipso*), 132.9 (C *ipso*), 130.5, 130.2, 130.0, 128.3, 122.7 (aromatic CH), 79.8 (OCH_2), 79.4 (OCH_2), 49.7 (CH_3). IR (KBr): ν 2064, 1986, 1948, 1220 cm^{-1}. $C_{27}H_{16}Cr_2O_{12}$: Calcd C 50.96, H 2.53. Found C 51.20, H 2.68.

Decacarbonyl[μ-(1,16-pentaethyleneglycoxy)bis(methyl)carbene)]-dichromium(0), 35. The general procedure was followed, using 1.5 g (4.85 mmol) of pentacarbonyl[(methyl)(tetramethylammonio)oxycarbene]-chromium(0), 0.36 mL (4.85 mmol) of freshly distilled acetyl bromide, and 0.61 g (2.42 mmol) of pentaethyleneglycol. **35** (0.74 g, 45%) was obtained as an orange oil. ^{1}H NMR (200 MHz): δ 4.95 (br s, 4H, OCH_2), 3.96 (m, 4H, OCH_2), 3.65 (m, 6H, OCH_2), 3.60 (s, 6H, OCH_2), 2.91 (s, 6H, CH_3). ^{13}C NMR (75 MHz): δ 359.3 (Cr═C), 223.2 (CO *trans*), 216.3 (CO *cis*), 79.8 (OCH_2), 70.9 (OCH_2), 70.5 (OCH_2), 69.1 (OCH_2), 48.8 (CH_3). IR (CCl_4): ν 2064, 1983, 1942, 1252 cm^{-1}. $C_{24}H_{26}Cr_2O_{16}$: Calcd C 42.74, H 3.89. Found C 42.99, H 4.02.

General Procedure for the Pd Catalyzed Reactions of Alkoxychromiun(0) and Alkoxytungsten(0) Carbene Complexes. A THF solution (4 mL/mmol) of the carbene was placed in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/backfill with argon (3 times). $Pd(OAc)_2$ (0.1 mmol, 10%) and Et_3N (1.1 mmol) were added at rt, and the mixture was stirred until the disappearance of the starting material (checked by TLC). The solvent was distilled under reduced pressure, and the residue was dissolved in ethyl acetate and filtered through Celite. The solvent was removed in vacuo, and the residue was purified by flash column chromatography (SiO_2, 10:1 hexane:EtOAc) or molecular distillation.

1,2-Dimethoxy-1,2-diphenylethene, 11a.[39] From carbene complex **10a** (312 mg, 1 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol) and 0.15 mL (1.1 mmol) of Et_3N after 1 h was obtained **11a** as a mixture of isomers *E/Z* (2:1), that were separated by flash column chromatography to give 22 mg (18%, *Z*-isomer) and 42 mg (35%, *E*-isomer). ***Z*-isomer:** ^{1}H NMR (300 MHz): δ 7.61 (d, $J = 7.3$ Hz, 4H, ArH), 7.34 (t, $J = 7.3$ Hz, 4H, ArH), 7.25 (t, $J = 7.3$ Hz, 2H, ArH), 3.33 (s, 6H, OCH_3). ^{13}C NMR (75 MHz) δ 145.1 (Cq), 134.0 (C *ipso*), 128.2, 128.1, 127.7 (aromatic CH), 58.5 (OCH_3). IR ($CHCl_3$): ν 1640, 1265 cm^{-1}. ***E*-isomer:** ^{1}H NMR (300 MHz): δ 7.07 (s, 10H, ArH), 3.52 (s, 6H, OCH_3). ^{13}C NMR (75 MHz): δ 143.2 (Cq), 134.6 (C *ipso*), 129.9, 128.0, 127.6 (aromatic CH), 58.2 (OCH_3). IR ($CHCl_3$): ν 1600, 1250 cm^{-1}. $C_{16}H_{16}O_2$: Calcd C 79.97, H 6.71. Found: C 80.25, H 6.95. The same experiment was carried out using 4.5 mg (0.02 mmol, 2%) of $Pd(OAc)_2$ to give, after 12 h, 70 mg (58%) of **11a** as an *E/Z* mixture (4:1).

Carbene Ligand Dimerization of Complex 10a Using Different Solvents. (Hexane). From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol) and 17 mg (0.17 mmol) of Et_3N in 1 mL of hexane after 20 h was obtained 9.6 mg (50%) of **11a** as a mixture of isomers *E/Z* (2.4:1). **(CH_2Cl_2).** From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol) and 17 mg (0.17 mmol) of Et_3N in 1 mL of CH_2Cl_2 after 1.5 h was obtained 13.0 mg (68%) of **11a** as a mixture of isomers *E/Z* (2.2:1). **(MeCN).** From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol)

(39) Bachmann, W. E. *J. Am. Chem. Soc.* **1934**, *56*, 963.

and 17 mg (0.17 mmol) of Et_3N in 1 mL of acetonitrile after 15 min was obtained 18.0 mg (94%) of **11a** as a mixture of isomers *E/Z* (2:1). **(Benzene).** From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol) and 17 mg (0.17 mmol) of Et_3N in 1 mL of benzene after 4 h was obtained 12.0 mg (63%) of **11a** as a mixture of isomers *E/Z* (2.2:1). **(Et_2O).** From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol) and 17 mg (0.17 mmol) of Et_3N in 1 mL of diethyl ether after 8 h was obtained 11 mg (57%) of **11a** as a mixture of isomers *E/Z* (2.6:1).

Carbene Ligand Dimerization of Complex 10a Using Additives. (PPh_3). From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol), 17 mg (0.17 mmol) of Et_3N,and 12.6 mg (0.048 mmol) of PPh_3 in 1 mL of THF after 45 min was obtained 12.4 mg (65%) of **11a** as a mixture of isomers *E/Z* (2.5:1). **($AsPh_3$).** From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol), 17 mg (0.17 mmol) of Et_3N, and 15.1 mg (0.048 mmol) of $AsPh_3$ in 1 mL of THF after 1.5 h was obtained 13.9 mg (72%) of **11a** as a mixture of isomers *E/Z* (3.6:1). **($SbPh_3$).** From carbene complex **10a** (50 mg, 0.16 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol), 17 mg (0.17 mmol) of Et_3N, and 17.1 mg (0.048 mmol) of $SbPh_3$ in 1 mL of THF after 3 h was obtained 10 mg (52%) of **11a** as a mixture of isomers *E/Z* (2:1).

Carbene Ligand Dimerization of Complex 10a Using Other Catalysts. (Pd on Charcoal, 5%). From carbene complex **10a** (50 mg, 0.16 mmol) and Pd(C) (17 mg, 0.008 mmol), in 1 mL of THF after 21 h was obtained 9.5 mg (49%) of **11a** as a mixture of isomers *E/Z* (5.1:1). **($PdCl_2(MeCN)_2$).** From carbene complex **10a** (50 mg, 0.16 mmol), $PdCl_2(MeCN)_2$ (2.1 mg, 0.008 mmol), and 18 mg (0.18 mmol) of Et_3N in 1 mL of THF after 45 min was obtained 13.9 mg (72%) of **11a** as a mixture of isomers *E/Z* (2:1). **($PdCl_2(PPh_3)_2$).** From carbene complex **10a** (50 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (5.6 mg, 0.008 mmol), and 18 mg (0.18 mmol) of Et_3N in 1 mL of THF after 75 min was obtained 12.3 mg (64%) of **11a** as a mixture of isomers *E/Z* (2.7:1). **($Pd_2(dba)_3{\cdot}CHCl_3$).** From carbene complex **10a** (100 mg, 0.32 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (16.6 mg, 0.016 mmol) in 2 mL of THF after 5 h was obtained 31 mg (80%) of **11a** as a mixture of isomers *E/Z* (2.1:1).

1,2-Bis(*p*-bromophenyl)-1,2-dimethoxyethene, 11b. From carbene complex **10b** (392 mg, 1 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), and 0.15 mL (1.1 mmol) of Et_3N after 1.5 h was obtained 170 mg of a mixture of **11b** and $Cr(CO)_6$. Molecular distillation of the mixture afforded 120 mg (62%) of a white solid identified as an *E/Z* (2:1) mixture of isomers of **11b**. The isomers could be separated by flash column chromatography to give 32 mg (16%, *Z*-isomer) and 72 mg (37%, *E*-isomer). ***Z*-isomer:** ^{1}H NMR (300 MHz): δ 7.48 (m, 8H, ArH), 3.29 (s, 6H, OCH_3). ^{13}C NMR (75 MHz): δ 144.7 (Cq), 132.6 (C *ipso*), 131.4, 129.8 (aromatic CH), 121.8 (C *ipso*), 58.5 (OCH_3). IR ($CHCl_3$): ν 1600, 1259 cm^{-1}. ***E*-isomer:** ^{1}H NMR (300 MHz) δ 7.25 (d, J = 8.5 Hz, 4H, ArH), 6.95 (d, J = 8.5 Hz, 4H, ArH), 3.51 (s, 6H, OCH_3). ^{13}C NMR (75 MHz): δ 142.7 (Cq), 133.4 (C *ipso*), 131.4, 131.3 (aromatic CH), 121.9 (C *ipso*), 58.5 (OCH_3). IR ($CHCl_3$): ν 1630, 1260 cm^{-1}. $C_{16}H_{14}Br_2O_2$: Calcd C 48.27, H 3.54, Br 40.14. Found C 48.43, H 3.28, Br 39.76. **Reaction with $Pd(PPh_3)_4$ (3% Molar Ratio).** Following an analogous procedure, from carbene complex **10b** (391 mg, 1 mmol) and $Pd(PPh_3)_4$ (39 mg, 0.033 mmol) after 2.5 h was obtained 280 mg of **11b** as a mixture of isomers *E/Z* (2:1) and $Cr(CO)_6$. The $Cr(CO)_6$ was eliminated by dissolving the residue in MeOH and filtering through Celite to give 110 mg (55%) of the pure alkene. **Reaction with $Pd(PPh_3)_4$ (0.6% Molar Ratio).** Following an analogous procedure, from carbene complex **10b** (391 mg, 1 mmol) and $Pd(PPh_3)_4$ (7.8 mg, 0.006 mmol) after 18 h was obtained 160 mg of **11b** as a mixture of isomers *E/Z* (2:1) and $Cr(CO)_6$. The $Cr(CO)_6$ was eliminated by dissolving the residue in MeOH and filtering through Celite to give 80 mg (40%) of the pure alkene.

1,2-Diethoxy-1,2-diphenylethene, 11c. From carbene complex **10c** (150 mg, 0.33 mmol), $Pd(OAc)_2$ (7.4 mg, 0.033 mmol), and 36 mg (0.36 mmol) of Et_3N after 5 h was obtained 120 mg of a mixture of **11c** and $W(CO)_6$. Molecular distillation of the mixture afforded 21 mg (46%) of a white solid identified as an *E/Z* (1:1) mixture of isomers of **11c**. ^{1}H NMR (300 MHz): δ 7.74 (d, J = 7.5 Hz, 4H, ArH), 7.32 (t, J = 7.8 Hz, 4H, ArH), 7.21 (t, J = 7.2 Hz, 2H, ArH), 7.09 (s, 10H, ArH), 3.71 (q, J = 7.0 Hz, 4H, OCH_2), 3.49 (q, J = 7.0 Hz, 4H, OCH_2), 1.25 (t, J = 7.0 Hz, 6H, CH_3), 1.06 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR (75 MHz): δ 144.1 (Cq), 142.6 (Cq), 135.4 (C *ipso*), 134.7 (C *ipso*), 129.8, 128.3, 127.9, 127.8, 127.5, 127.3 (aromatic CH), 66.4 (OCH_2), 65.9 (OCH_2), 15.6 (CH_3), 15.2 (CH_3). IR (CCl_4): ν 1665, 1599, 1551, 1259 cm^{-1}. $C_{18}H_{20}O_2$: Calcd C 80.56, H 7.51. Found C 80.41, H 7.65.

1,2-Dibenzyloxy-1,2-dimethyethene, 14a. From carbene complex **12a** (100 mg, 0.31 mmol) and Pd on charcoal (5%) (66 mg, 0.031 mmol) in 2 mL of THF after 20 h was obtained **14a** (28 mg, 70%) as a mixture of isomers *E/Z* (1.3:1). Compound **14a** was unstable for further purification. ^{1}H NMR (300 MHz): δ 7.40−7.23 (m, 20H, ArH), 4.71 (s, 4H, OCH_2), 4.56 (s, 4H, OCH_2), 1.77 (s, 6H, CH_3), 1.71 (s, 6H, CH_3). ^{13}C NMR (50 MHz): δ 137.9 (Cq), 137.3 (Cq), 128.3, 128.2, 127.9, 127.8, 127.7, 127.5 (aromatic CH), 71.7 (OCH_2), 71.2 (OCH_2), 15.1 (CH_3), 12.0 (CH_3). IR (CCl_4): ν 1608, 1587, 1261 cm^{-1}.

Carbene Ligand Dimerization of Complex 12a Using Other Catalysts. ($Pd(PPh_3)_4$). From carbene complex **12a** (50 mg, 0.15 mmol) and $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) in 1 mL of THF after 20 h was obtained 17.5 mg (87%) of **14a** as a mixture of isomers *E/Z* (1.1:1). **($Pd_2(dba)_3{\cdot}CHCl_3$).** From carbene complex **12a** (50 mg, 0.15 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (15.5 mg, 0.015 mmol) in 1 mL of THF after 5 h was obtained 15.2 mg (76%) of **14a** as a mixture of isomers *E/Z* (1.9:1). **($PdCl_2(PPh_3)_2$).** From carbene complex **12a** (50 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (10.7 mg, 0.015 mmol), and 17 mg (0.17 mmol) of Et_3N in 1 mL of THF after 3 h was obtained 14.4 mg (72%) of **14a** as a mixture of isomers *E/Z* (1.3:1) and 5% of **13a**. **($PdCl_2(MeCN)_2$).** From carbene complex **12a** (50 mg, 0.15 mmol), $PdCl_2(MeCN)_2$ (4.0 mg, 0.015 mmol), and 17 mg (0.17 mmol) of Et_3N in 1 mL of THF after 1 h was obtained 15.6 mg (78%) of **14a** as a mixture of isomers *E/Z* (1.1:1) and 8% of **13a**.

***E,Z,E*- and *E,E,E*-3,4-Diethoxy-1,6-diphenyl-1,3,5-hexatrienes, 22.** From carbene complex **16a** (176 mg, 0.5 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), and 80 μL (0.55 mmol) of Et_3N after 24 h was obtained 90 mg of a dark brown solid, that after flash column chromatography yielded 42 mg (53%) of an inseparable mixture of *E/Z* isomers of **22** (2:1 ratio). ^{1}H NMR (300 MHz): δ 7.42 (d, J = 7.6 Hz, M + m, 8H, ArH), 7.31−7.16 (m, M + m, 12H, ArH), 7.07 (d, J = 16.1 Hz, M, 2H, C*H*═CH−Ph), 6.99 (d, J = 15.5 Hz, m, 2H, C*H*═CH−Ph), 6.81 (d, J = 15.5 Hz, m, 2H, CH═C*H*−Ph), 6.72 (d, J = 16.1 Hz, M, 2H, CH═C*H*−Ph), 3.97 (q, J = 7.0 Hz, M, 4H, OCH_2), 3.84 (q, J = 7.0 Hz, m, 4H, OCH_2), 1.36 (t, J = 7.0 Hz, m, 6H, CH_3), 1.34 (t, J = 7.0 Hz, M, 6H, CH_3). ^{13}C NMR (75 MHz): δ 147.9 (Cq), 145.7 (Cq), 137.3 (C *ipso*), 128.6, 128.3, 128.0, 127.6, 127.5, 126.7, 126.6, 120.4, 119.2 (aromatic and CH), 69.5 (OCH_2), 67.9 (OCH_2), 15.8 (CH_3), 15.7 (CH_3). IR ($CHCl_3$): ν 1637, 1597, 1227, 1196 cm^{-1}. $C_{22}H_{24}O_2$: Calcd C 82.46, H 7.55. Found C 82.63, H 7.81. Following an analogous procedure, from carbene complex **16b** (100 mg, 0.21 mmol), $Pd(OAc)_2$ (4.7 mg, 0.021 mmol), and 23 mg (0.23 mmol) of Et_3N after 15 h was obtained 60 mg of a brown solid, that after flash column chromatography yielded 17 mg (50%) of an inseparable mixture of *E/Z* isomers of **22** (1:1 ratio).

3,4-Diethoxy-1,6-diphenyl-1,5-hexadiyn-3-ene, 23. From carbene complex **17a** (150 mg, 0.43 mmol), $Pd(OAc)_2$ (9.6 mg, 0.043 mmol), PPh_3 (33.7 mg, 0.13 mmol,) and 48 mg (0.48 mmol) of Et_3N after 16 h was obtained 110 mg of a brown oil identified as a mixture of *E/Z* isomers (2:1 ratio) of **23**. Further purification of the reaction mixture by flash column chromatography allowed the separation of 35 mg (51%) of the major isomer. **23 (major isomer):** ^{1}H NMR (200 MHz): δ 7.43−7.36 (m, 4H, ArH), 7.29−7.23 (m, 6H, ArH), 4.12 (q, J = 7.0 Hz, 4H, OCH_2), 1.31 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR (50 MHz): δ 131.3 (Cq), 131.0, 128.4 (aromatic CH), 122.8 (C *ipso*), 97.5 (C≡C), 82.9 (C≡C), 66.1 (OCH_2), 15.4 (CH_3). IR (KBr): ν 2201 (C≡C), 1577, 1256, 1198 cm^{-1}. $C_{22}H_{22}O_2$: Calcd C, 83.51, H 6.37. Found: C 83.41, H 6.32. **23 (minor isomer):** ^{1}H NMR (200 MHz): δ 7.43−7.36 (m, 4H, ArH), 7.29−7.23 (m, 6H, ArH), 4.04 (q, J = 7.0 Hz, 4H, OCH_2), 1.30 (t, J = 7.0 Hz, 6H, CH_3). Following an analogous procedure, from carbene complex **17b** (150 mg, 0.31 mmol), $Pd(OAc)_2$ (7.1 mg, 0.031 mmol), and 34 mg (0.34 mmol) of Et_3N after 15 h was obtained 150 mg of a black solid, that after flash column chromatography yielded 15.6 mg (32%) of a mixture of *E/Z* isomers of **23** (1:1 ratio).

***E,Z,E*- and *E,E,E*-3,4-Diethoxy-1,6-bis(2-furyl)-1,3,5-hexatrienes, 24.** From carbene complex **17** (150 mg, 0.44 mmol), $Pd(OAc)_2$ (10 mg, 0.04 mmol), and 70 μL (0.48 mmol) of Et_3N after 24 h was obtained 80 mg of a dark brown solid, that after flash column chromatography yielded 37 mg (54%) of an inseparable mixture of *E/Z* isomers of **24** (2:1 ratio). ^{1}H NMR (200 MHz): δ 7.33 (m, M + m, 4H, Furan), 6.93 (d, J = 15.3 Hz, m, 2H, C*H*═CH−Furyl), 6.92 (d, J = 15.9 Hz, M, 2H, C*H*═CH−Furyl), 6.57 (d, J = 15.9 Hz, M, 2H, CH═C*H*−Furyl), 6.49 (d, J = 15.3 Hz, m, 2H, CH═C*H*−Furyl), 6.34 (m, M + m, 4H, Furan), 6.24 (m, M + m, 4H, Furan), 3.92 (q, J = 7.1 Hz, M, 4H, OCH_2), 3.81 (q, J = 7.0 Hz, m, 4H, OCH_2), 1.34. (t, J = 7.0 Hz, m, 6H, CH_3), 1.30 (t, J = 7.1 Hz, M, 6H, CH_3). ^{13}C NMR (75 MHz): δ 153.6 (Cq, Furan), 147.8 (Cq), 145.6 (Cq), 142.4, 142.1, 119.1, 117.9, 115.7, 115.3, 111.8, 109.1, 108.8 (CH and Furan), 69.5 (OCH_2), 67.8 (OCH_2), 15.7 (CH_3). IR (KBr): ν 1599, 1261, 1229 cm^{-1}. $C_{18}H_{20}O_4$: Calcd C 71.98, H 6.71. Found: C 72.15, H 6.82.

***E,Z,E*- and *E,E,E*-3,4-Diethoxy-1,6-bis(ferrocenyl)-1,3,5-hexatrienes, 25.** From carbene complex **19** (230 mg, 0.5 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), and 80 μL (0.55 mmol) of Et_3N after 45 min was obtained 140 mg of a dark brown solid identified as a mixture of *Z/E* isomers (12:1 ratio) of **25**. Further purification of the reaction mixture by flash column chromatography led to a partial isomerization of one of the isomers to yield 31 mg (23%) of the former major isomer and 67 mg (50%) of the former minor isomer, respectively; both compounds were obtained as dark brown-red solids. **Triene 25 (major isomer):** ^{1}H NMR (200 MHz): δ 6.53 (d, J = 15.4 Hz, 2H, C*H*═CH−Fc), 6.44 (d, J = 15.4 Hz, 2H, CH═C*H*−Fc), 4.36 (m, 4H, Cp), 4.21 (m, 4H, Cp), 4.07 (s, 10H, Cp), 3.92 (q, J = 7.1 Hz, 4H, OCH_2), 1.33 (t, J = 7.1 Hz, 6H, CH_3). ^{13}C NMR (50 MHz): δ 144.2 (Cq), 125.9 (*C*H═CH−Fc), 118.3 (CH═*C*H−Fc), 83.7 (Cp), 69.2 (Cp), 69.0 (Cp), 67.7 (OCH_2), 66.9 (Cp), 15.8 (CH_3). IR (KBr): ν 1560, 1265, 1215 cm^{-1}. $C_{30}H_{32}Fe_2O_2$: Calcd C 67.19, H 6.01. Found: C 67.32, H 6.19. **Triene 25 (minor isomer):** ^{1}H NMR (200 MHz): δ 6.62 (d, J = 15.9 Hz, 2H, C*H*═CH−Fc), 6.44 (d, J = 15.9 Hz, 2H, CH═C*H*−Fc), 4.38 (m, 4H, Cp), 4.22 (m, 4H, Cp), 4.05 (s, 10H, Cp), 3.81 (q, J = 7.1 Hz, 4H, OCH_2), 1.36 (t, J = 7.1 Hz, 6H, CH_3). ^{13}C NMR (50 MHz): δ 146.1 (Cq), 126.2 (*C*H═CH−Fc), 117.3 (CH═*C*H−Fc), 83.6 (Cp), 69.3 (Cp), 69.2 (Cp), 69.1 (OCH_2), 67.0 (Cp), 15.8 (CH_3). IR (KBr): ν 1622, 1221 cm^{-1}.

***E,Z,E*- and *E,E,E*-3,4-Diethoxy-1,6-bis[(tricarbonylchromium)-phenyl]-1,3,5-hexatrienes, 26.** From carbene complex **20** (105 mg, 0.21 mmol), $Pd(OAc)_2$ (4.6 mg, 0.021 mmol), and 40 μL (0.23 mmol) of Et_3N after 10 min was obtained 80 mg of a dark brown solid that after flash column chromatography yielded 15.2 mg (25%) of **26** as a mixture of *E/Z* isomers (5:1 ratio). ^{1}H NMR (300 MHz): δ 6.88 (d, J = 16.0 Hz, m, 2H, C*H*═CH−Ar), 6.75 (d, J = 15.1 Hz, M, 2H, C*H*═CH−Ar), 6.35 (d, J = 15.1 Hz, M, 2H, CH═C*H*−Ar), 6.26 (d, J = 16.0 Hz, m, 2H, CH═C*H*−Ar), 5.44 (d, J = 6.0 Hz, M + m, 8H, ArH), 5.37 (t, J = 6.0 Hz, M + m, 8H, ArH), 5.22 (t, J = 5.7 Hz, M + m, 4H, ArH), 3.93 (q, J = 6.9 Hz, M, 4H, OCH_2), 3.80 (q, J = 6.9 Hz, m, 4H, OCH_2), 1.30 (t, J = 6.9 Hz, M + m, 12H, CH_3). ^{13}C NMR (50 MHz, major isomer): δ 232.9 (CO), 145.6 (Cq), 125.4 (*C*H═CH−Ar), 122.9 (CH═*C*H−Ar), 105.6 (C *ipso*), 92.8, 91.1, 91.0 (aromatic CH), 68.1 (OCH_2), 15.7 (CH_3). IR (KBr): ν 1973, 1904, 1551, 1217 cm^{-1}. The mixture of compounds was unstable and correct analytical data could not be obtained.

***E,E,E,E,E*- *and* *E,E,Z,E,E*-5,6-Diethoxy-1,10-diphenyl-1,3,5,7,9-decapentaene, 27.** Following the general procedure carbene complex **21** (150 mg, 0.40 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol) and 44 mg (0.44 mmol) of Et_3N were reacted for 14 h. Then, the crude reaction was dissolved in hexane and filtered through Celite to give 63 mg of a mixture of *E/Z* isomers (1.7:1 ratio) of **27** (85%) as a yellow solid. Compound **27** was too unstable for further purification, and all spectroscopic data of the mixture had to be obtained right after the reaction. Correct analytical data could not be obtained. ^{1}H NMR (300 MHz): δ 7.36−7.11 (m, M + m, 22H, ArH, and CH), 6.93−6.83 (m, M + m, 4H, CH), 6.79−6.48 (m, M + m, 10H, ArH, and CH), 3.91 (q, J = 7.2 Hz, M, 4H, OCH_2), 3.78 (q, J = 7.2 Hz, m, 4H, OCH_2), 1.33 (t, J = 7.2 Hz, m, 6H, CH_3), 1.30 (t, J = 7.2 Hz, M, 6H, CH_3). ^{13}C NMR (75 MHz): δ 148.1 (Cq), 146.0 (Cq), 137.5, 133.2, 132.8, 129.3, 129.2, 129.0, 128.6, 127.4, 126.4, 126.3, 124.7, 123.6, 118.8 (CH and aromatic), 69.4 (OCH_2), 67.9 (OCH_2), 15.8 (CH_3), 15.7 (CH_3). IR (KBr): ν 1626, 1599, 1581, 1215 cm^{-1}.

5,6-Diphenyl-2,3-dihydro-[1,4]dioxine, 29a. From bis-carbene complex **28a** (359 mg, 0.58 mmol), $Pd(OAc)_2$ (13.3 mg, 0.058 mmol), and 90 μL (0.63 mmol) of Et_3N after 2 h and further flash column chromatography was obtained **29a** (96 mg, 70%) as a white crystalline solid (mp 93−94 °C). ^{1}H NMR (300 MHz): δ 7.17−7.15 (m, 4H, ArH), 7.10−7.08 (m, 6H, ArH), 4.25 (s, 4H, OCH_2). ^{13}C NMR (75 MHz): δ 135.3 (Cq), 134.6 (Cq), 128.9, 127.8, 127.4 (aromatic CH), 65.1 (OCH_2). IR (KBr): ν 1634, 1597, 1288, 1107 cm^{-1}. Mass-spectra (EI), *m/z* (%): 238 (M^+, 7), 149 (40), 105 (100), 91 (15), 77 (36). $C_{16}H_{14}O_2$: Calcd C 80.65, H 5.92. Found C 80.93, H 6.13.

2,3-Diphenyl-6,7-dihydro-*5H*-[1,4]dioxepine, 29b. From bis-carbene complex **28b** (197 mg, 0.31 mmol), $Pd(OAc)_2$ (7.0 mg, 0.031 mmol), and 50 μL (0.34 mmol) of Et_3N after 45 min and further flash column chromatography was obtained **29b** (50 mg, 64%) as a white crystalline solid (mp 118−119 °C). ^{1}H NMR (200 MHz): δ 7.18−7.12 (m, 4H, ArH), 7.09−7.03 (m, 6H, ArH), 4.43 (t, J = 6.1 Hz, 4H, OCH_2), 2.14 (qt, J = 6.1 Hz, 2H, CH_2). ^{13}C NMR (50 MHz): δ 141.7 (Cq), 136.6 (C *ipso*), 129.5, 127.7, 127.4 (aromatic CH), 69.9 (OCH_2), 30.1 (CH_2). IR (KBr): ν 1616, 1261, 1101 cm^{-1}. $C_{17}H_{16}O_2$: Calcd C 80.93, H 6.39. Found C 81.02, H 6.51.

2,3-Diphenyl-5,6,7,8-tetrahydro-[1,4]dioxocine, 29c. From bis-carbene complex **28c** (245 mg, 0.38 mmol), $Pd(OAc)_2$ (8.6 mg, 0.038 mmol), and 60 μL (0.42 mmol) of Et_3N after 2 h and further flash column chromatography was obtained **29c** (21 mg, 21%) as a white crystalline solid (mp 102−104 °C). ^{1}H NMR (200 MHz): δ 7.18−7.14 (m, 4H, ArH), 7.10−7.05 (m, 6H, ArH), 4.29 (br s, 4H, OCH_2), 1.90 (br s, 4H, CH_2). ^{13}C NMR (50 MHz): δ 141.7 (Cq), 136.8 (C *ipso*), 129.3, 127.8, 127.3 (aromatic CH), 72.0 (OCH_2), 27.9 (CH_2). IR (KBr): ν 1616, 1277, 1086, 1068 cm^{-1}. $C_{18}H_{18}O_2$: Calcd C 81.17, H 6.81. Found C 81.25, H 6.95.

2,3-Diphenyl-6,7,8,9-tetrahydro-*5H*-[1,4]dioxonine, 29d. From bis-carbene complex **28d** (245 mg, 0.38 mmol), $Pd(OAc)_2$ (8.6 mg, 0.038 mmol), and 60 μL (0.42 mmol) of Et_3N after 2 h and further flash column chromatography was obtained **29d** (14 mg, 14%) as a very viscous colorless oil. ^{1}H NMR (300 MHz): δ 7.17−7.13 (m, 4H, ArH), 7.10−7.06 (m, 6H, ArH), 4.21 (t, J = 5.1 Hz, 4H, OCH_2), 1.84 (m, 4H, CH_2), 1.70 (m, 2H, CH_2). ^{13}C NMR (50 MHz): δ 142.1 (Cq), 136.5 (C *ipso*), 129.5, 127.8, 127.3 (aromatic CH), 72.4 (OCH_2), 29.4 (CH_2), 25.9 (CH_2). IR (KBr): ν 1549, 1275, 1254, 1084 cm^{-1}. $C_{19}H_{20}O_2$: Calcd C 81.40, H 7.19. Found C 81.65, H 7.26.

3,4-Diphenyl-1,6-dihydro-benzo[*f*][1,4]dioxocine, 31a. From bis-carbene complex **30a** (100 mg, 0.14 mmol), $Pd(OAc)_2$ (3.1 mg, 0.014 mmol), and 20 μL (0.15 mmol) of Et_3N after 2 h and further flash column chromatography was obtained **31a** (23.5 mg, 54%) as a white crystalline solid (mp 89−90 °C). ^{1}H NMR (200 MHz): δ 7.27−7.22 (m, 2H, ArH), 7.13−7.10 (m, 2H, ArH), 7.04−7.00 (m, 6H, ArH), 6.96−6.91 (m, 4H, ArH), 5.25 (s, 4H, OCH_2). ^{13}C NMR (50 MHz): δ 139.8 (Cq), 136.0 (C *ipso*), 135.4 (C *ipso*), 129.5, 129.2, 128.7, 127.7, 127.4 (aromatic CH), 72.4 (OCH_2). IR (KBr): ν 1641, 1261, 1063 cm^{-1}. $C_{22}H_{18}O_2$: Calcd C 84.05, H 5.77. Found C 84.30, H 5.94.

3,4-Dimethyl-1,6-dihydro-benzo[*f*][1,4]dioxocine, 31b. From bis-carbene complex **30b** (150 mg, 0.26 mmol), $Pd(OAc)_2$ (5.9 mg, 0.026 mmol) ,and 40 μL (0.29 mmol) of Et_3N after 2 h and further flash column chromatography was obtained **31b** (25.7 mg, 52%) as a white crystalline solid (mp 58−60 °C). ^{1}H NMR (200 MHz): δ 7.25−7.21 (m, 2H, ArH), 7.16−7.09 (m, 2H, ArH), 5.11 (s, 4H, OCH_2), 1.55 (s, 6H, CH_3). ^{13}C NMR (50 MHz): δ 136.3 (Cq), 133.7 (C *ipso*), 128.9, 128.3 (aromatic CH), 72.1 (OCH_2), 15.7 (CH_3). IR (KBr): ν 1689, 1618, 1236, 1174 cm^{-1}. $C_{12}H_{14}O_2$: Calcd C 75.76, H 7.42. Found C 75.87, H 7.61.

3-Methyl-4-phenyl-1,6-dihydro-benzo[*f*][1,4]dioxocine, 31c. From bis-carbene complex **30c** (150 mg, 0.24 mmol), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol), and 40 μL (0.26 mmol) of Et_3N after 2 h and further flash column chromatography was obtained **31c** (31.5 mg, 53%) as a dense light yellow oil. ^{1}H NMR (200 MHz): δ 7.26−7.08 (m, 9H, ArH), 5.34 (s, 2H, OCH_2), 4.97 (s, 2H, OCH_2), 1.65 (s, 3H, CH_3). ^{13}C NMR (50 MHz): δ 139.7 (Cq), 137.6 (Cq), 135.6 (Cq), 135.1, 134.5, 131.0, 128.7, 128.2, 127.9, 127.3, 127.1 (aromatic CH), 72.8 (OCH_2),

71.8 (OCH_2), 17.3 (CH_3). IR (CCl_4): ν 1697, 1269, 1164 cm^{-1}. $C_{17}H_{16}O_2$: Calcd C 80.93, H 6.39. Found C 81.15, H 6.49.

Reactions of β-Elimination in Chromium Carbene Complexes. Synthesis of Enol Ethers 13a, 13b, and 36. Benzyl vinyl ether, 13a.[40] From carbene complex **12a** (326 mg, 1 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), and 0.15 mL (1.1 mmol) of Et_3N after 1.5 h was obtained 230 mg of a mixture of the enol ether **13a** and $Cr(CO)_6$. Compound **12a** was very unstable and could not be further purified. ^{1}H NMR (300 MHz): δ 7.29−7.25 (m, 5H, ArH), 6.48 (dd, J_1 = 14.4 Hz, J_2 = 6.6 Hz, 1H, C*H*═CH_2), 4.71 (s, 2H, OCH_2), 4.22 (d, J = 14.4 Hz, 1H, CH═CH_2), 3.98 (d, J = 6.6 Hz, 1H, CH═CH_2). ^{13}C NMR (75 MHz): δ 151.5 (*C*H═CH_2), 136.7 (C *ipso*), 128.4, 127.7, 127.4 (aromatic CH), 87.2 (CH═*C*H_2), 69.9 (OCH_2).

(*o*-Methylbenzyl)vinyl Ether, 13b. From carbene complex **12b** (340 mg, 1 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), and 0.15 mL (1.1 mmol) of Et_3N after 45 min was obtained 230 mg of a mixture of **13b** and $Cr(CO)_6$. Compound **13b** was purified by molecular distillation to yield 96 mg (65%) of a colorless oil. ^{1}H NMR (300 MHz): δ 7.27−7.12 (m, 4H, ArH), 6.50 (dd, J_1 = 14.0 Hz, J_2 = 7.0 Hz, 1H, C*H*═CH_2), 4.66 (s, 2H, OCH_2), 4.25 (d, J = 14.0 Hz, 1H, CH═CH_2), 4.01 (d, J = 7.0 Hz, 1H, CH═CH_2), 2.26 (s, 3H, CH_3). ^{13}C NMR (75 MHz): δ 151.7 (*C*H═CH_2), 136.7 (C *ipso*), 134.7 (C *ipso*), 130.3, 128.6, 128.4, 125.9 (aromatic CH), 87.1 (CH═*C*H_2), 68.5 (OCH_2), 18.7 (CH_3). IR (KBr): ν 1645, 1620, 1500, 1250 cm^{-1}. $C_{10}H_{12}O$: Calcd C 81.04, H 8.16. Found: C 81.32, H 8.38.

(Pentaethylenglycol)divinyl Ether, 36. From carbene complex **35** (150 mg, 0.22 mmol), $Pd(OAc)_2$ (5.1 mg, 0.022 mmol), and 40 μL (0.24 mmol) of Et_3N after 3 h was obtained a mixture of **36** and $Cr(CO)_6$. The $Cr(CO)_6$ was removed by filtration after dissolving the mixture in cold MeOH to yield 54 mg (85%) of **36** as a light yellow oil. Compound **36** was obtained in pure form and further purification was not required. ^{1}H NMR (200 MHz): δ 6.42 (dd, J_1 = 14.3 Hz, J_2 = 6.8 Hz, 2H, C*H*═CH_2), 4.10 (d, J = 14.3 Hz, 2H, CH═CH_2), 3.93 (d, J = 6.8 Hz, 2H, CH═CH_2), 3.77 (m, 4H, OCH_2), 3.66 (m, 4H, OCH_2), 3.58 (s, 12H, OCH_2).^{13}C NMR (50 MHz): δ 151.7 (*C*H═CH_2), 86.6 (CH═*C*H_2) 70.7 (OCH_2), 70.6 (OCH_2), 69.2 (OCH_2), 67.2 (OCH_2). IR (CCl_4): ν 1614, 1549, 1244, 1205, 1126 cm^{-1}. $C_{14}H_{26}O_6$: Calcd C 57.91, H 9.03. Found C 58.02, H 9.20.

Pentacarbonyl[(6-methyl-2,5-dioxa-6-cycloheptenyliden)carbene]-chromium(0), 37. From carbene complex **32a** (n = 0) (170 mg, 0.34 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) and 50 μL (0.33 mmol) of Et_3N after 20 min were obtained 73 mg of a mixture of $Cr(CO)_6$ and **37**. Further purification of **37** by flash column chromatography gave 41 mg (40%) of **37** as a deep red solid. ^{1}H NMR (300 MHz): δ 6.98 (s, 1H, CH), 4.76 (br s, 2H, OCH_2), 4.31 (br s, 2H, OCH_2), 2.02 (s, 3H, CH_3). ^{13}C NMR (75 MHz): δ 302.4 (Cr═C), 224.6 (CO *trans*), 217.6 (CO *cis*), 156.4 (Cq), 119.0 (CH), 77.7 (OCH_2), 73.4 (OCH_2), 23.0 (CH_3). IR (CCl_4): ν 2080, 1990, 1940, 1560, 1280, 1195 cm^{-1}.

General Procedure for Pd-Catalyzed Reactions of Aminocarbene Complexes 15 with Methyl Acrylate and Acrylonitrile. A solution of the aminocarbene complex was placed in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (three cycles). Then, the indicated $Pd(OAc)_2$, Et_3N, and the indicated excess of the alkene were added at rt, and the mixture was refluxed at 70 °C during the stated time. The solvent was removed in vacuo, and the residue was dissolved in AcOEt, and filtered through Celite. Then the crude reaction was purified by flash column chromatography or molecular distillation.

Methyl 4-Phenyl-4-oxobutanoate, 48a.[41] From a mixture of carbene complex **15a** (250 mg, 0.76 mmol), $Pd(AcO)_2$ (3.4 mg, 0.015 mmol), Et_3N (0.21 mL, 1.5 mmol), and methyl acrylate (0.35 mL, 3.8 mmol) in 12 mL of THF after 4 h was obtained 160 mg of a residue that after molecular distillation afforded pure **48a** (116 mg, 80%). ^{1}H NMR (300 MHz): δ 7.92 (d, J = 7.2 Hz, 2H, ArH), 7.51−7.35 (m, 3H, ArH), 3.64 (s, 3H, OCH_3), 3.26 (t, J = 6.7 Hz, 2H, CH_2), 2.70 (t, J = 6.7 Hz, 2H, CH_2). ^{13}C NMR (75 MHz): δ 198.1 (CO), 173.5 (CO_2CH_3), 136.6 (C *ipso*), 133.3, 128.7, 128.1 (aromatic CH), 51.9 (CH_2), 33.5 (CH_2), 28.1 (CH_3). IR ($CHCl_3$): ν 1735, 1685 cm^{-1}. $C_{11}H_{12}O_3$: Calcd C 68.74, H 6.29. Found C 68.62, H 6.02.

Methyl 4-*p*-Bromophenyl-4-oxobutanoate, 48b.[42] From a mixture of carbene complex **15b** (200 mg, 0.5 mmol), $Pd(AcO)_2$ (2.2 mg, 0.009 mmol), Et_3N (0.15 mL, 1 mmol), and methyl acrylate (0.23 mL, 2.5 mmol) in 12 mL of THF after 8 h was obtained 120 mg of a residue that was purified by molecular distillation to afford pure **48b** (101 mg, 75%). ^{1}H NMR (300 MHz): δ 7.78 (d, J = 7.7 Hz, 2H, ArH), 7.54 (d, J = 7.7 Hz, 2H, ArH), 3.64 (s, 3H, OCH_3), 3.21 (t, J = 6.6 Hz, 2H, CH_2), 2.70 (t, J = 6.6 Hz, 2H, CH_2). ^{13}C NMR (75 MHz): δ 197.2 (CO), 173.3 (CO_2CH_3), 135.3 (C *ipso*), 132.0, 129.6 (aromatic CH), 128.5 (C *ipso*), 52.0 (CH_2), 33.4 (CH_2), 28.0 (CH_3). IR ($CHCl_3$): ν 1735, 1690 cm^{-1}. $C_{11}H_{11}BrO_3$: Calcd C 48.73, H 4.09, Br 29.47. Found C 48.44, H 4.34, Br 29.18. **Thermal Reaction of Aminocarbene Complex 15b and Methyl Acrylate.** A solution of aminocarbene complex **15b** (150 mg, 0.37 mmol) and methyl acrylate (159 mg, 1.85 mmol) was refluxed in 4 mL of THF for 48 h. Filtration through Celite and solvent evaporation gave 95 mg of a residue containing *N*,*N*-dimethyl-*p*-bromobenzamide and 4-*p*-bromophenyl-4-oxobutanoate, **48b**, in a 4:1 ratio. The reaction crude was not further purified.

4-*p*-Bromophenyl-4-oxobutanenitrile, 48c. From a mixture of carbene complex **15b** (400 mg, 0.9 mmol), $Pd(AcO)_2$ (4.4 mg, 0.02 mmol), Et_3N (0.3 mL, 1.98 mmol), and acrylonitrile (262 mg, 4.95 mmol) in 12 mL of THF after 8 h was obtained a residue that after column chromatography (hexane:EtOAc, 10:1) afforded **48c** (94 mg, 40%). ^{1}H NMR (300 MHz): δ 7.76 (d, J = 8.6 Hz, 2H, ArH), 7.58 (d, J = 8.6 Hz, 2H, ArH), 3.29 (t, J = 7.0 Hz, 2H, CH_2), 2.71 (t, J = 7.0 Hz, 2H, CH_2). ^{13}C NMR (75 MHz): δ 194.4 (CO), 134.3 (C *ipso*), 132.3, 129.5 (aromatic CH), 129.3 (C *ipso*), 119.1 (C≡N), 34.3 (CH_2), 11.8 (CH_2). IR (KBr): ν 2260 (C≡N), 1680 cm^{-1}. $C_{10}H_8BrNO$: Calcd C 50.45, H 3.39, N 5.88, Br 33.56. Found C 50.22, H 3.57, N 6.13, Br 33.22.

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