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Published on Web 10/07/2005

A General Method for Preparation of Metal Carbenes via Solution- and Polymer-Based Approaches

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Abstract: A new general, synthetically simple, and safe method for the preparation of metal carbene complexes, which is based on diphenyl sulfonium salts as carbenoid precursors, has been developed, and its scope and applications were studied. In general, deprotonation of a sulfonium salt with a base results in a sulfur ylide, which, in turn, reacts with an appropriate metal precursor to give the corresponding metal carbene complex. Thus, starting from benzyldiphenylsulfonium salt, the complexes $\mathrm{(PCX)Rh{=}CHPh}$ ($\mathrm{X = P, N}$) were prepared in quantitative yield. Syntheses of Grubbs' catalyst, $\mathrm{(PCy_3)_2Cl_2Ru{=}CHPh}$, and of Werner's carbene, $\mathrm{[Os({=}CHPh)HCl(CO)(P^iPr_3)_2]}$, were achieved by this method. Novel *trans*-bisphosphine Rh and Ir carbenes, $\mathrm{(^iPr_3P)_2(Cl)M{=}CHPh}$, which could not be prepared by other known methods, were synthesized by the sulfur ylide approach. The method is not limited to metal benzylidenes, as demonstrated by the preparation of the Ru vinyl-alkylidene, $\mathrm{(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CH_2}$, methoxycarbonyl-alkylidene, $\mathrm{(PCy_3)_2Cl_2Ru{=}CH(CO_2Me)}$, and alkylidene $\mathrm{(PCy_3)_2Cl_2Ru{=}CH(CH_3)}$, $\mathrm{(PCy_3)_2Cl_2Ru{=}CH_2}$ compounds. The problem of recycling of starting materials as well as the issue of facile purification of the product metal carbene complex were addressed by the synthesis of a polymer-supported diarylsulfide, the carrier of the carbenoid unit in the process. Based on the sulfur ylide route, a methodology for the synthesis of metallocarbenes anchored to a polymer via the carbene ligand, using a commercial Merrifield resin, was developed.

Introduction

Metal carbene complexes are of much interest in synthetic chemistry.[1] Being a source of the carbenoid unit, metallocarbenes (as isolated complexes or as apparent reactive intermediates) are widely utilized as mediators in different synthetic transformations. For example, cyclopropanation of alkenes with diazo compounds catalyzed by transition metal complexes is among the best methods for the synthesis of cyclopropane derivatives.[2] It is widely believed that this carbon−carbon bond-forming process proceeds via reactive metal carbene intermediates.[2] In addition, metallocarbenes are thought to be key reactive intermediates in catalytic intramolecular[2] and intermolecular[3] hydrocarbon C−H bond functionalization using transition metal complexes and diazo compounds.

Metallocarbenes are also utilized in the formation of C−C double bonds. Nucleophilic alkylidene complexes react with electophiles such as aldehydes and ketones to give olefins in a Wittig-like fashion.[4]

Most importantly, the Schrock molybdenum alkylidene[5] and Grubbs ruthenium alkylidene,[6] which efficiently catalyze olefin metathesis, have led to a myriad of synthetic applications.[7] Ring-closing metathesis, cross-metathesis, ring-opening metathesis, as well as combinations of these transformations, have provided access to organic molecules that would otherwise be difficult to prepare. Among the many applications of Mo-alkylidene based complexes is the effective catalytic asymmetric metathesis.[7i] The benzylidene complex $\mathrm{(PCy_3)_2Cl_2Ru{=}CHPh}$[6b] and its derivatives[8] have found broad applications in both organic[7b,c,g] and polymer synthesis[7d,e] due to its stability, functional group tolerance, and high activity.

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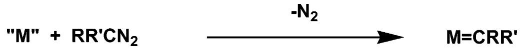
Scheme 1



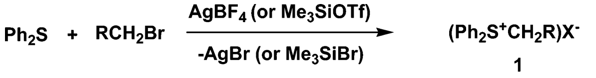
$$\text{"M"} + RR'CN_2 \xrightarrow{-N_2} M{=}CRR'$$

Considering the importance of metal carbenes, and particularly alkylidenes, synthetically simple and general routes for their preparation are highly desirable. There are several synthetic approaches toward alkylidene complexes, with the ones utilizing the corresponding diazoalkanes being the most general[9] (Scheme 1). However, the instability of diazo compounds and the safety issues involved in handling them seriously limit this method, particularly from the standpoint of industrial application.

In addition, metallocarbenes are not always the products of the reaction of transition metal complexes with diazo compounds. Instead, in some cases stable diazoalkane complexes[9b,10] or bridged species [M]−CHR−[M][11] are formed. Other approaches for the synthesis of specific alkylidenes include α-hydrogen abstraction routes,[12] alkylidene transfer from phosphoranes,[13] or ring-opening of cyclopropenes.[6a,14] Recently, reactions of Ru(0) complexes with alkyl dihalides[15] or reactions of Ru(II) compounds with alkynes or alkenes leading to the Ru alkylidenes[16] were reported.

Here, we present our studies on a new, safe, and synthetically simple method for the preparation of metal carbene complexes, utilizing sulfur ylides as carbenoid donors.[17] Applications of sulfur ylides in organic chemistry are well-documented.[18] Our new synthetic route is quite general and can be applied to a wide range of metal complexes. Different sulfur ylides can be utilized, resulting in complexes with various alkylidene units. Moreover, the synthesis of Rh and Ir carbenes, which could not be prepared by other methods, has been accomplished by this method. Some of the results presented here were communicated.[19]

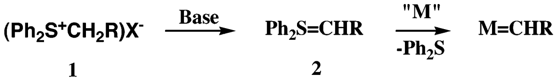
Scheme 2



$$Ph_2S + RCH_2Br \xrightarrow[-AgBr\ (\text{or } Me_3SiBr)]{AgBF_4\ (\text{or } Me_3SiOTf)} \underset{\mathbf{1}}{(Ph_2S^+CH_2R)X^-}$$

X = BF_4, OTf. **1a**: R = Ph; **1b**: R = CH=CH_2;
1c: R = CO_2CH_3; **1d**: R = CH_3; **1e**: R = H

Scheme 3



$$\underset{\mathbf{1}}{(Ph_2S^+CH_2R)X^-} \xrightarrow{\text{Base}} \underset{\mathbf{2}}{Ph_2S{=}CHR} \xrightarrow[-Ph_2S]{\text{"M"}} M{=}CHR$$

2a: R = Ph; **2b**: R = CH=CH_2; **2c**: CO_2CH_3; **2d**: R = CH_3; **2e**: R = H

Base: $KN(Me_3Si)_2$ or MN^iPr_2 (M = K, Li); NEt_3 in case of **2c**

The topic of recycling of diphenyl sulfide, which plays the role of carrier of the carbenoid unit in the new process, as well as the issue of simple purification of the product metal carbene complex, are addressed by the synthesis of a polymer-supported diarylsulfide. Using the sulfur ylide route, we also developed a method for the synthesis of metal carbenes in which the carbene ligand is anchored to a Merrifield resin.

Results and Discussion

Synthesis of Sulfonium Salts and a General Pathway of Metallocarbene Preparation. Alkyldiphenylsulfonium salts **1** were prepared in analogy to literature procedures.[20] Thus, a one-pot reaction of diphenyl sulfide with a large excess of the corresponding alkyl bromide, which also serves as a solvent, in the presence of silver tetrafluoroborare ($AgBF_4$), leads to the formation of salt **1** (Scheme 2). We found that this reaction proceeds in a similar fashion if dichloromethane is used as a solvent and a 10-fold excess of alkyl bromide is applied. In addition, we found that the use of silver salts can be avoided by utilizing trimethylsilyltriflate as a halide abstractor. This is of importance in the synthesis of polymer-supported sulfonium salts, avoiding the problem of separating the product silver halide from the polymer (vide infra).

The general pathway for the synthesis of metallocarbene using diphenyl sulfonium salts[21] is shown in Scheme 3. Deprotonation of the sulfonium salts by a base, such as potassium bis(trimethylsilyl)amide or potassium (or lithium) diisopropylamide, leads to the formation of the corresponding sulfur ylides. In turn, the sulfur ylide, as a carbenoid donor, reacts in situ with the appropriate metal precursor to give the metal carbene complex. Although transition metal complexes of sulfur ylides are reported,[22] there are no examples of the use of such compounds for metal carbene preparation.[23] The transfer of the carbenoid unit between heteroatoms of the main-group elements (so-called "transylidation" reaction) is well documented.[24]

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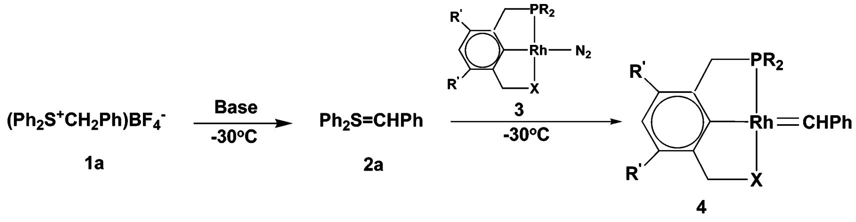
Scheme 4



Base: $KN(Me_3Si)_2$ or MN^iPr_2 (M = K, Li)
R= ^{i}Pr; R' = H; X= P^iPr_2: **3a**, **4a**
R= ^{t}Bu; R' = Me; X= NEt_2: **3b**, **4b**

Synthesis of PCP and PCN Carbenes. The new method was applied first to tridentate PCX-based (X = P, N, O) complexes, which are of current interest to us.[25] Being rigid, electron rich, and bulky, PCX systems proved to be very useful in studies of strong bond activation, stabilization of elusive species, and catalysis.[26] Our goal was to synthesize PCX (X = P, N) rhodium-based benzylidene compounds (Rh═CHPh) via the sulfur ylide route. The first Rh alkylidene complex of the type Rh═C*H*R was recently synthesized using phenyldiazomethane.[27]

The benzylidene sulfur ylide **2a** was prepared by deprotonation of the corresponding benzyl diphenylsulfonium salt **1a** in toluene or THF with $KN(SiMe_3)_2$ or MN^iPr_2 (M = K, Li) (Scheme 4). Because the ylide **2** is only moderately stable, the reaction was carried out at −30 °C. The reaction reached completion immediately, as indicated by a color change to deep yellow and precipitation of MBF_4 (M = K, Li). After filtration of the tetrafluoroborate salt, the resulting sulfur ylide was reacted in situ with PCX−Rh(I) complexes **3**[28] to give the corresponding Rh benzylidene compounds **4** quantitatively. Complexes **4** are relatively unstable and decompose within 24 h via, most likely, a dimerization mechanism,[29] resulting in the starting material **3** and stilbene.

Characterization of compounds **4** by multinuclear NMR techniques unequivocally proves their carbenoid molecular structure. Thus, the carbene protons exhibit very characteristic low-field doublets at 19.8 and 17.2 ppm for **4a** and **4b**, respectively, in the ^1H NMR spectrum, due to coupling with the Rh center. These shifts are similar to the one observed in the case of the only reported Rh benzylidene complex (20.41 ppm).[28] In ^{13}C NMR, the benzylidene carbon, Rh═*C*HPh gives rise to a very low-field resonance at 340.8 and 283.5 ppm for **4a** and **4b**, respectively. Indeed, such extremely low-field signals in ^{13}C NMR are very characteristic of the carbene ligand carbon of late transition metal carbenes.

The carbene complexes **4** can alternatively be obtained by reaction of the PCX-based Rh−dinitrogen complexes **3** with phenyldiazomethane. Experimental and theoretical studies of the mechanism of this reaction were recently reported.[28]

Synthesis of *trans*-($(^iPr_3P)_2$(Cl)M═CHPh (M = Rh, Ir). Interestingly, the sulfur ylide approach can be applied for the synthesis of metal carbenes, which could not be prepared by other known methods. In seminal work on metal carbenes by Werner and co-workers, a variety of dialkyl-substituted carbene Rh(I) complexes, *trans*-[RhCl(═CRR′)(P^iPr_3)$_2$], were synthesized by reaction of the corresponding diazoalkanes with a Rh(I) stibine complex followed by phosphine/stibine ligand exchange, and their chemistry was extensively explored.[30] However, reaction of the rhodium dimer **5a** with phenyldiazomethane, aimed at the preparation of the corresponding *trans*-[RhCl(═CHPh)(P^iPr_3)$_2$], did not lead to the desired results.[31] Applying the new method, the bis(isopropylphosphine)Rh(I) chloride dimer **5a** was reacted with an equimolar amount of the in situ prepared sulfur ylide **2a**, resulting in the Rh benzylidene complex **6a** in quantitative yield (Scheme 5). A low-field signal at 20.17 ppm (doublet of triplets) in the ^1H NMR spectrum and a resonance at 317.86 ppm in the ^{13}C NMR spectrum unambiguously establish the carbenoid structure of complex **6a**. Complex **6a** is moderately stable and undergoes decomposition at room temperature within 3−4 days.

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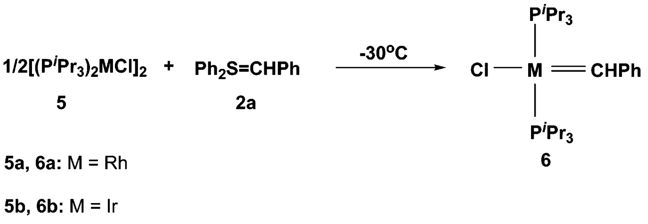
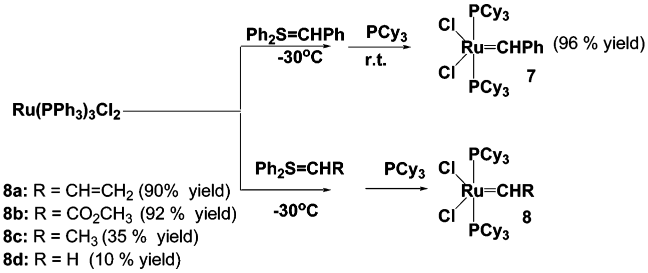
Scheme 5



Scheme 6



The bisphosphine iridium carbenes, *trans*-$[IrCl({=}CRR')(P^iPr_3)_2]$, were synthesized by Werner et al.[32] utilizing a mixed phosphine−stibine iridium compound as a starting material followed by substitution of triisopropylstibine with the bulky triisopropylphosphine ligand. To our knowledge, the analogous monoalkyl-substituted carbene *trans*-$[IrCl({=}CHPh)(P^iPr_3)_2]$ has not been reported. This complex can be synthesized by the new approach and without the aid of the stibine ligand. When bis(triisopropylphosphine)iridium chloride dimer **5b**, prepared in situ from $[(COE)_2IrCl]_2$ (COE = cyclooctene) and P^iPr_3 in pentane,[33] was reacted with 1 equiv of the sulfur ylide **2a** at −30 °C, an immediate color change from yellow to deep green was observed and formation of the iridium benzylidene complex **6b** was confirmed by NMR (Scheme 5).

The ^{31}P NMR spectrum of **5b** shows a singlet at 11.69 ppm. The carbene proton exhibits a low-field triplet at 25.49 ppm in ^{1}H NMR, due to coupling with two P atoms. The carbenoid carbon resonates at 235.6 ppm, which is in excellent agreement with the signal at 234.7 ppm observed for the analogous carbon of Werners' diphenylcarbene *trans*-$[IrCl({=}CPh_2)(P^iPr_3)_2]$.[32a] Contrary to the rhodium benzylidene **6a**, the iridium benzylidene **6b** is thermally stable and can be kept at room temperature without decomposition. The difference in the stability of **6b** versus **6a** may be due to the stronger binding of the P^iPr_3 ligand to the iridium center, which prevents dissociative decomposition pathways of **6b**. To the best of our knowledge, complex **6b** represents the first isolated Ir benzylidene (Ir═CHPh) compound. The observation of an unstable Ir(III) benzylidene at low temperatures was reported.[34] In addition, iridium methylene complexes ($Ir{=}CH_2$) are known.[35]

Synthesis of Ru and Os Carbenes. To further examine the scope of the sulfur ylide method, we applied it to the preparation of the widely used Grubbs' catalyst, $(PCy_3)_2Cl_2Ru{=}CHPh$ **7**.[6b] The reaction of the sulfur ylide **2a** with the commercially available $RuCl_2(PPh_3)_3$ at −30 °C, followed by in situ substitution of the triphenylphosphine ligands by tricyclohexylphosphines at room temperature, led to the Ru carbene complex **7** (Scheme 6). The reaction proceeded cleanly under mild conditions with an excellent isolated yield of 96%.

The sulfur ylide method is not limited to benzylidene carbenes and can be applied to the preparation of other thermodynamically stable metal carbenes. For example, we synthesized the known vinyl diphenylsulfonium tetrafluoroborate **1b**[20b] and applied this carbenoid precursor to the synthesis of $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CH_2$ (**8a**). The preparation of this complex via metathesis of 1,3-butadiene with $(PCy_3)_2Cl_2Ru{=}CHPh$ was reported.[6b] Complex **8a** was directly synthesized by reaction of the freshly prepared vinylalkylidene sulfur ylide with $RuCl_2(PPh_3)_3$ at −30 °C, followed by substitution of the triphenylphosphine ligands with the bulky tricyclohexylphosphines at room temperature (Scheme 6). The NMR spectra of this complex, after work up, were identical to the reported ones.

The sulfur ylide method can also be utilized for generation of carbenes bearing functional groups. For example, diphenyl(methoxycarbonylmethyl)sulfonium fluoroborate salt **1c**[20c] was synthesized and deprotonated by triethylamine to form the corresponding sulfur ylide, which was reacted with $RuCl_2(PPh_3)_3$ at −30 °C to give, after exchange of Ph_3P for Cy_3P, the methoxycarbonyl-substituted Ru carbene $(PCy_3)_2Cl_2Ru{=}CH(CO_2Me)$ **8b** in 92% yield. The NMR spectra of **8b** are identical to those reported in the literature for this complex.[6c]

In addition, the use of simple alkyldiphenylsulfonium salts (methyldiphenyl sulfonium and ethyldiphenylsulfonium) as precursors of the corresponding $M{=}CH(CH_3)$ and $M{=}CH_2$ carbenes was studied. $[CH_3CH_2SPh_2]^+BF_4^-$ **1d**[20d] and $[CH_3SPh_2]^+BF_4^-$ **1e**[20e] salts have been prepared and reacted with the base $KN(SiMe_3)_2$ to generate the corresponding very unstable[18] sulfur ylides at −30 °C. Reaction of the generated $CH_3CH{=}SPh_2$ sulfur ylide with $RuCl_2(PPh_3)_3$ at −30 °C, followed by substitution of triphenylphosphine by tricyclohexylphosphines at room temperature, resulted, after work up, in a 35% yield of the complex $(PCy)_2Cl_2Ru{=}CH(Me)$ **8c**.[6b] The NMR spectra of this complex were identical to the reported ones.[6b] An analogous reaction of the in-situ generated ylide $CH_2{=}SPh_2$ with $RuCl_2(PPh_3)_3$ led to formation of the corresponding known $(PCy)_2Cl_2Ru{=}CH_2$ **8d**[6b] complex, but a poor yield was obtained (10%).[36] Hence, the successful generation of various carbene complexes is dependent on the stability of the corresponding sulfur ylides, and in cases of appropriated sulfur ylide precursors this method can be quite general.

Osmium carbenes are also included in the scope of the new method. As an example, Werner's (hydrido)(benzylidene)osmium complex **9**[37] was quantitatively synthesized via the smooth reaction of $[OsHCl(CO)(P^iPr_3)_2]$ with the freshly prepared sulfur ylide **2** at −30 °C, followed by stirring for 30 min at room temperature (Scheme 7).

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(36) Attempts to prepare a Ru−vinylidene complex were not successful, because deprotonation of the corresponding arylethenyl(diphenyl)sulfonium salt led to formation of an unstable sulfur ylide, which decomposed even at low temperatures (formation of diphenyl sulfide was detected by GC). As a result, a reaction analogous to the preparation of complex **7** led to a mixture of complexes, including the starting $RuCl_2(PPh_3)_3$. Arylethenyl(diphenyl)sulfonium salt was prepared according to: Matsuo, J.; Yamanaka, H.; Kawana, A.; Mukaiyama, T. *Chem. Lett.* **2003**, *32*, 392.

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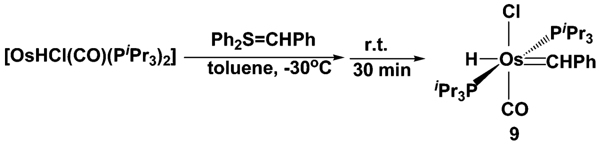
Scheme 7



Synthesis of Metal Carbenes via a Polymer-Supported Sulfonium Precursor. A significant problem in chemical processes is the recycling of starting materials and efficient utilization of reaction byproducts. As follows from Schemes 1 and 2, 1 mol of diphenyl sulfide is involved in the preparation of sulfonium salt precursor, and then liberated in the final step of metal carbene formation. Because Ph_2S plays the role of a mediator of alkylidene transfer from the alkyl bromide to the appropriate metal precursor, its recycling is desirable. Another attractive target is the purification of the metal carbene complex from the product sulfide by simple filtration.

Addressing the above-mentioned issues, the synthesis of the polymeric diaryl sulfide **10** as a sulfur ylide precursor was planned. Brominated polystyrene (1% cross-linked) was swollen in THF and lithiated by two successive treatments with *n*-butyllithium, in a fashion similar to the one described in a literature procedure (Scheme 8).[38] The resulting lithiated polystyrene was reacted with diphenyl disulfide in THF at 70 °C to give, after washings, the polymer-supported diaryl sulfide **10**. A similar reaction of lithiated polystyrene with dimethyl disulfide, leading to a methyl-aryl thioether functionalized polymer, was reported.[39] The overall yield of the lithiation-sulfidation steps is 85%. The resulting polymeric compound was swollen in CH_2Cl_2, mixed with benzyl bromide, and Me_3SiOTf was added dropwise. Overnight stirring at room temperature resulted in formation of the polymer-supported sulfonium salt **11** in 83% yield. The use of Me_3SiOTf as a bromide abstractor instead of $AgBF_4$ is essential to avoid the need to separate between the insoluble solids **11** and AgBr.

The polymeric compound **11** can be used for the preparation of metal carbene complexes in a fashion similar to the soluble sulfonium salt **1a**. This was demonstrated in the preparation of the Grubbs' catalyst **7**. Deprotonation of **11**, swollen in THF, with $KN(SiMe_3)_2$ resulted in a deep yellow color, characteristic of sulfur ylides (presumably **12**). Reaction of the resulting polymer with $RuCl_2(PPh_3)_3$ and concomitant substitution of PPh_3 by PCy_3 (Cy = cyclohexyl) cleanly resulted in the Grubbs' carbene **7** (and free PPh_3) in the homogeneous phase. The aryl sulfide polymer was separated by simple filtration, and subsequent workup resulted in pure **7** in a good yield (77%). Significantly, the separated aryl sulfide polymer was recycled and proved to be active in the synthesis of the sulfonium salt **11** and subsequent carbene transfer. Thus, the polymeric sulfur ylide method is attractive from the points of view of facile metallocarbene separation and the recycling of the carbenoid carrier.

Synthesis of Metal Carbenes on Polymer. The use of polymers as supports in organometallic catalysis is well documented.[39,40] The synthesis and applications of polymer-supported metal carbene complexes are of special interest.[41] As part of the development of sulfur ylide approach, we have demonstrated the facile applicability of the method for the synthesis of polymer-supported metallocarbenes. The readily available Merrifield peptide resin (1% cross-linked) Poly-$C_6H_4-CH_2-Cl$ (**13**) can be used as a solid support, utilizing the benzylic group as a precursor to a carbene unit. Thus, reaction of **13**, swollen in CH_2Cl_2, with Ph_2S in the presence of Me_3SiOTf formed a polymer-supported sulfonium triflate salt formulated as **14** (Scheme 9). After being washed with ether and dried, the salt **14** was deprotonated with $KN(SiMe_3)_2$ in THF to give a characteristically colored yellow sulfur ylide **15**. Notably, ylide **15** is bound to the solid support via the carbene unit rather than via diphenyl sulfide as was the case of ylide **12**. Now, the reaction of **15** with the appropriate metal precursor will result in the corresponding metallocarbene incorporated onto the polymer. For example, when sulfur ylide **15** was reacted with $RuCl_2(PPh_3)_3$ in THF, followed by PPh_3 exchange with PCy_3, the polymer-supported Grubbs' catalyst **16** was formed. This Ru carbene on polymer can be easily separated from other products of the reaction by simple filtration and washings. The ^{31}P NMR of **16** swollen in THF exhibits a singlet at 40.10 ppm, which is in good agreement with the ^{31}P NMR of the soluble monomer **7**.

To chemically confirm the presence of Grubbs' catalyst on the polymer beads, the activity of **16** in olefin metathesis was examined. Indeed, the polymer-supported ruthenium carbene **16** catalyzed the metathesis of allyl benzene under conditions similar to the ones reported for the analogous reaction with soluble Ru benzylidene 7.[42] The product of self-metathesis, 1,4-diphenyl-2-butene, was observed by GC and GC/MS of the reaction solution in 70% yield, 8:1 *E*/*Z* ratio after 3 h.

Supported Grubbs' carbene complexes, attached to polymers via the carbene ligand, have been reported,[40b,c,i] and found to be useful as "boomerang", recyclable metathesis catalysts. As reported, these supported complexes operate by release of the Ru catalyst into the solution upon metathesis with the substrate alkene, generating an alkene-substituted polymer. At the end of the reaction, the carbene complex is recaptured by metathesis with the polymer-bound alkene. The carbene-based polymer-supported catalysts are made by cross metathesis of vinyl-modified polystyrene resins with the Ru Grubbs' carbenes. Our methodology for the preparation of polymer attached metal carbenes (via the carbene ligand) is not limited to metathesis catalysts and in principle can be applied generally to any complex capable of being generated by the sulfur ylide method.

In conclusion, the new sulfur ylide method allows the straightforward synthesis of metallocarbene complexes supported on a polymer, utilizing the commercially available Merrifield resin. It can be utilized also in the site-isolation of otherwise unstable metallocarbenes. The synthesis of such

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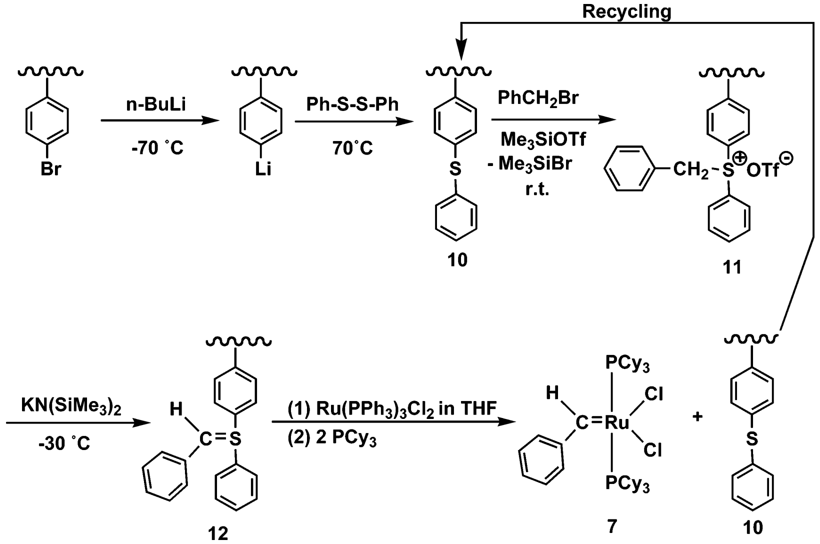
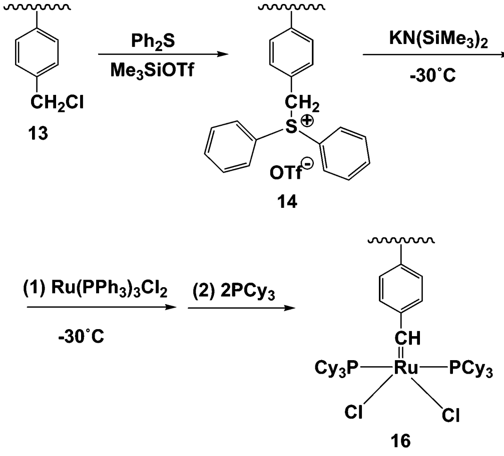
Scheme 8



Scheme 9



polymer-supported carbene complexes of various metals is currently sought in our group. The trapping of unstable carbenes on polymer should retard the widely accepted bimolecular decomposition in solution and thus may help in the investigation of their properties.

Summary

A new, selective, and safe method for the synthesis of metal carbene complexes has been developed, involving the reaction of metal complexes with a sulfur ylide as the carbenoid donor. The new route is synthetically simple, the sulfonium salt being prepared in a one-step synthesis. The method can be applied to various metals and alkylidene units. Thus, carbene complexes of rhodium, iridium, ruthenium, and osmium were synthesized. Also, compounds with different alkylidene units, such as benzylidene (=CHPh), vinylalkylidene (=CH−CH=CH$_2$), methoxycarbonyl alkylidene (=CH−CO$_2$CH$_3$), and alkylidene (=CH−CH$_3$, =CH$_2$), were prepared. Moreover, this approach allows the direct synthesis of new metal carbene complexes, which could not be prepared by known methods.

The method was extended by the incorporation of the sulfonium salt precursor onto a polymer. The use of the corresponding polymer-supported sulfur ylide allows recycling of the diarylsulfide (which is the carbenoid unit carrier in the process), as well as the easy separation of the product metallocarbene from other byproducts by simple filtration. In addition, a route for the synthesis of polymer-supported metal carbene complexes based on a Merrifield resin was developed. As an example, a Grubbs'-type catalyst with a polymeric benzylidene unit was prepared and shown to be active in olefin metathesis. The straightforward synthesis of metal carbenes on polymer by our new method opens the possibility for simple site isolation and investigation of a variety of carbenes.

Experimental Section

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in MBraun MB 150B-G and Vacuum Atmospheres Nexus System gloveboxes. The complexes [Rh(COE)$_2$Cl]$_2$,[43] [Ir(COE)$_2$Cl]$_2$,[44] RuCl$_2$(PPh$_3$)$_3$,[45] and [OsHCl(CO)(P^{i}Pr$_3$)$_2$][46] were prepared according to literature procedures. Butyllithium (1.6 M solution in hexane, Aldrich) was titrated immediately before use.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 400.1, 100.6, and 162.0 MHz, respectively, at 295 K (if not specified otherwise), using a Bruker Avance-400 NMR spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents, and in ^{13}C{^{1}H} NMR the ^{13}C signal of the deuterated solvents was used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H$_3$PO$_4$ and referenced to an external 85% solution of phosphoric acid in D$_2$O. Abbreviations used in the description of NMR data are as follows: Ar − aryl, br − broad, s − singlet, d − doublet, t − triplet, q − quartet, m − multiplet, v − virtual. Elemental analyses were performed at the Microanalytical Laboratories, The Hebrew University of Jerusalem, Israel.

Synthesis of 1. Diphenyl sulfide (3 g, 16 mmol) was mixed with a 10-fold excess of benzyl bromide in 20 mL of CH$_2$Cl$_2$. 1 equiv of AgBF$_4$ (3.12 g, 16 mmol) was gradually added during 30 min. Alternatively, Me$_3$SiOTf (2.9 mL, 16 mmol) can be used instead of AgBF$_4$. The reaction mixture was stirred for an additional 2 h and left overnight without stirring. CH$_2$Cl$_2$ (20 mL) was added, and the AgBr precipitate was filtered off (when Me$_3$SiOTf was used, the formed Me$_3$SiBr was removed under vacuum together with the solvent in the next step). The solvent from the filtrate was removed under vacuum, resulting

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in a yellowish oil. Addition of ether to the oil led to precipitation of crude **1a** as a white solid, which was filtered and recrystallized from a CH_2Cl_2/ether solution to give 5.36 g (92% yield) of pure **1a** as white crystals. ^{1}H NMR ($CDCl_3$): 7.86 (m, 4H, Ar−H), 7.56 (m, 6H, Ar−H), 7.20 (m, 5H, Ar−H), 5.28 (s, 2H, S−CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 134.54−123.75 (aromatic carbons), 50.82 (s, S−CH_2).

For convenience, we also describe a literature procedure:[20a] diphenyl sulfide (3 g, 16 mmol) was dissolved in 20 mL of benzyl bromide. To the resulting stirred solution was gradually added $AgBF_4$ (3 g, 16 mmol) during 30 min. The reaction mixture was stirred for additional 2 h and left overnight without stirring. CH_2Cl_2 (20 mL) was added, and the AgBr precipitate was filtered off. The solvent from the filtrate was removed under vacuum, resulting in a yellowish oil. Addition of ether to the oil led to precipitation of crude **1a** as a white solid, which was filtered and recrystallized from a CH_2Cl_2/ether solution to give 5.12 g (88% yield) of pure **1a**.

Reaction of 3a with Ph_2SCHPh. Formation of Complex 4a. A toluene solution (3 mL) of $KN(SiMe_3)_2$ (27 mg, 0.133 mmol) was added dropwise to a stirred suspension of $[Ph_2SCH_2Ph]BF_4$ (48 mg, 0.132 mmol) in 2 mL of toluene at −30 °C. The resulting yellow solution was filtered into a toluene solution of **3a** (60 mg, 0.132 mmol) precooled to −30 °C. A color change from brown to dark green-brown took place upon warming the mixture to room temperature. ^{31}P{^{1}H} NMR revealed formation of complex **4a** in almost quantitative yield. Complex **4a** is stable at temperatures below −30 °C and was spectroscopically characterized at −40 °C. ^{31}P{^{1}H} NMR (toluene-d_8): 71.90 (d, $^1J_{RhP}$ = 165.0 Hz). ^{1}H NMR (toluene-d_8): 19.75 (d, $^2J_{RhH}$ = 2.7 Hz, 1H, Rh═C*H*Ph), 8.18 (d, J_{HH} = 7.1 Hz, 2H, Ar−H), 7.32 (d, J_{HH} = 8.1 Hz, 2H, Ar−H), 7.16 (m, 4H, Ar−H), 3.29 (vt, J_{HH} = 4.2 Hz, 4H, Ar−CH_2−P), 1.70 (m, 4H, C*H*$(CH_3)_2$), 0.91 (m, 24H, CH(CH_3)$_2$). Selected ^{13}C{^{1}H} NMR signals (toluene-d_8): 340.80 (m, Rh═*C*HPh), 182.60 (dt, J_{RhC} = 19.4 Hz, J_{PC} = 10.0 Hz, C_{ipso}).

Reaction of 3b with Ph_2SCHPh. Formation of Complex 4b. To a stirred suspension of $[Ph_2SCH_2Ph]BF_4$ (48 mg, 0.132 mmol) in 2 mL of toluene was added a solution of $KN(TMS)_2$ (27 mg, 0.133 mmol) in 3 mL of toluene at −30 °C. The resulting yellow solution of **2** was filtered into a cold (−30 °C) toluene solution of **3b** (63 mg, 0.132 mmol). The reaction mixture was warmed to room temperature, and almost quantitative conversion to complex **4b** was observed by ^{31}P{^{1}H} NMR. Compound **4b** was not stable at room temperature and was characterized at −40 °C. ^{31}P{^{1}H} NMR (toluene-d_8): 92.72 (d, $^1J_{RhP}$ = 218.23 Hz). ^{1}H NMR (toluene-d_8): 17.21 (d, $^2J_{RhH}$ = 7.8 Hz, 1H, Rh═C*H*Ph), 8.37 (d, J_{HH} = 7.6 Hz, 2H, Ar−*H*), 7.75 (m, 1H, Ar−*H*), 7.53 (d, 1H, *J* = 7.3 Hz, Ar−*H*), 7.12 (m, 1H, Ar−*H*), 6.63 (bs, 1H, Ar−*H*), 3.99 (s, 2H, Ar−CH_2−N), 3.63 (bd, 2H, J_{PH} = 8.4 Hz, Ar−CH_2−P), 3.03 (m, 2H, N−CH_2−CH_3), 2.92 (m, 2H, N−CH_2−CH_3), 2.84 (m, 6H, N−CH_2−CH_3), 2.39 (s, 3H, Ar−CH_3), 2.19 (s, 3H, Ar−CH_3), 1.23 (d, 18H, J_{PH} = 12.6 Hz, C(CH_3)$_3$). Selected ^{13}C{^{1}H} NMR signals (toluene-d_8): 283.51 (m, Rh═*C*HPh), 186.15 (dd, J_{RhC} = 18.6 Hz, J_{PC} = 9.4 Hz, C_{ipso}), 32.41 (d, J_{PC} = 16.3 Hz, P−*C*$(CH_3)_3$).

Preparation of 6a. Complex **6a** was prepared analogously to complexes **4**, using 30 mg (0.033 mmol) of the dimer **5a**, 24 mg (0.066 mmol) of $[Ph_2SCH_2Ph]BF_4$, and 14 mg (0.066 mmol) of $KN(TMS)_2$. Yield: 85%. ^{31}P{^{1}H} NMR (toluene-d_8): 32.10 (d, $^1J_{RhP}$ = 167.4 Hz). ^{1}H NMR (toluene-d_8): 20.17 (dt, $^2J_{RhH}$ = 3.2 Hz, $^3J_{PH}$ = 6.1 Hz, 1H, Rh═C*H*Ph), 8.12 (d, J_{HH} = 7.2 Hz, 1H, Ar−H), 7.30−6.92 (m, 4H, Ar−H), 2.21 (m, 6H, C*H*$(CH_3)_2$), 1.83 (m, 36H, CH(CH_3)$_2$). ^{13}C NMR (toluene-d_8): 317.86 (m, Rh═*C*HPh), 25.53 (vt, *C*H$(CH_3)_2$), 20.34 (s, CH(*C*H_3)$_2$).

Preparation of 6b. The iridium dimer **5b** (30 mg, 0.034 mmol) was stirred with P^iPr_3 (21 mg, 0.134 mmol) in 2 mL of pentane for 10 min. To the resulting yellow solution was added at −30 °C the sulfur ylide **2a**, prepared by reaction of **1a** (24 mg, 0.067 mmol) and $KN(TMS)_2$ (14 mg, 0.067 mmol) in toluene (2 mL). An immediate change of color from yellow to deep green took place. The resulting mixture was filtered through a cotton pad, and the solvent from filtrate was removed under vacuum. The residue was washed with cold pentane and ether (3 × 2 mL), successively. Complex **6b** was extracted with benzene from the remaining solid. Evaporation of benzene resulted in the clean carbene **6b** in 80% yield. ^{31}P{^{1}H} NMR (toluene-d_8): 11.40 (s). ^{1}H NMR (toluene-d_8): 25.49 (t, $^3J_{PH}$ = 7.1 Hz, 1H, Ir═C*H*Ph), 7.12−6.91 (m, 5H, Ar−H), 2.35 (m, 6H, C*H*$(CH_3)_2$), 1.44 (dvt, *N* = 12.7 Hz, J_{HH} = 7.2 Hz, 36H, CH(CH_3)$_2$). Selected ^{13}C NMR (toluene-d_8): 235.6 (t, J_{PC} = 7.5 Hz, Ir═*C*HPh), 155.8 (Ar, *ipso*), 26.5 (vt, N = 24.2 Hz, *C*H$(CH_3)_2$), 20.9 (s, CH(*C*H_3)$_2$).

Preparation of 7. $[Ph_2SCH_2Ph]BF_4$ (212 mg, 0.584 mmol) was dissolved in THF (5 mL) and cooled to −30 °C. A solution of $KN(SiMe_3)_2$ (140 mg, 0.584 mmol) in THF (5 mL) was added, resulting in a rapid change of color to yellow. $KN(^iPr)_2$ (81 mg, 0.584 mmol) or $LiN(^iPr)_2$ (62 mg, 0.584 mmol) can be alternatively used as bases. The yellow solution was added at −30 °C to a solution of $Ru(PPh_3)_3Cl_2$ (552 mg, 0.576 mmol) in CH_2Cl_2 (10 mL). The mixture was kept at −30 °C for an additional 30 min, after which a solution of tricyclohexylphosphine (352 mg, 1.240 mmol) in CH_2Cl_2 (7 mL) was added and the mixture was warmed to room temperature and stirred for 2 h. The solvent was removed under vacuum, and the residue was washed with ethanol (3 × 25 mL) to remove the residual phosphine, sulfide, and silyl byproducts. The remaining solid was dried under high vacuum to give the pure Grubbs' carbene (510 mg, 0.553 mmol) in 96% yield. Its spectral data are identical to those reported in the literature.[6b]

Preparation of 8a. The previously reported[6b] complex **8** was prepared in 90% yield analogously to complex **7**, using 30 mg (0.096 mmol) of $[Ph_2SCH_2CH{=}CH_2]BF_4$ (**1b**), 20 mg (0.067 mmol) of $KN(SiMe_3)_2$, 91 mg (0.095 mmol) of $RuCl_2(PPh_3)_3$, and 58 mg (0.20 mmol) of tricyclohexylphosphine. The washings were performed with acetone.

Preparation of 8b. To a benzene/toluene suspension (0.5 mL) of $[Ph_2SCH_2CO_2CH_3]BF_4$[20c] (23 mg, 0.067 mmol) at −30 °C was added 11 μL (0.074 mmol) of Et_3N, and after 15 min ylide solution was added to a benzene/toluene suspension (0.5 mL) of $RuCl_2(PPh_3)_3$ (54 mg, 0.057 mmol) at −30 °C. The color immediately became green. The presumably generated $(Ph_3P)_2Cl_2Ru({=}CHCO_2CH_3)$ complex was reacted with PCy_3 (57 mg, 0.170 mmol) to form the more stable $(Cy_3P)_2Cl_2Ru({=}CHCO_2CH_3)$ complex **8b**, which was obtained in 92% yield. This moderately stable complex exhibited NMR spectra identical to the reported ones.[6c]

Preparation of 8c. The previously reported[6b] complex **8c** was prepared in 35% yield (65% of the initial $RuCl_2(PPh_3)_3$ complex remained unchanged), analogously to complex **7**, using 11 mg (0.035 mmol) of $[Ph_2SCH_2CH_3]BF_4$ (**1d**), 8 mg (0.038 mmol) of $KN(SiMe_3)_2$, 30 mg (0.032 mmol) of $RuCl_2(PPh_3)_3$, and 30 mg (0.10 mmol) of tricyclohexylphosphine. The washings were performed with pentane and benzene.

The $Ph_2S(CH_2CH_3)OTf$ salt can also be used instead of $[Ph_2SCH_2CH_3]BF_4$.

Preparation of 8d. The previously reported[6b] complex **8d** was observed in 10% yield (90% of the initial $Ru(PPh_3)_3Cl_2$ complex remained unreacted), when 10.5 mg (0.035 mmol) of $[Ph_2SCH_3]BF_4$ (**1e**), 8 mg (0.038 mmol) of $KN(SiMe_3)_2$, 30 mg (0.032 mmol) of $RuCl_2(PPh_3)_3$, and 30 mg (0.10 mmol) of tricyclohexylphosphine were reacted in a procedure analogous to complex **7** formation.

Preparation of 9. A toluene solution (3 mL) of $KN(SiMe_3)_2$ (27 mg, 0.133 mmol) was added dropwise to a suspension of $[Ph_2SCH_2Ph]BF_4$ (48 mg, 0.132 mmol) in 2 mL of toluene at −30 °C. The resulting yellow solution was filtered into a cold (−30 °C) toluene solution of $[OsHCl(CO)(P^iPr_3)_2]$ (75 mg, 0.132 mmol). After the reaction mixture was stirred for 30 min, the solvent and volatile products were removed under high vacuum. The product was extracted from the dry residue with ether (3 × 4 mL) and the solvent was evaporated, resulting in compound **9** as an orange solid in 88% yield.

Synthesis of Grubbs' Catalyst 7 via Polymer. Synthesis of Diarylsulfide 10. 1% cross-linked brominated polystyrene resin (1 g, 4 mmol Br/g, purchased from Fluka) was swollen in 30 mL of THF with stirring for 1 h, and then 10 mL of 1.6 M *n*-BuLi in hexane was added. After additional stirring (1 h), the liquid phase was removed and 30 mL of THF was added followed by a second portion of 30 mL of 1.6 M *n*-BuLi in hexane. This reaction mixture was stirred at 70 °C overnight. The resulting lithiated beads were cooled to room temperature and washed repeatedly with THF. Afterward, the beads were suspended in 30 mL of THF and a solution containing 3.5 g (6 mmol) of Ph_2S_2 in 20 mL of THF was added. After 1 h of stirring at room temperature and 5 h at 70 °C under argon, the beads were collected on a sintered glass funnel, washed successively with THF, THF−ether (1:1), ether, ether−benzene (1:1), benzene, benzene−methanol (1:1), and finally methanol. After drying under high vacuum, 1.015 g of polymer beads was obtained. Anal. Calcd (for 100% conversion): S, 11.47 (3.58 mmol S/g). Found: S, 9.59 (3.0 mmol S/g); Br, 0.0. Yield: 84%.

Synthesis of [Ph−CH$_2$−S(Ph)−Poly]OTf, 11. 100 mg (3.0 mmol of S/g) of the diaryl sulfide derivative **10** was swollen in 5 mL of CH_2Cl_2, and 0.46 mL (3.0 mmol) of benzyl bromide was added. After 30 min of stirring, 0.06 mL (0.30 mmol) of Me_3SiOTf was added, and the mixture was stirred overnight. The resulting beads, [Ph−CH$_2$−S(Ph)−Poly]$^{\oplus}$OTf$^{\theta}$, were filtered, washed with ether, and dried under high vacuum, resulting in 146 mg of the polymer **11**.

Synthesis of Grubbs' Catalyst 7 from [Ph−CH$_2$−S(Ph)−Poly]-OTf, 11. Beads **11** (146 mg) were swollen in 5 mL of THF and cooled to −30 °C. A THF solution (2 mL) of $KN(SiMe_3)_2$ (73 mg, 0.30 mmol) was added, resulting in a rapid change of color to yellow. The yellow beads were filtered, washed with THF from silyl byproducts, and suspended in THF. A solution of $RuCl_2(PPh_3)_3$ (284 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was added at −30 °C to an efficiently stirred mixture of the yellow beads **12** in THF. The mixture was stirred at −30 °C for an additional 1 h. A solution of tricyclohexylphosphine (171 mg, 0.61 mmol) in CH_2Cl_2 (3 mL) was then added, and the mixture was warmed to room temperature and stirred for 2 h. The soluble carbene **7** was separated from the insoluble polymer-supported sulfide **10** by filtration. Polymer **10** was kept for the recycling process. The solvent from the filtrate was removed under vacuum, and the residue was washed with dry ethanol (3 × 25 mL). The resulting solid was dried to give the clean Grubbs' catalyst **7** (190 mg, 0.23 mmol) as evident from its spectral data as compared to the literature.[6b] Total yield (based on **10**): 77%.

Synthesis of Grubbs' Catalyst on Polymer. 1% cross-linked Merrifield's resin Poly−C_6H_4−CH_2Cl (100 mg, 4.71 mmol Cl/g) was swollen in 10 mL of CH_2Cl_2 for 3 h. Diphenyl sulfide (1 mL, 59 mmol) was added followed by Me_3SiOTf (0.1 mL, 0.55 mmol), and the mixture was stirred for 6 h, resulting in compound **14**. The resulting polymer was filtered off, washed with ether (3 × 5 mL), and dried under vacuum. The dry beads of **14** were swollen in 5 mL of THF and cooled to −30 °C. A THF (3 mL) solution of $KN(SiMe_3)_2$ (100 mg, 0.49 mmol) was added, resulting in a rapid color change to yellow. The yellow beads were filtered, washed with THF, and suspended in an additional portion of THF (3 mL). To this suspension, a solution of $RuCl_2(PPh_3)_3$ (386 mg, 0.47 mmol) in 7 mL of CH_2Cl_2 at −30 °C was added, and the resulting mixture was stirred at −30 °C. After being stirred for 2 h, a solution of tricyclohexylphosphine (280 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was added, and the resulting mixture was warmed to room temperature followed by stirring for 2 h. The beads were separated by filtration, washed with dry methanol, and dried under vacuum to give the polymer-supported carbene **16**. ^{31}P NMR: 40.10 ppm (s). Anal. Calcd (for 100% conversion): Cl, 7.82; P, 6.8. Found: Cl, 4.14; P, 3.24. Yield: 52%.

Self-Metathesis of Allyl Benzene Catalyzed by the Polymeric Carbene 16. Polymer **16** (20 mg, 0.01 mmol) was placed in allyl benzene (0.5 mL, 3.77 mmol), and the mixture was stirred under vacuum. After 3 h, a white solid was observed on the walls of the reactor. The metathesis product, 1,4-diphenyl-2-butene, was formed in 70% yield. Formation of this product was confirmed by GC/MS ($M^+ + 1 = 209.4$) and ^{1}H NMR.

Acknowledgment. This work was supported by the Israel Science Foundation, Jerusalem, Israel, and by the Helen and Martin Kimmel Center for Molecular Design. D.M. is the Israel Matz Professor of Organic Chemistry.

JA050781+