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A New General Method for the Preparation of Metal Carbene Complexes

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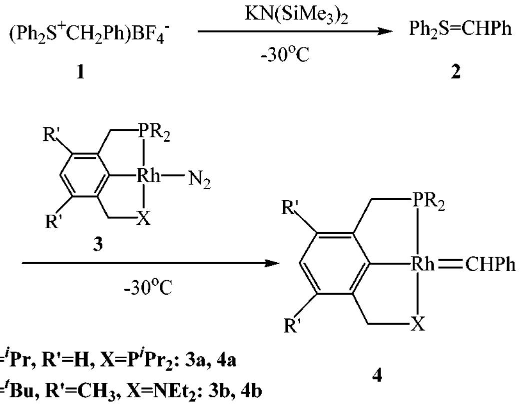
The chemistry of late-transition-metal carbene complexes has recently received much attention, primarily due to the high catalytic activity of phosphine ruthenium carbene complexes in olefin metathesis.[1,2] The most useful Ru carbene in these series is Grubbs' catalyst, $(PCy_3)_2Cl_2Ru{=}CHPh$, bearing a benzylidene unit.[1] Being highly active and remarkably tolerant to common functional groups, this compound found broad applications in both organic[2b,c] and polymer chemistry.[2d,e] Therefore, synthesis and investigation of late-metal benzylidene complexes ($M{=}CHPh$) is a topic of great interest.[1−4a] There are several synthetic approaches toward alkylidene complexes,[4] with the ones utilizing the corresponding diazoalkane being the most popular.[1,2,5] However, the instability of diazo compounds and the safety issues involved in handling them seriously limit this method. Another recent approach, involving the reaction of precursors to unstable Ru(0) complexes with alkyl dihalides,[6] is limited by the difficult synthesis of the unstable Ru(COD)(COT) precursor.[7] New approaches toward Ru−alkylidenes starting from Ru−hydride complexes and utilizing alkyne or alkene functions were reported recently.[8] Here, we present a new, synthetically simple and safe method toward carbene preparation by using sulfur ylides as carbenoid precursors.[9] Such ylides are extensively used in organic chemistry.[10] To our knowledge, there are no examples for the synthesis of metal carbene complexes by using these compounds, although metal complexes of sulfur ylides are reported.[11,12] Also, the "transylidation" reaction, transfer of a carbenoid unit between heteroatom centers, is well-known among main group elements.[13] The new synthetic route is general and can be applied to different metals. Moreover, it can be used for the synthesis of carbene complexes which could not be prepared by known methods.

Scheme 1

$$\underset{\mathbf{1}}{(Ph_2S^+CH_2Ph)BF_4^-} \xrightarrow{\text{Base}} \underset{\mathbf{2}}{Ph_2S{=}CHPh} \xrightarrow[\text{-}Ph_2S]{\text{"M"}} M{=}CHPh$$

Scheme 2



R=^{i}Pr, R'=H, X=P^{i}Pr$_2$: 3a, 4a
R=^{t}Bu, R'=CH$_3$, X=NEt$_2$: 3b, 4b

The general pathway of metal carbene preparation is presented in Scheme 1. Benzyldiphenylsulfonium tetrafluoroborate **1**, the precursor of the corresponding ylide compound, can be easily prepared by a one-pot reaction of diphenylsulfide and benzyl bromide in the presence of $AgBF_4$.[14] Deprotonation of this sulfonium salt by base results in the formation of the benzyl ylide **2**, that readily reacts with the appropriate metal complex to give the metal carbene complex.

In continuation of our interest in pincer-type PCX complexes,[15] we have studied the possibility of synthesis of rhodium PCX-type (X = P, N) carbene complexes by this approach. When the sulfonium salt **1** was reacted with 1 equiv of $KN(SiMe_3)_2$ at −30 °C in toluene, immediate formation of a yellow solution and precipitation of KBF_4 took place (Scheme 2). After filtration of KBF_4, the sulfur ylide **2** was reacted with complexes **3**[16] at

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(16) The synthesis of compounds **3** will be reported elsewhere.

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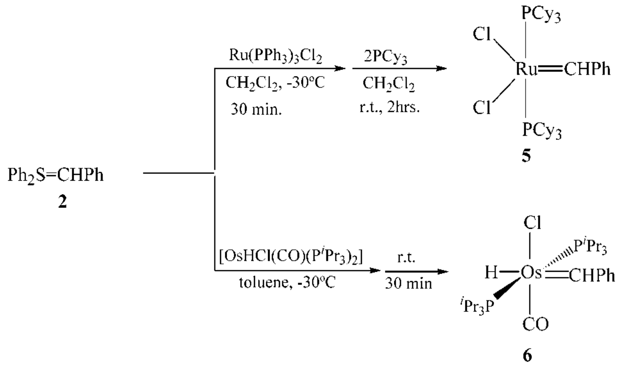
Scheme 3

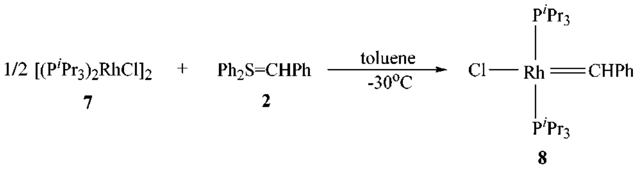


−30 °C resulting in clean conversion to the Rh−benzylidene complexes **4**. The Rh(I)−benzylidene complexes are not stable at room temperature and were characterized by multinuclear NMR spectroscopy at −40 °C. The carbene protons exhibit very characteristic low-field doublets at 19.8 and 17.2 ppm for **4a** and **4b**, respectively, in the ^{1}H NMR spectrum, due to coupling with the Rh center. For comparison, the sole isolated alkylidene complex of the type Rh═C*H*R shows a resonance of the carbene proton at 20.41 ppm.[17] The carbenoid carbon gives rise to an extremely low-field signal in ^{13}C NMR at 340.8 and 283.6 ppm for **4a** and **4b**, respectively, that provides unequivocal proof of the M═*C*HR structure. Indeed, both Ru and Rh carbenes show extremely low-field signals for the carbenoid carbon atom.[1,17,18] Carbenes **4** can alternatively be prepared by reaction of the PCX based Rh(I) complexes **3** with phenyldiazomethane.[19]

Stable, well-known metal carbenes can also easily and cleanly be prepared by the sulfur ylide approach. An example is the preparation of the synthetically very useful Grubbs' catalyst, $(PCy_3)_2Cl_2Ru{=}CHPh$ (**5**).[1] The reaction of $(PPh_3)_3RuCl_2$ in CH_2Cl_2 with the freshly prepared sulfur ylide **2** in THF at −30 °C and concomitant substitution of the PPh_3 ligands by tricyclohexylphosphine at room-temperature results, after the workup, in the Ru−benzylidene complex **5** in 96% yield[20] (Scheme 3). The NMR spectra of this complex are identical to the reported ones.[1]

The scope of this method is not limited to rhodium and ruthenium carbenes. For instance, Werner's hydrido-osmium carbene **6**[3] was also successfully prepared by this approach (Scheme 3). Ylide **2** was added to the osmium complex $[OsHCl(CO)(P^iPr_3)_2]$[21] in toluene at −30 °C, resulting in an immediate color change to orange. Stirring for additional 30 min at room temperature and workup results in quantitative formation of the benzylidene complex **6**. Spectroscopic data for **6** were identical to the reported literature values.[3b]

Scheme 4



Significantly, the approach described above can be applied also to the synthesis of carbenes, which could not be prepared by existing methods. Werner and co-workers have synthesized and extensively studied the chemistry of novel disubstituted Rh(I) carbene complexes *trans*-$[RhCl({=}CRR')(P^iPr_3)_2]$.[18] These complexes have been prepared with the aid of SbR_3 ligands, which later were substituted by the bulky triisopropylphosphine ligands. However, attempts to prepare similar monosubstituted carbene *trans*-$[RhCl({=}CHPh)(P^iPr_3)_2]$ by use of phenyldiazomethane did not lead to the desired results.[22] Remarkably, this complex can be synthesized by the new approach and without the aid of stibine ligands. When bis-(triisopropylphosphine)rhodium chloride dimer **7** reacts with 1 equiv of the sulfur ylide **2** at −30 °C in toluene, selective formation of the Rh benzylidene complex **8** is observed (Scheme 4).

The ^{31}P NMR spectrum of **8** shows a doublet at 32.1 ppm, due to coupling with the Rh center (d, J_{RhP} = 167.4 Hz). The carbene proton exhibits a low-field doublet of triplets at 20.17 ppm in ^{1}H NMR, due to coupling with Rh and P atoms. The carbenoid carbon resonates at 317.86 ppm, which is in excellent agreement with the signal at 316.11 ppm observed for the analogous carbon of Werner's diphenylcarbene *trans*-$[RhCl({=}CPh_2)(P^iPr_3)_2]$.[18a] Compound **8** is moderately stable and decomposes at room temperature within 3−4 days.

In summary, a new, general, synthetically simple and safe method for the synthesis of metal carbene complexes is described. The method involves the reaction of a metal precursor with a sulfur ylide as the carbene donor. The reaction is selective and can be applied to different metals: alkylidenes of ruthenium, osmium, and rhodium were synthesized. Moreover, this approach allows the direct synthesis of new metal carbene complexes, which are difficult to prepare by known methods.

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Supporting Information Available: Text describing the synthesis of compounds **1**, **4**−**6**, **8** and the characterization of compounds **1**, **4**, and **8** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] This procedure was performed under a nitrogen atmosphere. $[Ph_2SCH_2Ph]BF_4$ **1** (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 (2 mL) was added, resulting in a rapid change of color to yellow. 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. A solution of tricyclohexylphosphine (352 mg, 1.240 mmol) in CH_2Cl_2 (7 mL) was then 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 clean Grubbs' carbene **5** (510 mg, 0.553 mmol) in 96% yield.

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