A New General Method for the Preparation of Metal Carbene Complexes

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Received March 1, 2001
Revised Manuscript Received April 19, 2001

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, (PCy3)2ClRuCp*, bearing a benzylidene unit.1 Being highly active and remarkably tolerant to common functional groups, this compound found broad applications in both organic20ze and polymer chemistry.2d-e Therefore, synthesis and investigation of late-metal benzylidene complexes (M=CHPh) is a topic of great interest.1

Approaches toward alkylidene complexes,4 with the ones utilizing diazo compounds and the safety issues involved in handling them seriously limit this method. Another approach toward carbene preparation by using sulfur ylides as precursors to unstable Ru(0) complexes with alkyldihalides,5 is limited by the difficult synthesis of the unstable Ru(COD)(COT) precursor.6 New approaches toward Ru–alkylidene starting from Ru–hydrate complexes and utilizing alkyl or alkenes functions were reported recently.7

Here, we present a new, synthetically simple and safe method toward carbene preparation by using sulfur ylides as carbonoid precursors.8 Such ylides are extensively used in organic chemistry.9 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.10,11 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. The general pathway of metal carbene preparation is presented in Scheme 1. Benzylidiphensulfonyl tetrfluoroborate 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 AgBF4.14 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(SiMe3)2 at −30 °C in toluene, immediate formation of a yellow solution and precipitation of KBF4 took place (Scheme 2). After filtration of KBF4, the ylide 2 was reacted with complexes 3a at

![Scheme 1](Image)

![Scheme 2](Image)

(14) Frazzen, V.; Schmidt, H.-J.; Mertz, C. Ber. 1961, 94, 2942. See also Supporting Information.
(16) The synthesis of compounds 3 will be reported elsewhere.

10.1021/ja0157393 CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/11/2001
−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 1H NMR spectrum, due to coupling with the Rh center. For comparison, the sole isolated alkylidene complex of the type Rh=CHR shows a resonance of the carbene proton at 20.41 ppm.17 The carbene carbon gives rise to an extremely low-field signal in 13C NMR at 340.8 and 283.6 ppm for 4a and 4b, respectively, that provides unequivocal proof of the M=CHR structure. Indeed, both Ru and Rh carbones show extremely low-field signals for the carbene carbon atom.1,17,18 Carbones can alternatively be prepared by reaction of the PCX based Rh(I) complexes 3 with phenylidiazomethane.19

Stable, well-known metal carbones can also easily and cleanly be prepared by the sulfur ylide approach. An example is the preparation of the synthetically very useful Grubbs’ catalyst, (PC3)2Ru=CHPh (5).20 The reaction of (PPh3)2RuCl2 in CH2Cl2 with the freshly prepared sulfur ylide 2 in THF at −30 °C and concomitant substitution of the PPh3 ligands by tricyclohexylphosphine at room-temperature results, after the workup, in the Ru−benzylidene complex 5 in 96% yield (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 carbones. For instance, Werner’s hydrido-osmium carbene 6 was also successfully prepared by this approach

![Scheme 3](https://example.com/scheme3.png)

**Scheme 3**

\[
\text{Ph}_{3}S=\text{CHPh} \quad 2 \\
\text{[Ru(PPh)}_{3}]_{2}\text{Cl}_{2} \quad \rightarrow \quad \text{PC}_{3} \quad \text{Cl} \quad \text{Ru=CHPh} \quad 5 \\
\text{[OsHCl(}CO\text{)(PPh)}_{3}]_{2} \quad \text{Cl} \quad \text{Os=CHPh} \quad 6
\]

(Scheme 3). Ylide 2 was added to the osmium complex [OsHCl(CO)(PPh3)2]1 in toluene at −30 °C in an immediate color change to orange. Stirring for additional 30 min at room temperature and workup resulted in quantitative formation of the benzylidene complex 6. Spectroscopic data for 6 were identical to the reported literature values.20

Significantly, the approach described above can be applied also to the synthesis of carbones, which could not be prepared by existing methods. Werner and co-workers have synthesized and extensively studied the chemistry of novel disubstituted Rh(I) carbone complexes trans-[RhCl(CHR)2(PPh3)2].18 These complexes have been prepared with the aid of SbR3 ligands, which later were substituted by the bulky triisopropylphosphan ligands. However, attempts to prepare similar monosubstituted carbene trans-[RhCl(=CHPh)(PPh3)2] by use of phenylidiazomethane did not lead to the desired results.22 Remarkably, this complex can be synthesized by the new approach and without the aid of sulfane ligands. When bis-(triisopropylphosphophosphate)ruthodium 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 31P NMR spectrum of 8 shows a doublet at 32.1 ppm, due to coupling with the Rh center (d, J_RP = 167.4 Hz). The carbene proton exhibits a low-field doublet of triplets at 20.17 ppm in 1H NMR, due to coupling with Rh and P atoms. The carbene carbon resonates at 317.86 ppm, which is in excellent agreement to the reported literature values.3b The carbene proton exhibits a low-field doublet of triplets at 20.17 ppm in 1H NMR, due to coupling with Rh and P atoms. The carbene carbon resonates at 317.86 ppm, which is in excellent agreement to the reported literature values.3b

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.

**Acknowledgment.** This work was supported by the Israel Science Foundation, Jerusalem, Israel, and by the Tasheliot program of the Israeli Ministry of Science. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry. We thank Yehoshua Ben-David for technical assistance.

**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.

JA0157393