Catalytic Activity of a New Ruthenium−(Trimethylsilyl)diazomethane Complex

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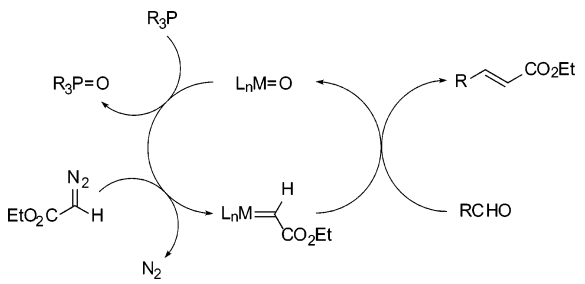
Summary: The ruthenium catalyst $RuCl(NO)(PPh_3)_2$ is shown to be an active catalyst for the methylenation of aldehydes in the presence of (trimethylsilyl)diazomethane, triphenylphosphine, and 2-propanol. Spectroscopic investigations have revealed the unusual formation of an octahedral $\eta^2(C,N)$-coordinated (trimethylsilyl)diazomethane ruthenium complex that, upon treatment with triphenylphosphine and 2-propanol, produces methylenetriphenylphosphorane.

The synthesis of alkenes by the olefination of carbonyl compounds is a very important transformation in organic synthesis.[1] In addition to phosphorus ylides,[2] other related stoichiometric processes involving sulfur[3] and silicon[4] ylides have been developed together with organometallic stoichiometric reagents derived from titanium, chromium, and zinc.[5,6] Recently, several transition-metal complexes, including those of Mo,[7] Re,[8] Fe,[9] Ru,[9c,10] and Rh,[11] have been disclosed as efficient catalysts for the olefination of carbonyl compounds with diazo reagents. Both carbene and phosphorane have been proposed as intermediates in these processes. The two mechanistic pathways suggested for the olefination of carbonyl derivatives with ethyl diazoacetate are shown in Schemes 1 and 2. In the first place, a nucleophilic carbene species is formed from the transition-metal complex and ethyl diazoacetate. The carbene species reacts with the carbonyl compound to produce the desired alkene and the corresponding metal−oxo species, which is then reduced by the phosphorus reagent (Scheme 1).

Scheme 1



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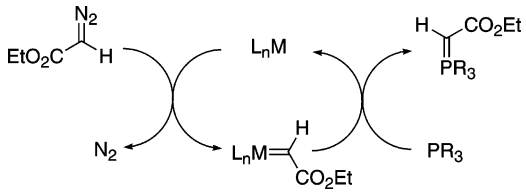
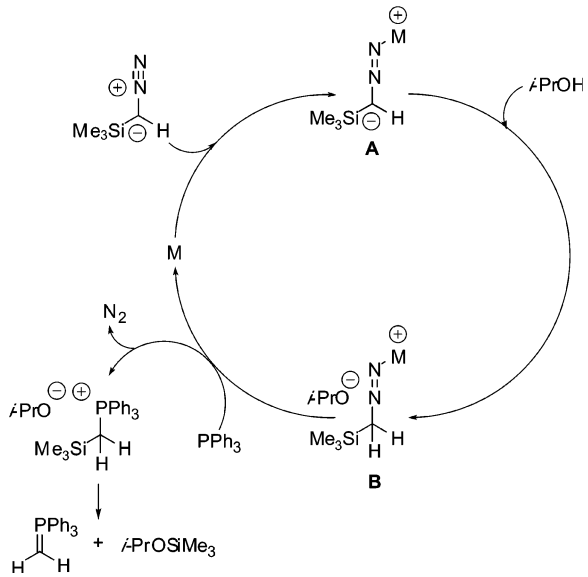
Scheme 2



Alternatively, the reaction between the transition-metal complex and ethyl diazoacetate produces an electrophilic carbene species, which is then attacked by the phosphorus reagent, thus forming a phosphorus ylide species that adds to the carbonyl derivative (Scheme 2).

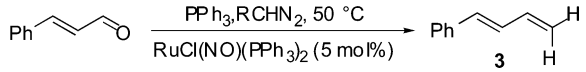
We have recently proposed a distinct catalytic cycle for our rhodium-catalyzed methylenation reaction with (trimethylsilyl)diazomethane that relies on the formation of methylenetriphenylphosphorane without the involvement of a carbene intermediate (Scheme 3).[11]

Scheme 3



Protonation of the (trimethylsilyl)diazomethane metal complex **A** with 2-propanol, followed by a triphenylphosphine attack, generates the corresponding phosphonium salt. Desilylation then leads to the methylenetriphenylphosphorane, which has been characterized by NMR spectroscopy. In an effort to support the existence of an intermediate such as **A**, we have investigated a number of other transition-metal complexes that produce phosphorus ylides under similar reaction conditions. Herein, we wish to report our study of a new ruthenium−(trimethylsilyl)diazomethane complex that catalyzes the methylenation of aldehydes.

Table 1. Ruthenium-Catalyzed Methylenation of Cinnamaldehyde: Optimization of the Reaction Conditions



entry	reacn conditions	conversn, %[a]
1	CH_2N_2/THF	≤5
2	CH_2N_2/benzene	≤5
3	Me_3SiCHN_2/THF, 16 h	≥98
4	Me_3SiCHN_2, *i*-PrOH, THF, 2 h	≥98
5	Me_3SiCHN_2, *i*-PrOH, THF, 16 h[b]	20
6	Me_3SiCHN_2, *i*-PrOH, THF, 16 h[c]	≤5
7	Me_3SiCHN_2, *i*-PrOH, toluene, 16 h	87
8	Me_3SiCHN_2, *i*-PrOH, benzene, 16 h	82
9	Me_3SiCHN_2, *i*-PrOH, TBME, 16 h	32
10	Me_3SiCHN_2, *i*-PrOH, CH_2Cl_2, 16 h	≤5

[a] Determined by GC. [b] Reaction at 25 °C. [c] Without triphenylphosphine.

Our interest in the de novo synthesis of terminal alkenes prompted us to study the generation of either methylenetriphenylphosphoranes or methylene metal carbenes from diazo reagents. In principle, the generation of such species requires the use of diazomethane as the diazo precursor. The syntheses of a few methylene metal carbenes using this strategy have been disclosed in the literature.[12] For instance, Roper has reported the synthesis of the air-stable methylene carbene **2** from diazomethane and the chloronitrosylbis(triphenylphosphine)ruthenium complex (**1**) (eq 1).[13]

$$\underset{\mathbf{1}}{RuCl(NO)(PPh_3)_2} \xrightarrow[\text{benzene}]{CH_2N_2/Et_2O} \underset{\mathbf{2}}{CH_2{=}RuCl(NO)(PPh_3)_2} \quad (1)$$

Unfortunately, the methylene carbene **2** is completely unreactive toward aldehydes, and no olefination product is observed when carbene **2** is added to a mixture of cinnamaldehyde and triphenylphosphine (Table 1, entries 1 and 2). However, quite surprisingly, the methylenation of cinnamaldehyde took place in the presence of catalyst **1** and (trimethylsilyl)diazomethane,[14] a safe alternative to diazomethane (entry 3). In the presence of 1 equiv of triphenylphosphine and 2-propanol, the methylenation of cinnamaldehyde proceeded smoothly at 50 °C to produce diene **3** in a quantitative yield (entry 4). The methylenation reaction occurred very slowly at room temperature and did not proceed in the absence of triphenylphosphine (entries 5 and 6). Although the reaction conditions are compatible with other solvents,

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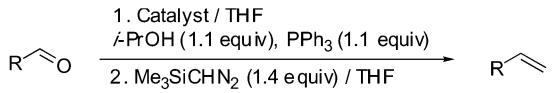
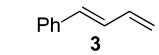
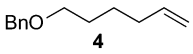
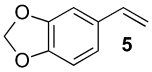
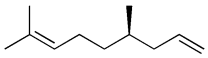
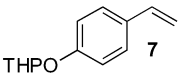
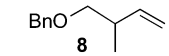
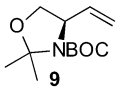
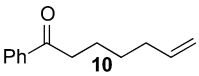
Table 2. Transition-Metal-Catalyzed Methylenation of Aldehydes with Me_3SiCHN_2



Entry	Product	$RuCl(NO)(PPh_3)_2$[a] Yield[b]; Time	$RhCl(PPh_3)_3$[c] Yield[b]; Time
1	 **3**	74%; 0.5 h	88%; 0.5 h
2	 **4**	68%; 1 h	74%; 0.5 h
3	 **5**	60%; 2 h	74%; 1 h
4	 **6**	41%; 3 h	84%; 7 h
5	 **7**	81%; 3 h	93%; 1 h
6	 **8**	62%; 3 h	78%; 3 h
7[d]	 **9**	63%; 6 h (92% ee)	86%; 4 h (92% ee)
8	 **10**	56%; 3 h	87%; 0.5 h

[a] Reaction was run with 5 mol % catalyst at 50 °C. [b] Isolated yield. [c] Reaction was run with 25 mol % catalyst at 25 °C. [d] The starting material was 95% ee.

such as toluene and benzene, longer reaction times are required to reach reasonable conversions (entries 7 and 8). The reaction proceeded very slowly in TBME, whereas no reaction occurred when dichloromethane was used as the solvent (entries 9 and 10).

A comparison of the catalytic reactivities of ruthenium complex **1** and Wilkinson's catalyst for the methylenation of aldehydes in the presence of (trimethylsilyl)diazomethane, triphenylphosphine, and 2-propanol is shown in Table 2. The reaction with Wilkinson's catalyst proceeds efficently at room temperature, whereas good conversions are obtained with catalyst **1** only when the reaction is performed at 50 °C. In addition, the isolated yields of terminal alkenes are usually lower when using the ruthenium catalyst; thus, from a synthetic point of view, the rhodium system is more attractive.

However, from a mechanistic standpoint, the discrepancy between the reactivities of the ruthenium complex with diazomethane and (trimethylsilyl)diazomethane is quite intriguing and prompted us to study these complexes by spectroscopic analysis. As reported by Roper,[13] the reaction of ruthenium complex **1** and diazomethane generated the ruthenium carbene **2**, which was isolated and characterized at room temperature. The ruthenium carbene **2** displayed a singlet in phosphorus NMR (see the Supporting Information for details). This is consistent with a trigonal-bipyramidal geometry in which both triphenylphosphine groups are trans, and thus both phosphorus atoms are equivalent. In addition, the proton NMR spectrum showed a triplet at 13.5 ppm, for the methylene carbene moiety (see the Supporting Information for details).

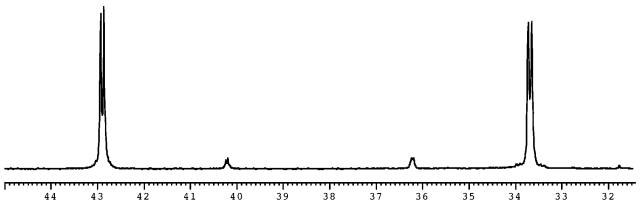


Figure 1. ^{31}P NMR spectrum of $RuCl(NO)(PPh_3)_2$ (**1**) and Me_3SiCHN_2 in d_8-THF at −40 °C.

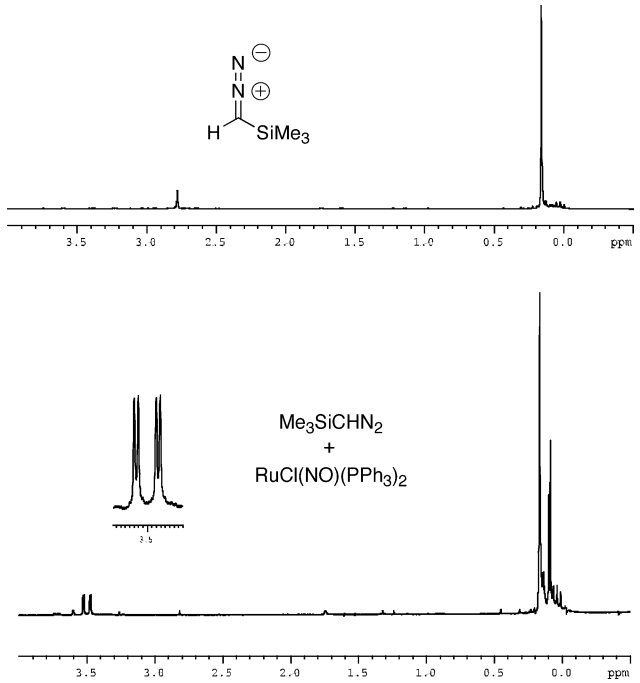


Figure 2. ^1H NMR spectra of Me_3SiCHN_2 and a mixture of $RuCl(NO)(PPh_3)_2$ and Me_3SiCHN_2 in d_8-THF at −40 °C.

The situation is quite different with regard to the reaction of ruthenium complex **1** and (trimethylsilyl)diazomethane. When an equimolar amount of Me_3SiCHN_2 was added to complex **1** at −40 °C in THF, no nitrogen evolution was observed, and a new species appeared which was characterized by multinuclear NMR at −40 °C. This new complex gives rise to two doublets at 33.7 and 42.9 ppm ($^1J_{PP}$ = 12 Hz) in $^{31}P\{^1H\}$ NMR, which is consistent with two nonequivalent phosphorus atoms (Figure 1). The absence of nitrogen evolution during the formation of this new species suggests the formation of a (trimethylsilyl)diazomethane−ruthenium complex. Indeed, new signals appear in the ^1H and ^{13}C NMR spectra. For instance, the proton of (trimethylsilyl)diazomethane, originally at 2.78 ppm, is shifted to 3.50 ppm and now appears as a doublet of doublets ($^1J_{HP}$ = 20, 4 Hz) (Figure 2). In the ^{13}C NMR spectrum, the coordinated Me_3SiCHN_2 gives rise to a doublet of doublets at 9.4 ppm ($^1J_{CP}$ = 57, 26 Hz) (Figure 3).

The chemical shifts of both the proton and the carbon of the coordinated Me_3SiCHN_2 are not consistent with the formation of a carbene or an azine species.[12] Nevertheless, in both cases, phosphorus coupling suggests a

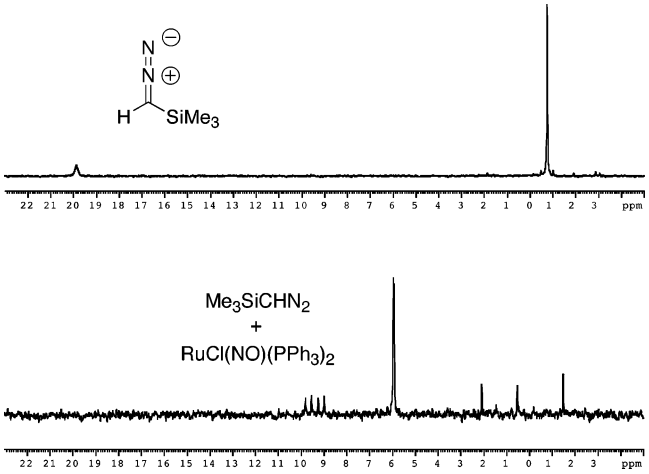
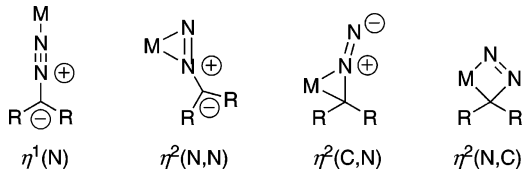


Figure 3. ^{13}C NMR spectra of Me_3SiCHN_2 and a mixture of $RuCl(NO)(PPh_3)_2$ and Me_3SiCHN_2 in d_8-THF at −40 °C.

close relationship between the carbon of Me_3SiCHN_2 and the ruthenium atom.[15] Among the stable diazoalkane complexes that have been isolated from reactions between transition-metal complexes and diazoalkanes, the most common are either η^2-diazoalkane ligands coordinated through the N−N multiple bonds (η^2(N,N)) or η^1-diazoalkane ligands coordinated at the terminal nitrogen atom (η^1(N)) (Chart 1).[16] Although the chemical

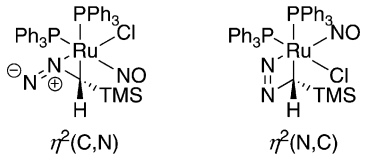
Chart 1



shifts observed for the new coordinated Me_3SiCHN_2 species suggest such complexes, usually no phosphorus−carbon or phosphorus−hydrogen coupling is detected for η^1(N) and η^2(N,N) coordination.[16g] Other suggested coordination modes of diazoalkane ligands include η^2-coordination through the C−N multiple bonds (η^2(C,N)) and the formation of metallacyclobutanes with 1,3-N,C coordination (η^2(N,C)). Such complexes have been proposed as intermediates in the mechanism of decomposition of diazoalkanes but have never been fully characterized.[17]

The observed NMR data of the Me_3SiCHN_2−ruthenium complex reported herein can, however, be rationalized through an octahedral η^2(C,N)-coordinated diazoalkane metal complex (Chart 2). Not only can the formation of either a metallacyclobutane or a η^2(C,N) complex account for the observed chemical shifts but it is also consistent with the observed phosphorus coupling constants.[18]

Chart 2



The sensitivity of the (trimethylsilyl)diazomethane−ruthenium complex precludes its characterization by other techniques that cannot be run at low temperature.[19] The THF solution of this new Me_3SiCHN_2−ruthenium species is stable at −40 °C but starts to slowly decompose when warmed above 0 °C. No ruthenium carbene was observed upon warming the mixture, and the ruthenium complex decomposed with nitrogen evolution to generate $Me_3SiCH{=}CHSiMe_3$ (72% yield by GC-MS) and an insoluble amorphous inorganic mixture.[20] The Me_3SiCHN_2−ruthenium complex is stable at −40 °C in THF in the presence of triphenylphosphine and 2-propanol. When this mixture was warmed to 50 °C, the formation of 71% of methylenetriphenylphosphorane and 50% of isopropoxytrimethylsilane was observed (see the Supporting Information for details).

In conclusion, we have described a new Me_3SiCHN_2−ruthenium complex which is catalytically active in the presence of triphenylphosphine and 2-propanol to generate methylenetriphenylphosphorane. Upon treatment with aldehydes, the latter gives rise to the corresponding alkenes. NMR spectroscopic analysis is consistent with the unusual formation of an octahedral η^2(C,N)-coordinated (trimethylsilyl)diazomethane−ruthenium complex.

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Supporting Information Available: Text and figures giving characterization data for new compounds and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The observed phosphorus coupling could not be due to a coordinated phosphorus azine, as the formation of such a species from triphenylphosphine and (trimethylsilyl)diazomethane does not proceed, even at 50 °C. For instance, when a 1:1 mixture of (trimethylsilyl)-diazomethane and triphenylphosphine was heated at 50 °C in THF for 3 days, the GC-MS spectra and the phosphorus NMR revealed the presence of 90% of the starting materials together with 10% of $Me_3SiCH{=}CHSiMe_3$ and 10% of triphenylphosphine oxide. See the Supporting Information for details.

(16) For reviews, see: (a) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, *180*, 623−663. (b) Putala, M.; Lemenovskii, D. A. *Russ. Chem. Rev. (Engl. Transl.)* **1994**, *63*, 197. For selected examples, see: (c) Cowie, M.; Loeb, S. J.; McKeer, I. R. *Organometallics* **1986**, *5*, 854−860. (d) Polse, J. L.; Kaplan, A. W.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6316−6328. (e) Kwen, H.; Young, V. G.; Maatta, E. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1145−1146. (f) Albertin, G.; Antoniutti, S.; Bordignon, E.; Carrera, B. *Inorg. Chem.* **2000**, *39*, 4646−4650. (g) Dias, E. L.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **2001**, *123*, 2442−2443. (h) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 6532−6546.

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(18) At this time, it is not possible to specifically assign which isomer is formed, although the NMR spectra clearly showed the formation of only one isomeric species.

(19) For instance, no valuable information could be obtained from in situ React-IR analysis, because of the heterogenicity of the mixture.

(20) No discrete species could be characterized from this mixture. Unfortunately, the new Me_3SiCHN_2−ruthenium species was not stable in the solid state and could not be crystallized from the mixture even at low temperature under argon.