

Articles

Direct Synthesis of Thermally Stable PCP-Type Rhodium Carbenes

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Dinitrogen rhodium(I) complexes with bis-chelating diphosphine ligands are shown to be robust precursors toward Rh carbene complexes. While the Rh aryl N₂ complex **1** reacts with phenyldiazomethane, giving the phenylcarbene complex **2**, the Rh alkyl N₂ precursor **3** reacts with 2 equiv of phenyldiazomethane to yield the Rh vinyl carbene complex **5**. The more stable diphenyldiazomethane does not form carbene complexes under similar conditions, giving instead the stable diazomethane complex **10**.

Introduction

The chemistry of the late-transition-metal carbene complexes has recently received much attention, primarily due to high catalytic activity of the ruthenium phosphine carbene complexes in olefin metathesis.^{1,2} There are several synthetic approaches toward the carbene complexes, with the ones utilizing the corresponding diazoalkanes being the most attractive.^{1,3} Indeed, this direct method normally results in excellent yields of pure compounds. Another recent method involves the reacting of precursors to unstable Ru(0) complexes with alkyl dihalides.⁴ Surprisingly, despite the wide interest in late-transition-metal carbenes Werner's system remains the sole example of isolated Rh carbene complexes.⁵ These complexes have been prepared with the aid of SbR₃ ligands, which later can be substituted by bulky phosphines. To our knowledge, no direct method for the synthesis of Schrock-type phosphine Rh carbenes has been reported. Also, no

rhodium carbene complex with a proton at the carbene atom has been isolated—the corresponding ruthenium complexes are among the most active metathesis catalysts.¹ In continuation of our interest in PCP-type complexes,⁶ we have studied the possibility of synthesis of rhodium PCP-type carbene complexes of this family. Here we present a direct approach toward stable Rh carbene complexes with chelated phosphine ligands that utilizes a diazomethane derivative. Preparation of an iridium carbene complex by deprotonation of an Ir(III) methyl halide precursor in a chelating phosphine system was reported.^{7,8}

Results and Discussion

The dinitrogen complex **1** was prepared in high yield by treatment of the known methyl chloride Rh(III) complex⁹ with 1.2 equiv of NaBEt₃H in benzene under a dinitrogen atmosphere (eq 1).¹⁰

Complex **1** exhibits a doublet in the ³¹P NMR spectrum at 79.65 ppm (*J*_{RhP} = 157.0 Hz). The ipso carbon atom appears in the ¹³C NMR spectrum as a doublet of triplets at 167.73 ppm. The coordinated N≡N ligand

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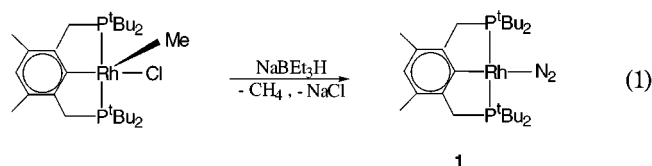
(6) For example: (a) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1996**, 1673. (b) Vigalok, A.; Kraatz, H.-B.; Konstantinovskiy, L.; Milstein, D. *Chem. Eur. J.* **1997**, *3*, 253. (c) Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 7873. (d) Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539. (e) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *19*, 895.

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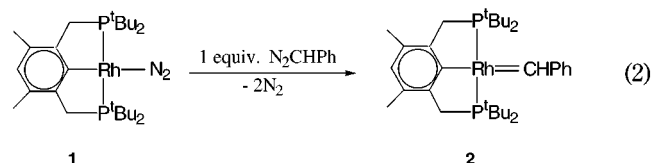
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(10) For similar unsaturated PCP-type Rh(I) complexes see: (a) Nemeš, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442–1447. (b) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.



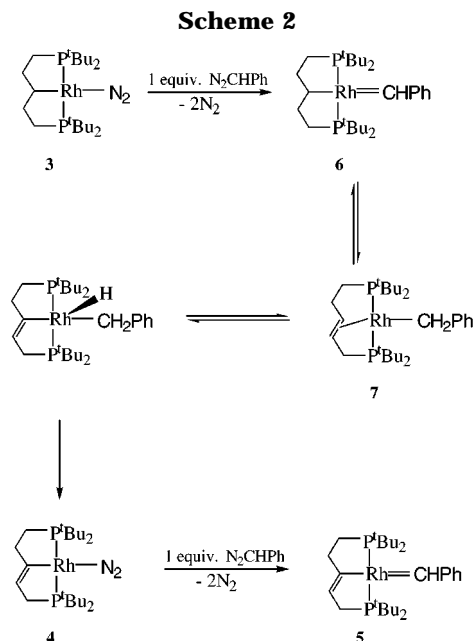
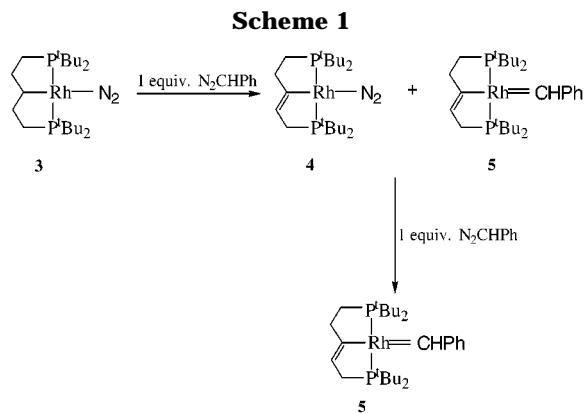
gives rise to a strong IR band at 2120 cm^{-1} . When **1** was reacted with 1 equiv of phenyldiazomethane in pentane, quantitative formation of the new Rh carbene complex **2** was immediately observed (eq 2). Complex **2** is an air-sensitive red solid, highly soluble in common organic solvents.



The ^{31}P NMR spectrum of **2** shows a doublet at 88.31 ppm (d, $J_{RhP} = 169.1\text{ Hz}$). The carbene proton exhibits a low-field doublet at 20.41 ppm in the 1H NMR spectrum, due to coupling with the Rh center. The corresponding Ru and Ir carbene protons normally resonate at 13–19 ppm.^{1,11} While the low-field shifts are characteristic for $M=CHR$ species, unequivocal proof of the carbenoid structure can be deduced from the ^{13}C NMR spectra. Both Ru and Rh carbenes show extremely low field signals for the carbenoid carbon atom.^{1,5} In the case of **2** this carbon atom gives rise to a signal at ca. 344.10 ppm, which appears as a multiplet due to coupling to Rh and two phosphorus atoms.^{1,5} Complex **2** is thermally stable both in the solid state and in solution. It did not react with olefins even under moderate heating. The lack of reactivity of complex **2** toward the olefin metathesis reaction may be associated with the high stability of the bis-chelates toward phosphine dissociation. It should also be kept in mind that these are d^8 complexes, while d^6 Ru(II) carbene complexes are metathesis catalysts.¹²

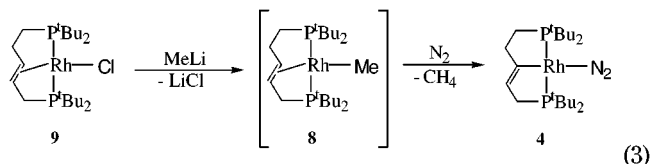
Interestingly, reaction of the aliphatic analogue of **1**, complex **3**,¹³ with 1 equiv of phenyldiazomethane gave a mixture of two products: the vinyl dinitrogen complex **4** and the carbene complex **5** derived from **4**. Addition of 1 equiv more of phenyldiazomethane to this mixture gave pure **5** in excellent yield (Scheme 1). Complex **5** is an air-sensitive violet-red solid. It exhibits a double AB quartet in the ^{31}P NMR spectrum centered at 106.43 ppm with a large J_{PP} value of 210.3 Hz due to the inequivalent phosphorus atoms in a mutually trans arrangement. Similarly to **2**, the carbenoid proton in **5** appears in the 1H NMR spectrum as a doublet at 20.11 ppm ($J_{RhH} = 2.2\text{ Hz}$), while its carbon gives a multiplet at 343.52 ppm in the ^{13}C NMR spectrum.

As it is known that complex **3** undergoes a fast, reversible β -hydrogen-elimination process,¹³ it is likely that the initially formed saturated carbene complex **6** undergoes rapid hydride migration to give the benzyl



olefin complex **7** (Scheme 2).¹⁴ C–H bond activation by the Rh center followed by elimination of toluene would result in **4**. Addition of phenyldiazomethane to **4** gives complex **5**.

To verify the C–H activation hypothesis, we attempted to prepare the Rh(I) alkyl olefin complex **8**. Interestingly, reaction of the olefinic complex **9** with 1 equiv of MeLi resulted exclusively in complex **4**, the presumed intermediate alkyl olefin complex **8** probably undergoing metal insertion into the C_{ipso} -H bond giving after alkane elimination the vinyl dinitrogen complex **4** (eq 3). Complex **4** shows a double AB quartet in the



(11) Iridium: Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079. See also ref 7.

(12) It was demonstrated that olefin metathesis at a ruthenium d^6 center is facilitated by dissociation of a phosphine ligand: Dias, E. L.; Nguyen, S. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.

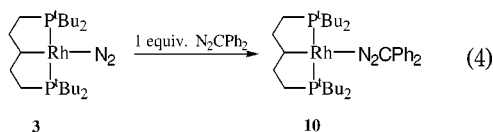
(13) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1838.

^{31}P NMR spectrum centered at 94.70 ppm ($J_{PAPB} = 287.7\text{ Hz}$). The vinylic proton appears at 6.18 ppm as a doublet of doublets with large coupling constants to the phosphine atoms ($J_{PH} = 37.8$ and 9.5 Hz). The ipso carbon atom gives rise to a doublet of broad triplets at 181.92

(14) For formal C–H insertion in Rh carbenes see: Herber, U.; Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **1998**, *17*, 10.

ppm ($J_{\text{RhC}} = 37.0$ Hz). The coordinated dinitrogen ligand strongly absorbs in the IR spectrum at 2124 cm^{-1} .

In contrast to the reactivity of phenyldiazomethane, when the less reactive diphenyldiazomethane was added to **3** no carbene formation was observed. Instead, the diphenyldiazomethane complex **10** was quantitatively formed (eq 4). Complex **10** shows NMR data similar to



that of the starting complex **3** and its IR spectrum exhibits an intense band at 2038 cm^{-1} , which is higher than $\nu(\text{N}\equiv\text{NCPh}_2)$ of the reported Rh diphenyldiazomethane complexes.¹⁵ The diazo carbon atom appears as a multiplet at 74.55 ppm, just a few ppm upfield from the starting diazo alkane, confirming that no dinitrogen elimination took place.

Summary

A direct synthetic method toward phosphine-containing Rh carbene complexes is described. The dinitrogen Rh(I) PCP chelates are shown to be suitable precursors for carbenes containing a hydrogen atom at the carbenoid carbon atom. When a rhodium alkyl complex is used, initial dehydrogenation takes place, resulting in formation of a rhodium vinyl complex, which reacts further to give a rhodium carbene. Diphenyldiazomethane forms a stable diazomethane complex with no dinitrogen elimination to give the corresponding rhodium carbene taking place.

Experimental Section

General Procedures. All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres with an MO-40 purifier). All solvents were reagent grade or better. Pentane, benzene, and THF were distilled over sodium/benzophenone ketyl. All solvents were degassed and stored under high-purity nitrogen after distillation. All deuterated solvents (Aldrich) were stored under high-purity nitrogen on molecular sieves (3 Å). Phenyldiazomethane¹⁶ and diphenyldiazomethane¹⁷ were prepared as reported.

¹H, ³¹P, and ¹³C NMR spectra were recorded at 400, 162, and 100 MHz, respectively, using a Bruker AMX400 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm downfield from TMS and referenced to the residual solvent *h*₁ (7.24 ppm, chloroform-*d*, chloroform; 128.00 ppm, benzene), respectively. ³¹P chemical shifts are in ppm downfield from H₃PO₄ and referenced to an external 85% phosphoric acid sample. All measurements were performed at 20 °C unless otherwise specified. Attempts to obtain elemental analyses for the PCP Rh(I) complexes were unsuccessful due to their high air sensitivity.

Preparation of 1. To a solution of PCP–Rh(Me)Cl⁹ (50 mg, 0.085 mmol) in 2 mL of benzene was added 100 μL of a 1 M solution of NaBEt₃H in toluene, resulting in a color change from red to brown. The solvent was evaporated, and the

remaining solid was extracted with pentane (2 \times 2 mL). Evaporation of pentane under vacuum gave 43 mg (90%) of **1**.

³¹P{¹H} NMR (C₆D₆; δ , ppm): 79.65 (d, $J_{\text{RhP}} = 157.0$ Hz). ¹H NMR (δ , ppm): 6.69 (s, 1H, Ar H), 3.10 (vt, 4H, $J = 3.9$ Hz, CH₂P), 2.28 (s, 6H, Ar CH₃), 1.29 (vt, $J_{\text{PH}} = 6.2$ Hz, 36H, t-Bu). ¹³C{¹H} NMR (δ , ppm): 167.73 (dvt, $J = 38.7$ Hz, $J = 5.7$ Hz, ipso C), 150.57 (vtd, $J = 9.4$ Hz, $J = 3.3$ Hz, Ar), 124.02 (vtd, $J = 8.9$ Hz, $J = 1.4$ Hz, Ar), 121.88 (s, Ar), 35.21 (vtd, $J = 6.6$ Hz, $J = 0.5$ Hz, C(CH₃)₃), 34.46 (vtd, $J = 10.7$ Hz, $J = 3.6$ Hz, CH₂P), 29.89 (vt, $J = 3.4$ Hz, C(CH₃)₃), 16.21 (s, Ar CH₃). IR (film; cm⁻¹): ν 2120 (s, Rh–N≡N).

Preparation of 2. To a solution of **1** (20 mg, 0.035 mmol) in pentane (1 mL) was added 40 μL of a 1 M solution of N₂CHPh in cyclohexane, giving a dark red solution. Evaporation of the solvent under vacuum gave 21 mg (91%) of **2**.

³¹P{¹H} NMR (C₆D₆; δ , ppm): 88.31 (d, $J_{\text{RhP}} = 169.1$ Hz). ¹H NMR (δ , ppm): 20.41 (d, $J_{\text{RhH}} = 3.0$ Hz, 1H, Rh=CHPh), 8.69 (s, 1H, Ar H), 8.18 (d, 2H), 7.27 (m, 2H, Ar H), 3.40 (vt, 4H, $J = 3.7$ Hz, CH₂P), 2.39 (s, 6H, Ar CH₃), 1.14 (vt, $J = 6.2$ Hz, 36H, t-Bu). ¹³C{¹H} NMR (δ , ppm): 344.10 (m, Rh=CHPh), 184.45 (dvt, $J = 20.1$ Hz, $J = 10.8$ Hz, α -C), 156.04 (s, Ar), 144.09 (vtd, $J = 12.2$ Hz, $J = 2.2$ Hz, Ar), 134.94 (s, Ar), 133.26 (s, Ar), 131.08 (s, Ar), 129.88 (s, Ar), 37.86 (vtd, $J = 12.5$ Hz, $J = 1.2$ Hz, CH₂P), 35.59 (vtd, $J = 6.4$ Hz, $J = 2.5$ Hz, C(CH₃)₃), 29.82 (vt, $J = 2.9$ Hz, C(CH₃)₃), 23.07 (s, Ar CH₃).

Preparation of 5. To a cold solution of **3** (14 mg, 0.029 mmol) in pentane (2 mL) was added 60 μL of a 1 M solution of N₂CHPh in cyclohexane. After several minutes at room temperature the solution turned dark reddish brown. Evaporation of the solvent under vacuum gave 16 mg (98.5%) of **5**.

³¹P{¹H} NMR (C₆D₆; δ , ppm): 106.43 (d of AB quartets, $J_{\text{PA}} = 210.3$ Hz, $J_{\text{PB}} = 174.9$ Hz, $J_{\text{PB}} = 172.7$ Hz). ¹H NMR (δ , ppm): 20.11 (d, $J_{\text{RhH}} = 2.2$ Hz, 1H, Rh=CHPh), 8.68 (s, 1H, Ar H), 8.06 (d, 2H, Ar H), 7.29 (m, 2H, Ar H), 6.12 (dm, $J_{\text{PH}} = 44.8$ Hz, 1H), 2.87 (m, 2H), 2.78 (m, 2H), 1.29 (m, 4H), 1.17 (d, 18H, t-Bu), 1.11 (d, 18H, t-Bu). ¹³C{¹H} NMR (δ , ppm): 343.52 (m, Rh=C), 191.28 (m, α -C), 156.27 (m), 133.02 (s), 129.75 (s), 120.37 (ddd, $J = 20.9$ Hz, $J = 3.8$ Hz, $J = 1.7$ Hz, Rh–C=CH), 46.48 (ddd, $J = 19.7$ Hz, $J = 2.9$ Hz, $J = 1.4$ Hz, (=CCH₂P)), 35.70 (m, C(CH₃)₃), 35.35 (dd, $J_{\text{PC}} = 21.2$ Hz, $J_{\text{RhC}} = 2.4$ Hz, CH₂(CH₂P)), 29.94 (t, $J_{\text{PC}} = 6.1$ Hz, C(CH₃)₃), 27.35 (dm, $J_{\text{PC}} = 20.6$ Hz, CH₂P).

Preparation of 4. To a solution of **6** (40 mg, 0.08 mmol) in 1 mL of THF was added 6 μL of MeLi (0.084 mmol, 1.4 M in diethyl ether) at –30 °C, resulting in a color change from pale brown to reddish. Evaporation of the solvent followed by extraction of the product with pentane gave pure **4** as an air-sensitive red solid in 85% yield.

³¹P{¹H} NMR (C₆D₆; δ , ppm): 94.70 (d of AB quartets, $J_{\text{PA}} = 287.7$ Hz, $J_{\text{PB}} = 162.6$ Hz, $J_{\text{PB}} = 161.3$ Hz). ¹H NMR (δ , ppm): 6.18 (dd, $J_{\text{PH}} = 37.8$ Hz, $J_{\text{PH}} = 9.5$ Hz, 1H, C=CHCH₂), 2.53 (m, 3H), 2.42 (m, 3H), 1.31 (m, 18H, t-Bu), 1.25 (m, 18H, t-Bu). ¹³C{¹H} NMR (δ , ppm): 181.92 (d br t, $J_{\text{RhC}} = 37.0$ Hz, α -C), 130.66 (dt, $J_{\text{RhC}} = 17.9$ Hz, $J_{\text{PC}} = 5.4$ Hz, Rh(C=CH)), 45.28 (dt, $J_{\text{RhC}} = 15.4$ Hz, $J_{\text{PC}} = 5.0$ Hz, (=CCH₂P)), 35.65 (m, C(CH₃)₃), 35.11 (m, C(CH₃)₃), 30.12 (br dd, C(CH₃)₃), 29.50 (br dd, C(CH₃)₃), 24.75 (dt, $J_{\text{PC}} = 3.6$ Hz, $J_{\text{RhC}} = 14.4$ Hz, CH₂P). IR (film; cm⁻¹): ν 2124 (s, Rh–N≡N).

Preparation of 10. To a solution of **3** (14 mg, 0.029 mmol) in pentane (2 mL) was added 6 mg (0.03 mmol) of N₂CPh₂. The solution immediately turned green. Evaporation of the solvent gave pure **10** in quantitative yield.

³¹P{¹H} NMR (C₆D₆; δ , ppm): 89.84 (br d $J_{\text{RhP}} = 166.1$ Hz). ¹H NMR (δ , ppm): 7.54 (d, $J = 7.8$ Hz, 4H, Ar H), 7.21 (7, $J = 7.8$ Hz, 2H, Ar H), 6.89 (m, 4H, Ar H), 1.92 (m, 4H), 1.46 (m, 4H), 1.24 (vt, $J = 6.0$ Hz, 18H, t-Bu), 1.18 (vt, $J = 6.2$ Hz, 18H, t-Bu). ¹³C{¹H} NMR (δ , ppm): 131.29 (s, Ar), 128.83 (s, Ar), 124.21 (s, Ar), 122.90 (s, Ar), 74.55 (br m, N₂CPh₂), 55.13 (dvt, $J = 26.8$ Hz, $J = 1.8$ Hz, α -C), 40.46 (vtd, $J = 8.7$ Hz, $J = 1.9$ Hz, CH₂(CH₂P)), 36.05 (vtd, $J = 5.3$ Hz, $J = 1.3$ Hz, C(CH₃)₃), 34.43 (vt, $J = 5.8$ Hz, C(CH₃)₃), 29.78 (vt, $J = 3.6$ Hz,

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C(CH₃), 25.46 (vtd, $J = 8.2$ Hz, $J = 2.6$ Hz, CH₂P). IR (film; cm⁻¹): ν 2038 (s, Ph₂CN \equiv N).

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