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 N_2 complex **1** reacts with phenyldiazomethane, giving the phenylcarbene complex **2**, the Rh alkyl N_2 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 SbR_3 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) complex[9] with 1.2 equiv of $NaBEt_3H$ in benzene under a dinitrogen atmosphere (eq 1).[10]

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

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(3) For reviews see: (a) Putala, M.; Lemenovskii, D. A. *Russ. Chem. Rev. (Engl. Transl.)* **1994**, *63*, 1994. (b) Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800. See also: (d) Polse, J. L.; Kaplan, A. W.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6316.

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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.; Konstantinovsky, 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.

(7) (a) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708. (b) Fryzuk, M. D.; Gao, X.; Joshi, K.; MacNeil, P. A.; Massey, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10581.

(8) For a rare example of an intramolecular Ir carbene complex in a bis-chelating system see: Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1271.

(9) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406.

(10) For similar unsaturated PCP-type Rh(I) complexes see: (a) Nemeh, 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.

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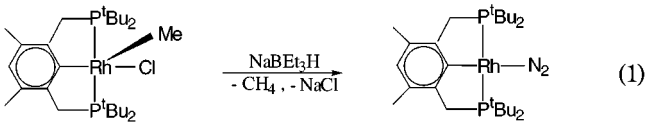
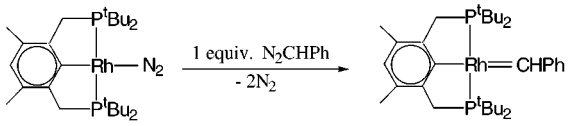


(1)

1

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.



(2)

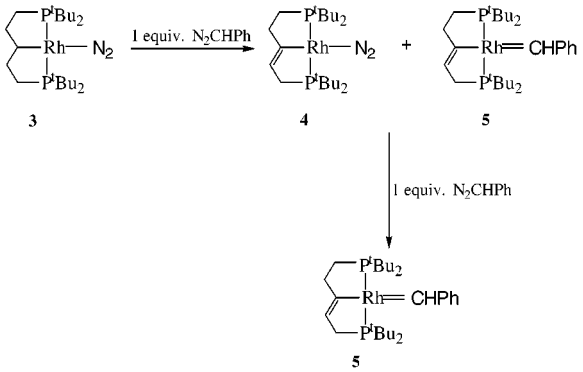
1 **2**

The ^{31}P NMR spectrum of **2** shows a doublet at 88.31 ppm (d, J_{RhP} = 169.1 Hz). The carbene proton exhibits a low-field doublet at 20.41 ppm in the ^{1}H 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=C*H*R 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 ^{1}H NMR spectrum as a doublet at 20.11 ppm (J_{RhH} = 2.2 Hz), while its carbon gives a multiplet at 343.52 ppm in the ^{13}C NMR spectrum.

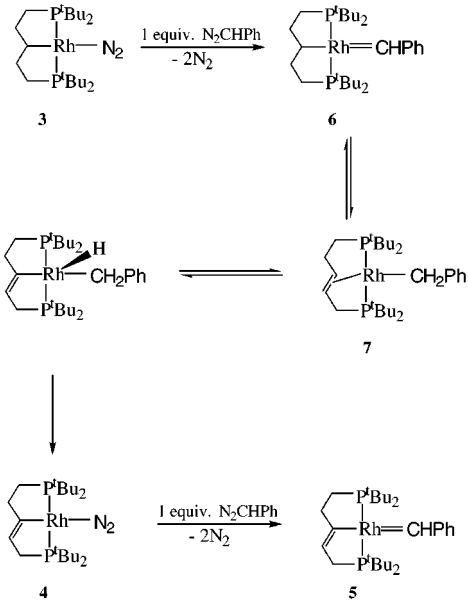
As it is known that complex **3** undergoes a fast, reversible β-hydrogen-elimination process,[13] it is likely that the initially formed saturated carbene complex **6** undergoes rapid hydride migration to give the benzyl

Scheme 1



3 **4** **5** **5**

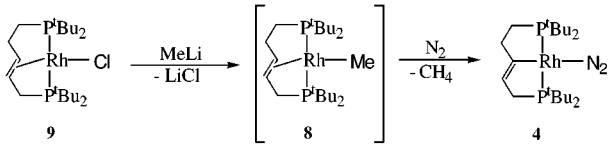
Scheme 2



3 **6** **7** **4** **5**

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



9 **8** **4**

(3)

^{31}P NMR spectrum centered at 94.70 ppm ($J_{P_AP_B}$ = 287.7 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

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

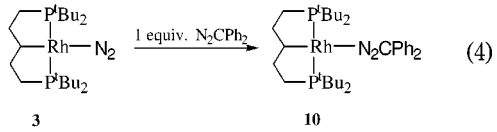
(12) It was demonstrated that olefin metathesis at a ruthenium d^6 center is facilitated by dissociation of a phosphine ligand: Dias, E. L.; Nguyen, S. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.

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

(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_{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



3 **10** (4)

that of the starting complex **3** and it's IR spectrum exhibits an intense band at 2038 cm^{-1}, which is higher than ν(N≡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 upfiled 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). Phenyldiazomethane[16] and diphenyldiazomethane[17] were prepared as reported.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at 400, 162, and 100 MHz, respectively, using a Bruker AMX400 spectrometer. ^{1}H and ^{13}C 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. ^{31}P chemical shifts are in ppm downfield from H_3PO_4 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)Cl[9] (50 mg, 0.085 mmol) in 2 mL of benzene was added 100 μL of a 1 M solution of $NaBEt_3H$ in toluene, resulting in a color change from red to brown. The solvent was evaporated, and the remaining solid was extracted with pentane (2 × 2 mL). Evaporation of pentane under vacuum gave 43 mg (90%) of **1**.

^{31}P{^{1}H} NMR (C_6D_6; δ, ppm): 79.65 (d, J_{RhP} = 157.0 Hz). ^{1}H NMR (δ, ppm): 6.69 (s, 1H, Ar H), 3.10 (vt, 4H, J = 3.9 Hz, CH_2P), 2.28 (s, 6H, Ar CH_3), 1.29 (vt, J_{PH} = 6.2 Hz, 36H, t-Bu). ^{13}C{^{1}H} 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*(CH$_3$)$_3$), 34.46 (vtd, J = 10.7 Hz, J = 3.6 Hz, *C*H$_2$P), 29.89 (vt, J = 3.4 Hz, C(*C*H$_3$)$_3$), 16.21 (s, Ar *C*H$_3$). 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 N_2CHPh in cyclohexane, giving a dark red solution. Evaporation of the solvent under vacuum gave 21 mg (91%) of **2**.

^{31}P{^{1}H} NMR (C_6D_6; δ, ppm): 88.31 (d, J_{RhP} = 169.1 Hz). ^{1}H NMR (δ, ppm): 20.41 (d, J_{RhH} = 3.0 Hz, 1H, Rh=C*H*Ph), 8.69 (s, 1H, Ar *H*), 8.18 (d, 2H), 7.27 (m, 2H, Ar *H*), 3.40 (vt, 4H, J = 3.7 Hz, CH_2P), 2.39 (s, 6H, Ar CH_3), 1.14 (vt, J = 6.2 Hz, 36H, t-Bu). ^{13}C{^{1}H} NMR (δ, ppm): 344.10 (m, Rh=*C*HPh), 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, *C*H$_2$P), 35.59 (vtd, J = 6.4 Hz, J = 2.5 Hz, *C*(CH$_3$)$_3$), 29.82 (vt, J = 2.9 Hz, C(*C*H$_3$)$_3$), 23.07 (s, Ar *C*H$_3$).

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 N_2CHPh 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**.

^{31}P{^{1}H} NMR (C_6D_6; δ, ppm): 106.43 (d of AB quartets, $J_{P_AP_B}$ = 210.3 Hz, J_{RhP_A} = 174.9 Hz, J_{RhP_B} = 172.7 Hz). ^{1}H NMR (δ, ppm): 20.11 (d, J_{RhH} = 2.2 Hz, 1H, Rh=C*H*Ph), 8.68 (s, 1H, Ar *H*), 8.06 (d, 2H, Ar *H*), 7.29 (m, 2H, Ar *H*), 6.12 (dm, J_{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). ^{13}C{^{1}H} 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=*C*H), 46.48 (ddd, J = 19.7 Hz, J = 2.9 Hz, J = 1.4 Hz, (=C*C*H$_2$P)), 35.70 (m, *C*(CH$_3$)), 35.35 (dd, J_{PC} = 21.2 Hz, J_{RhC} = 2.4 Hz, *C*H$_2$(CH$_2$P)), 29.94 (t, J_{PC} = 6.1 Hz, C(*C*H$_3$)), 27.35 (dm, J_{PC} = 20.6 Hz, *C*H$_2$P).

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.

^{31}P{^{1}H} NMR (C_6D_6; δ, ppm): 94.70 (d of AB quartets, $J_{P_AP_B}$ = 287.7 Hz, J_{RhP_A} = 162.6 Hz, J_{RhP_B} = 161.3 Hz). ^{1}H NMR (δ, ppm): 6.18 (dd, J_{PH} = 37.8 Hz, J_{PH} = 9.5 Hz, 1H, C=C*H*CH$_2$), 2.53 (m, 3H), 2.42 (m, 3H), 1.31 (m, 18H, t-Bu), 1.25 (m, 18H, t-Bu). ^{13}C{^{1}H} NMR (δ, ppm): 181.92 (d br t, J_{RhC} = 37.0 Hz, α-*C*), 130.66 (dt, J_{RhC} = 17.9 Hz, J_{PC} = 5.4 Hz, Rh(C=*C*H)), 45.28 (dt, J_{RhC} = 15.4 Hz, J_{PC} = 5.0 Hz, (=C*C*H$_2$P)), 35.65 (m, *C*(CH$_3$)), 35.11 (m, *C*(CH$_3$)), 30.12 (br dd, C(*C*H$_3$)), 29.50 (br dd, C(*C*H$_3$)), 24.75 (dt, J_{PC} = 3.6 Hz, J_{RhC} = 14.4 Hz, *C*H$_2$P). 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 N_2CPh_2. The solution immediately turned green. Evaporation of the solvent gave pure **10** in quantitative yield.

^{31}P{^{1}H} NMR (C_6D_6; δ, ppm): 89.84 (br d J_{RhP} = 166.1 Hz). ^{1}H 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). ^{13}C{^{1}H} NMR (δ, ppm): 131.29 (s, *Ar*), 128.83 (s, *Ar*), 124.21 (s, *Ar*), 122.90 (s, *Ar*), 74.55 (br m, N$_2$*C*Ph$_2$), 55.13 (dvt, J = 26.8 Hz, J = 1.8 Hz, α-*C*), 40.46 (vtd, J = 8.7 Hz, J = 1.9 Hz, *C*H$_2$(CH$_2$P)), 36.05 (vtd, J = 5.3 Hz, J = 1.3 Hz, *C*(CH$_3$)), 34.43 (vt, J = 5.8 Hz, *C*(CH$_3$)), 29.78 (vt, J = 3.6 Hz,

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(17) Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 351.

C(CH_3)), 25.46 (vtd, J = 8.2 Hz, J = 2.6 Hz, CH_2P). IR (film; cm^{-1}): ν 2038 (s, $Ph_2CN{\equiv}N$).

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