

# Reaction between Ruthenium(0) Complexes and Dihalo Compounds. A New Method for the Synthesis of Ruthenium Olefin Metathesis Catalysts

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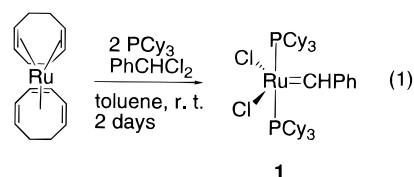
The synthesis of ruthenium carbenes by the reaction of a Ru(0) compound or Ru(0) precursors with dihalo compounds is reported. A new procedure for the preparation of  $[\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{PCy}_3)_2]$  and the use of this complex as a starting material for the synthesis of ruthenium carbenes are presented.

In recent years, the uses of ruthenium carbene complexes as catalysts in olefin metathesis processes (ring-closing metathesis, RCM, and ring-opening metathesis polymerization, ROMP) have increased<sup>1</sup> due mainly to their remarkable stability toward functional groups and protic media and their ease of handling. Two existing methods of synthesizing ruthenium carbene complexes have been developed in our group: the reaction between  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and diphenylcyclopropene<sup>2</sup> or diazo compounds<sup>3</sup> to yield  $[\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PPh}_3)_2]$  and  $[\text{RuCl}_2(=\text{CHR})(\text{PPh}_3)_2]$ , respectively. In the first case, the multistep synthesis and the instability of diphenylcyclopropene limited the availability of catalyst. In the second case, the method was limited by the danger of handling diazo compounds.

The reported preparations by Roper<sup>4</sup> of nonreactive dihalocarbene complexes generated from  $\text{CCl}_4$  and Ru(0) suggested that carbenes similar to those mentioned above could be formed using dihalo compounds and an appropriate Ru(0) compound or Ru(0) precursor. In the present contribution, we report the synthesis of five-coordinate ruthenium carbenes by the reaction of  $\text{XCHCl}_2$  ( $\text{X} = \text{Ph}, \text{CO}_2\text{Me}, \text{H}$ ) with  $[\text{Ru}(\eta^4\text{-COD})(\eta^6\text{-COT})]$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ;  $\text{COT} = \text{cyclooctatriene}$ ) in the presence of tricyclohexylphosphine ( $\text{PCy}_3$ ) or with Ru(0) precursors which contain coordinated  $\text{PCy}_3$ .

Addition of  $\text{PhCHCl}_2$  to solutions of  $[\text{Ru}(\text{COD})(\text{COT})]$  and  $\text{PCy}_3$  in toluene at room temperature lead to the formation of  $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]$ , **1**, which is isolated as a purple solid in 50% yield (eq 1).

The mechanism of formation of the carbene could involve two steps: oxidative addition of the alkyl



dihalide to the Ru(0) species<sup>5</sup> followed by  $\alpha$ -chloro elimination<sup>6</sup> (Scheme 1).

This synthetic route presents two limitations: (1)  $[\text{Ru}(\text{COD})(\text{COT})]$  is difficult to synthesize (although good yields in the synthesis of this complex have been reported,<sup>7</sup> its preparation is tedious) and (2) the above route could not be successfully applied to the synthesis of other carbenes, e.g.  $\text{Ru}=\text{CHCO}_2\text{Me}$  using  $\text{Cl}_2\text{CHCO}_2\text{Me}$ , because of the formation of the phosphonium salt  $\{[\text{Cy}_3\text{PCHCl}(\text{X})]^+\text{Cl}^-\}$  as a side reaction. One way to avoid this phosphonium salt formation is to use Ru(0) compounds or Ru(0) precursors in which the phosphines are already coordinated to the metal center. Of possible utility is  $[\text{Ru}(\text{H})(\text{C}_2\text{H}_2)_2(\eta^1\text{-(C}_6\text{H}_{10})\text{P(C}_6\text{H}_{11})}(\text{PCy}_3)]$ , **3**,<sup>8</sup> since **3** rearranges to a Ru(0) species upon reductive elimination of the hydride and alkyl group.<sup>8b</sup>

Complex **3** is conveniently obtained by the reaction of  $[\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{PCy}_3)_2]$ , **2**, and ethylene.<sup>8</sup> Although the previously reported preparation of **2** used  $[\text{Ru}(\text{COD})(\text{COT})]$  as the starting material,<sup>8b</sup> we present here a new method for the synthesis of **2**. This procedure provides a readily available source of that key starting material and catalyst.<sup>9</sup> High yields of **2** are obtained by the

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(1) (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (b) Meng, D.; Su, D.-S.; Balog, A.; Bertinato, P.; Sorensen, E. J.; Danishefsky, S. J.; Zheng, Y.-H.; Chou, T.-C.; He, L.; Horwitz, S. B. *J. Am. Chem. Soc.* **1997**, *119*, 2733. (c) Snapper, M. L.; Tallarico, J. A.; Randall, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 1478. (d) Miller, S. J.; Blackwell, H. E.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 9606. (e) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718. (f) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 5765.

(2) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

(3) (a) Schwab, P.; France, M. B.; Miller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(4) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167.

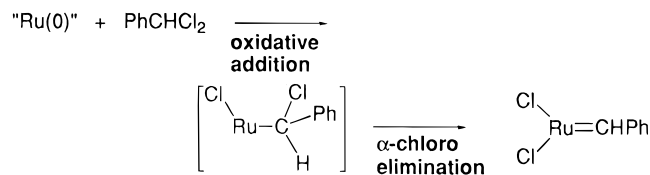
(5) This kind of process is well-known in the chemistry of Ru(0) compounds, see: (a) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Oxford, 1984. (b) Tsuji, Y.; Mukai, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1989**, *369*, C51. (c) Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem.* **1985**, *296*, 269. (d) Komiyama, S.; Kabashima, T.; Yamashita, K.; Hirano, M.; Fukuoka, A. *J. Organomet. Chem.* **1994**, *471*, C6.

(6) Similar processes have been observed in studies developed recently in our group about the generation of carbenes by insertion of vinyl chloride into the Ru–H bond followed by  $\alpha$ -chloro elimination, see: Wilhelm, T. E.; Brown, S. M.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.

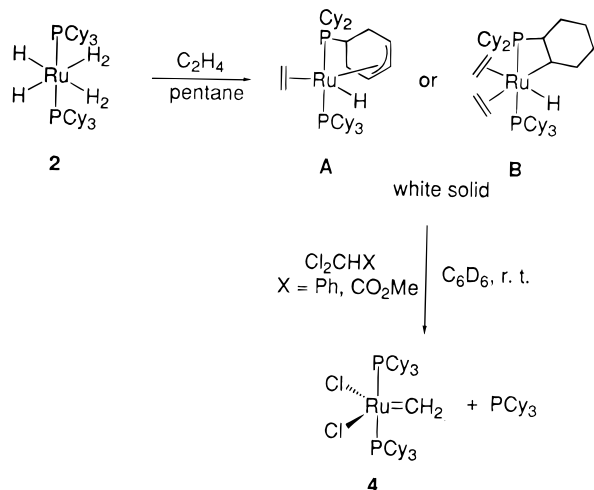
(7) (a) Itoh, K.; Nagashima, H.; Oshima, T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179. (b) Frosin, K. M.; Dahlenburg, L. *Inorg. Chim. Acta* **1990**, *167*, 83.

(8) Two structures have been reported for this compound,  $[\text{Ru}(\text{H})(\text{C}_2\text{H}_2)(\eta^3\text{-(C}_6\text{H}_5)_3\text{P(C}_6\text{H}_{11})}(\text{PCy}_3)]$  (A) and  $[\text{Ru}(\text{H})(\text{C}_2\text{H}_2)_2(\eta^1\text{-(C}_6\text{H}_{10})\text{P(C}_6\text{H}_{11})}(\text{PCy}_3)]$  (B) see: (a) Christ, M. L.; Sabo-Étienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082. (b) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722.

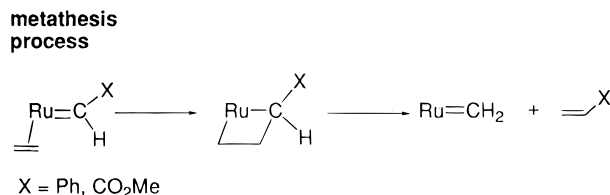
## Scheme 1



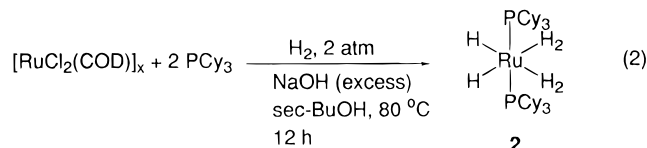
## Scheme 2



## Scheme 3



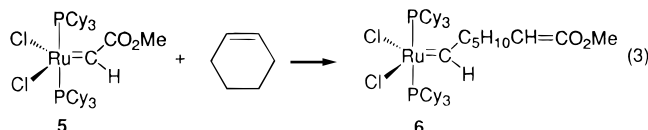
hydrogenation (2 atm) of [RuCl<sub>2</sub>(COD)]<sub>x</sub> in the presence of 2 equiv of PCy<sub>3</sub> and NaOH (excess) in *sec*-butyl alcohol (eq 2).



When the dihalo compounds Cl<sub>2</sub>CHX (X = Ph, CO<sub>2</sub>Me), were added to solutions of **3**, the methylidene complex, **4**, was obtained (Scheme 2). The formation of the methylidene complex, **4**, instead of the expected benzylidene and ester carbene, is most likely due to the subsequent metathesis of ethylene after these carbenes are generated (Scheme 3). Observation of the carbene proton resonances of the intermediates ( $\delta = 20.59$  (**1**) and 20.15 (**5**)) as well as formation of styrene and methyl methacrylate confirms this hypothesis.

The use of cyclohexene, an olefin which does not readily undergo metathesis, allowed the preparation and isolation of **1**, **4**, and **5**. When cyclohexene was added to a suspension of [Ru(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>], **2**, a pale yellow solid was obtained. <sup>31</sup>P NMR analysis of the reaction mixture showed a single peak ( $\delta = 59.63$ ). On the basis of the structure proposed by Chaudret and co-

workers for the product of the reaction of **2** and dimethyl fumarate,<sup>10</sup> an intermediate bis(hydrido)(olefin)Ru(II) complex is proposed. Addition of Cl<sub>2</sub>CHX (X = Ph, CO<sub>2</sub>Me, H) to the intermediate suspended in pentane afforded the corresponding carbenes **1**, **3**, and **5** in good yield. The conversions were quantitative, as monitored by <sup>31</sup>P NMR using triphenylphosphine oxide as the internal standard (Scheme 4). When excess cyclohexene was present in the preparation of **5**, a new unexpected product, **6**, was formed from the ring opening of cyclohexene (eq 3). NMR studies of the reaction of **5** with



an excess of cyclohexene confirmed this observation.

Addition of styrene to a solution of **5** in C<sub>6</sub>D<sub>6</sub> led to the formation of **1**. We therefore reasoned that styrene could be used as the olefin instead of ethylene or cyclohexene as a method to synthesize the benzylidene complex, **1**. When styrene was added to a suspension of **2**, a red solution was obtained. The <sup>31</sup>P NMR spectrum of that solution showed only one broad resonance ( $\delta = 62.41$ ). Addition of Cl<sub>2</sub>CHCO<sub>2</sub>Me to the solution led to the formation of **1** in a quantitative yield (by NMR) (Scheme 5). Further investigations focusing on the structures of the possible ruthenium olefin intermediates are in progress, along with attempts to increase the isolated yield of the carbenes generated.

The studies presented in this contribution demonstrate that reactions of Ru(0) complexes or Ru(0) precursor species with dihalo compounds provide an easy method for the preparation of a variety of ruthenium carbenes. Ongoing investigations focus on the enhanced activity displayed by **5** vs **1** and the characterization of the ruthenium olefin intermediates.

## Experimental Section

**Synthesis of 1 from [Ru(COD)(COT)].** To a solution of [Ru(COD)(COT)] (0.11 g, 0.33 mmol) and PCy<sub>3</sub> (0.19 g, 0.67 mmol) in toluene (15 mL),  $\alpha,\alpha$ -dichlorotoluene (50 mL, 0.39 mmol) was added. The reaction mixture was stirred at room temperature for 2 days. The resulting deep brown solution was evaporated, and the residue was washed with acetone and methanol (twice with 5 mL portions), affording 0.13 g of a purple solid. The NMR spectra of this product were identical to those reported for [RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>].<sup>3</sup> Yield: 50%.

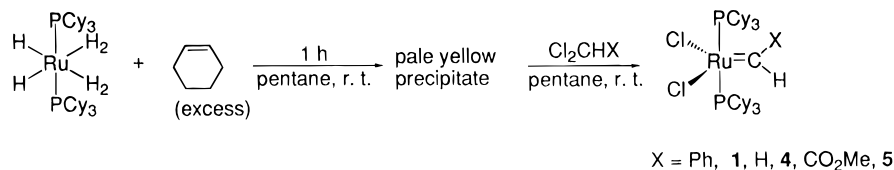
**Reaction of 3 with Cl<sub>2</sub>CHCO<sub>2</sub>Me.** To a suspension of **3** (14 mg, 0.020 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL), Cl<sub>2</sub>CHCO<sub>2</sub>Me (5  $\mu$ L) was added. After the addition of methyl dichloroacetate two resonances appeared downfield in the <sup>1</sup>H NMR spectrum, one small singlet,  $\delta$  20.15, corresponding to the proton of the carbene moiety in [RuCl<sub>2</sub>(=CHCO<sub>2</sub>Me)(PCy<sub>3</sub>)<sub>2</sub>], **5**, and the main peak, a singlet at  $\delta$  19.36, corresponding to the methylidene moiety protons in [RuCl<sub>2</sub>(=CH<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>].<sup>3</sup> After 5 min, only the final resonance (s,  $\delta$  19.36) for the methylidene moiety protons was observed. Methacrylate resonances were also in the final <sup>1</sup>H NMR spectrum. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed two peaks at  $\delta$  44.0 and 10.8 corresponding to [RuCl<sub>2</sub>(=CH<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>], **4**,<sup>3</sup> and free phosphine PCy<sub>3</sub>, respectively.

**Reaction of 3 with PhCHCl<sub>2</sub>.** To a suspension of **3** (16 mg, 0.023 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL), PhCHCl<sub>2</sub> (5  $\mu$ L) was added.

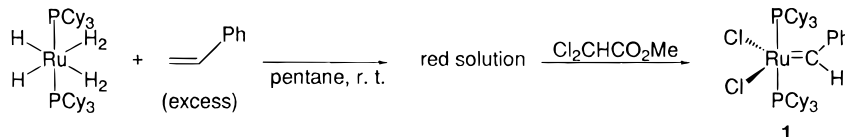
(9) For a similar synthetic procedure and use of [Ru(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>], **2**, as a hydrogenation catalyst, see: Beatty, R. P.; Paciello, R. A. U.S. Pat. 5,555,778, 1996.

(10) Borowski, A. F.; Sabo-Etienne, S.; Christ, M. L.; Donnadieu, B.; Chaudret, B. *Organometallics* **1996**, *15*, 1427.

Scheme 4



Scheme 5



After the addition, the <sup>1</sup>H NMR spectrum showed two down-field singlets. The main resonance, a singlet at  $\delta$  20.59, corresponding to the protons of the carbene moiety in [Ru(=CHPh)Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>], **1**,<sup>3</sup> and a small singlet,  $\delta$  19.36, for the carbenic protons in [RuCl<sub>2</sub>(=CH<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>], **4**.<sup>3</sup> After 30 min, only the final resonance (s,  $\delta$  19.36) for the methylenide protons in **4** was observed. The final <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed two peaks at  $\delta$  44.0 and 10.8 corresponding to [RuCl<sub>2</sub>(=CH<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>] and PCy<sub>3</sub>, respectively.

**Improved Preparation of Ru(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>, **2**.** [RuCl<sub>2</sub>(COD)]<sub>x</sub> (6.0 g, 21.43 mmol), PCy<sub>3</sub> (12.0 g, 42.86 mmol), and NaOH (7.2 g) were placed in a 500 mL Fisher–Porter bottle. Degassed *sec*-butyl alcohol (250 mL) was added, and the suspension was pressurized under H<sub>2</sub> (2 atm) and heated at 90 °C. The system was repressurized several times, an indication of H<sub>2</sub> uptake. The reaction mixture was stirred overnight. The system was allowed to cool to room temperature under H<sub>2</sub> pressure. A pale yellow crystalline precipitate was obtained. All of the following manipulations were carried out under H<sub>2</sub> atmosphere. Water (30 mL) was added to the resulting mixture, and the mixture was filtered through a glass frit filter. The filtrate was washed twice with water (30 mL portions) and with methanol (twice with 20 mL portions). The solid was dried under a H<sub>2</sub> stream. An 83% yield (11.8 g) of a pale yellow crystalline compound was obtained. The NMR spectra of this product were identical to those reported by Chaudret and co-workers for [Ru(H)<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>], **2**.<sup>8b</sup>

**Synthesis of 1 from 2 (Using Cyclohexene).** To a suspension of **2** (1.0 g, 1.50 mmol) in pentane (40 mL), cyclohexene (1.5 mL, 14.80 mmol) was added. After 2 min a yellow solution is obtained, and after 15 min, a pale yellow precipitate is formed. The reaction mixture was stirred for 1 h. The volatiles were removed under vacuum. Pentane was added to the solid. Addition of PhCHCl<sub>2</sub> (0.4 mL, 3.11 mmol) lead to the formation of a red solution, which was stirred for

45 min. The solvent was evaporated, and the residue was washed with cold methanol (three times with 10 mL portions). A 0.75 g (61%) yield of a purple solid was obtained, whose NMR spectra were identical to the compound [RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>], **1**, previously reported by our group.<sup>3</sup> [RuCl<sub>2</sub>(=CH<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>], **4**, and [RuCl<sub>2</sub>(=CHCO<sub>2</sub>Me)(PCy<sub>3</sub>)<sub>2</sub>], **5**, were prepared in an analogous manner by the addition of Cl<sub>2</sub>CH<sub>2</sub> and Cl<sub>2</sub>CHCO<sub>2</sub>Me as the dihalo compounds, respectively. In the case of the synthesis of **4**, the reaction mixture was stirred overnight after the addition of Cl<sub>2</sub>CH<sub>2</sub> (the reaction is slower as monitored by NMR). Selected spectroscopic data for **5**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  20.15 (s, Ru=CH), 3.53 (s, CO<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (125.71, CD<sub>2</sub>Cl<sub>2</sub>, -30 °C)  $\delta$  276.37 (t, *J*(P,C) = 5.1 Hz, Ru=CH), 178.69 (s, CO<sub>2</sub>Me), 50.84 (s, CO<sub>2</sub>CH<sub>3</sub>); <sup>31</sup>P (161.9 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  38.66 (s, PCy<sub>3</sub>); IR (Nujol)  $\nu$  1721 cm<sup>-1</sup> (C=O-ester).

**Reaction of 5 with an Excess of Cyclohexene.** To a solution of **5** (4.7 mg) in C<sub>6</sub>D<sub>6</sub> (0.5 mL), cyclohexene (20  $\mu$ L, 34 equiv) was added. The ester carbene <sup>1</sup>H NMR resonance disappeared within 3 h, and a new carbene proton resonance appeared (t,  $\delta$  19.62, *J*(H,H) = 5.0 Hz), which can be attribute to a ring-opening species, **6** (the chemical shift and coupling constant (H,H) are similar to those reported for other alkylidene complexes).<sup>3</sup>

**Synthesis of 1 from 2 (Using Styrene and Cl<sub>2</sub>CHCO<sub>2</sub>Me).** Styrene (5 mL) was added to a suspension of **2** (3.0 g, 4.50 mmol) in pentane (50 mL). The red solution immediately obtained was stirred for 1 h, and Cl<sub>2</sub>CHCO<sub>2</sub>Me (0.9 mL, 8.7 mmol) was then added. The reaction mixture was stirred for 45 min. The solvent was removed, and the residue was washed with acetone and methanol (twice with 20 mL portions). A purple solid (2.0 g, 54% yield) was isolated whose NMR data were identical to those of [RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>].<sup>3</sup>

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