

New Fischer Carbene Complexes of Rhodium(I): Preparation and 2-Cyclopentenone Ring Synthesis by Annelation to Alkynes

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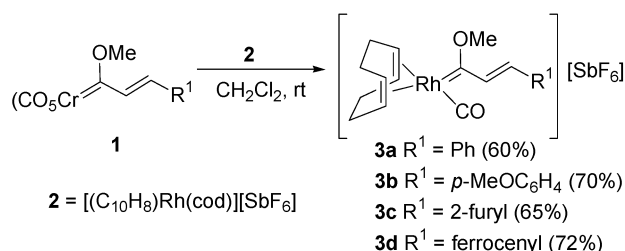
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Heteroatom-stabilized transition metal carbene complexes, particularly those derived from group 6, are recognized as versatile organometallic intermediates in organic synthesis.¹ Surprisingly, late transition metal carbene complexes have been scarcely studied despite the special features of these metals in carbon–carbon bond-forming reactions. A few examples have been reported wherein the chromium–palladium(0),² –rhodium(I),³ and –copper(I)^{3c,4} exchange from chromium alkoxycarbene complexes results in increased reactivity. A major goal consisting in qualitative modification of the reactivity of chromium carbenes has been recently achieved by us via chromium–nickel exchange, specifically new [2 + 2 + 2 + 1] and [3 + 2 + 2] carbocyclization reactions.⁵ Because of our interest in this area, as well as the importance of rhodium carbenes as intermediate species for fundamental organic processes,⁶ we now report the preparation of novel cationic rhodium(I) alkoxycarbene complexes⁷ and their potential for cyclopentenone synthesis.

Carbene complexes of rhodium(I) were prepared by stirring at room temperature a CH₂Cl₂ solution of chromium methoxycarbene complexes **1** and readily available rhodium complex **2** (Scheme 1). The reaction went to completion after 1 h, affording cationic rhodium(I) alkenyl(methoxy)carbene complexes **3** in yields higher than 60%. The solid-state structure of **3b** could be determined by a single-crystal analysis.⁸

Scheme 1. Synthesis of Cationic Carbonyl Rhodium(I) Carbene Complexes **3a–d**

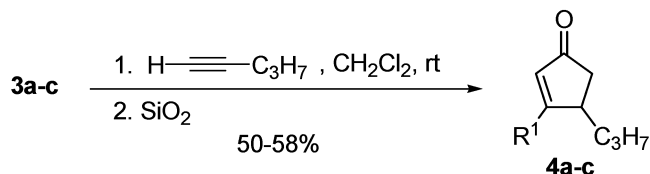


The simultaneous transfer of two ligands (carbene and CO) observed in this case represents a rare process.⁹ On other hand, cationic rhodium(I) carbene complexes are scarcely found in the literature.¹⁰

The treatment of complexes **3a–c** with 1-pentyne in CH₂Cl₂ at room temperature for 16 h resulted in the regioselective formation of cyclopentenones **4a–c** (Scheme 2).⁸ Therefore, a new and specific reactivity toward alkynes is encountered for rhodium(I) carbene complexes which is different from that found for transition metal carbene complexes.¹¹

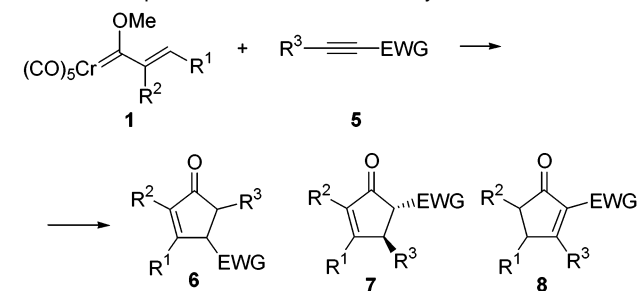
Next, we decided to check the reactivity of rhodium complexes toward electrophilic alkynes, since the reaction of these systems with group 6 carbene complexes presents severe limitations.¹² In

Scheme 2. [3 + 2] Cyclization of Carbenes **3a–c** with 1-Pentyne



this case, the rhodium-catalyzed reaction was found very effective. Thus, stirring a CH₂Cl₂ solution of chromium carbene complexes **1**, terminal electron-poor alkynes **5** (R³ = H), and **2** (10 mol %) yielded cyclopentenone derivatives **6a–g** with complete selectivity (64–89%, Table 1, entries 1–7).⁸ Carbene complexes with different substitution patterns were successfully used toward alkynyl esters and alkynyl ketones.

Table 1. Rh-Catalyzed [3 + 2] Cyclization of Alkenyl Chromium Carbene Complexes with Electron-Poor Alkynes^a



entry	R ¹	R ²	R ³	EWG	compd (yield, %) ^b
1	Ph	H	H	COOMe	6a (75)
2	<i>p</i> -MeOC ₆ H ₄	H	H	COOMe	6b (81)
3	2-furyl	H	H	COOMe	6c (88)
4	ferrocenyl	H	H	COOMe	6d (71)
5	<i>n</i> -Bu	H	H	COOMe	6e (70)
6	–CH ₂ CH ₂ CH ₂ O–	H	H	COOMe	6f (89)
7	2-furyl	H	H	COMe	6g (64)
8	2-furyl	H	Ph	COOEt	7a (75)
9	2-furyl	H	1-cyclohexenyl	COOMe	7b (85)
10	2-furyl	H	Me	COOMe	8 (81)

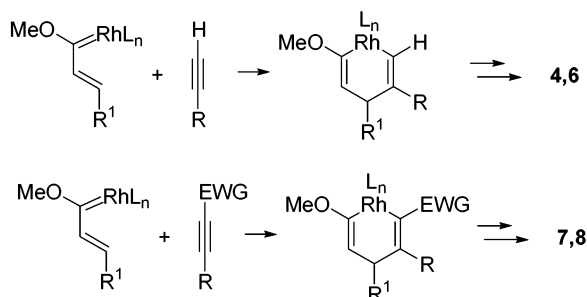
^a Reagents and conditions: [(naphthalene)Rh(cod)][SbF₆] (10 mol %), CH₂Cl₂, 25 °C, 12–36 h, and then chromatographic workup. ^b Yields of isolated products.

Representative electron-poor internal alkynes **5** (R³ = Ph, 1-cyclohexenyl, Me) also undergo efficiently the [3 + 2] cyclization, affording **7** or **8** depending on the alkyne nature (Table 1, entries 8–10).⁸ It should be noted in these cases that the cyclization occurs with reversal of regiochemistry (**6** vs **7**, **8**).

A mechanistic proposal to explain the behavior of these new rhodium systems seems at this point rather speculative.¹³ On the

basis of previous models where metalladienes are involved, we think that a metalla-Diels–Alder reaction would account well for the observed results (Scheme 3).^{14,15} Thus, the regiochemistry observed in the case of the terminal alkynes (cycloadducts **4**, **6**) would be dictated simply by steric discrimination, the larger alkyne substituent being placed away from rhodium. In the case of internal electron-poor alkynes (cycloadducts **7**, **8**) the steric differentiation is not so large and the electronic factors, which favor the interaction between the electrophilic metal center and the nucleophilic C α -alkyne, would dominate, leading to cycloadducts with opposite regiochemistry.

Scheme 3. Proposed Mechanism for the [3 + 2] Cyclization



In summary, a new type of metal carbene complexes of group 9, specifically a cationic Fischer carbene of rhodium(I), has been synthesized from chromium carbene complexes via double transfer of carbene and CO ligands and characterized in solution and in the solid state. These complexes reveal a different reactivity than other transition metal carbenes, including their chromium precursors, toward neutral and electron-poor alkynes. Synthetically, polysubstituted cyclopentenones are readily synthesized from chromium Fischer carbene complexes and alkynes by a [3 + 2] cyclization mediated (for neutral alkynes) or catalyzed (for activated alkynes) by rhodium(I).¹⁶ Most of these types of cyclopentenones are not at all straightforwardly accessible by the intermolecular Pauson–Khand reaction because of a lack of either reactivity (for unstrained alkenes and electron-poor alkenes) or regioselectivity (2,5-disubstituted cyclopentenones are generally formed).¹⁷

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Supporting Information Available: Detailed experimental procedures and characterization data for all compounds (PDF); X-ray crystallographic data for compound **3b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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