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A Ruthenium-Mediated $[C_1 + C_2]$ Coupling Reaction: Formation of π-Allyl Complexes from Carbenemetal Precursors

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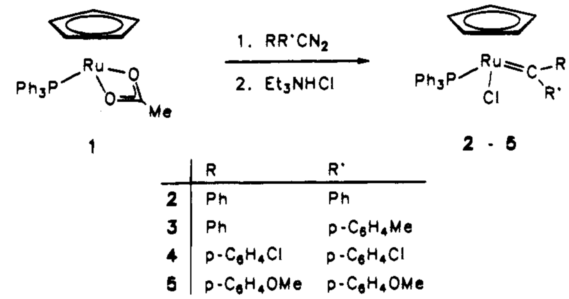
During the last decade, carbenemetal complexes, mainly of the Fischer type, have become an extremely useful tool in organic synthesis.[1] It is, in particular, the electron deficiency at the carbene carbon atom which facilitates the attack by nucleophiles and thus promotes, inter alia, the formation of C−C bonds. As far as the reactivity of metal-bonded *unsaturated* carbenes :C(=C)$_n$=CRR′ is concerned, it was recently shown that stereoselective coupling of an alkyl, aryl, or vinyl group with a vinylidene unit can occur in the coordination sphere of rhodium.[2] The vinyl or dienylmetal compounds obtained on this route react with acetic acid to give exclusively the *E* olefins RCH=CHR′ and CH_2=CHCH=CHR′, respectively. In this Communication, we describe both a novel ruthenium-mediated carbene-plus-vinyl coupling reaction leading to η^3-1,1-diarylallylmetal complexes and an analogous carbene-plus-methyl coupling which yields a hydrido(olefin)metal derivative.

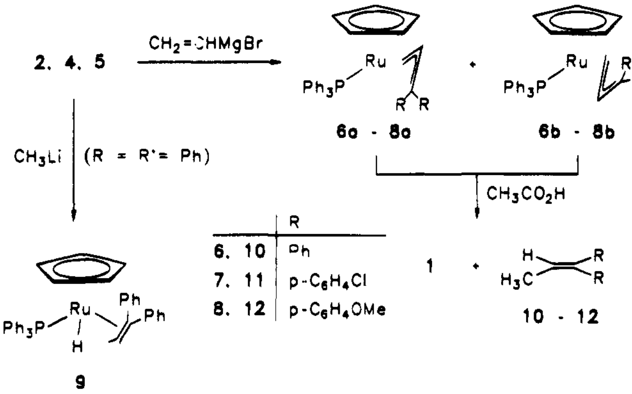
The key to success is the acetatoruthenium(II) compound **1**,[3] which reacts with diaryldiazomethanes in toluene at room temperature to give, after removal of the solvent and subsequent treatment with Et_3NHCl in acetone, green crystalline solids which correctly analyze as $[C_5H_5RuCl(=CRR')(PPh_3)]$ (**2−5**, Scheme 1).[4,5] The most characteristic feature of the spectroscopic data of **2−5** is the low-field position of the carbene carbon signal in the ^{13}C NMR spectrum, which appears at δ 315−330 (in C_6D_6). As established by the X-ray crystal structure analysis, compound **2** has the expected piano stool configuration, with a Ru−C(carbene) distance of 1.91(2) Å.[6] We note that structurally related carbeneruthenium complexes of composition $[C_5H_5RuX(=C(OEt)Ph)(CO)]$ (X = $SnPh_3$, I) are known but have been prepared on the classical Fischer route by converting a CO ligand with LiPh and $[OEt_3]BF_4$ into a carbene moiety.[7]

Scheme 1



	R	R'
2	Ph	Ph
3	Ph	p-C_6H_4Me
4	p-C_6H_4Cl	p-C_6H_4Cl
5	p-C_6H_4OMe	p-C_6H_4OMe

Scheme 2



	R
6. 10	Ph
7. 11	p-C_6H_4Cl
8. 12	p-C_6H_4OMe

The reaction of **2**, **4**, and **5** with vinyl Grignard reagent leads, in C_6H_6/THF at room temperature, to the displacement of the chloro ligand and formation of the 1,1-diarylallyl complexes **6−8** (Scheme 2) in 45−65% yield.[5,8] We assume that a carbene(η^1-vinyl)metal species is formed as an intermediate, which by intramolecular C-C coupling rearranges to give the products. An alternative pathway, addition of the nucleophile to the carbene carbon followed by elimination of Cl^- with concomitant η^1/η^3 allyl rearrangement, could equally be considered. The ^1H, ^{13}C, and ^{31}P NMR data of **6−8** illustrate that in each case a mixture of the *exo* (**a**) and *endo* (**b**) isomers is formed, the ratio of which is approximately 2:1. As a typical feature for the *exo* isomers, the ^1H NMR spectra display a signal for the allyl proton H^3 at the terminal carbon atom at δ 1.4−1.5 (doublet-of-doublet-of-doublets) with a much larger P−H coupling (~16−17 Hz) than found for the *endo* isomers.[5]

Attempts to separate the isomeric mixture of **6a/b** by low-temperature chromatography and fractional crystallization have led to the isolation of single crystals, which as shown by X-ray crystallography contain exclusively the *exo* isomer. The results of the structural analysis[9] are summarized in Figure 1, along with the principal bond lengths and interbond angles. Although the stereochemistry of **6a** is very similar to that of $[C_5H_5Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$[10] and $[C_5H_5Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(CO)]$,[11] compounds which both have been prepared from appropriate

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(4) A typical procedure is as follows. A solution of **1** (93 mg. 0.19 mmol) in 5 mL of toluene was treated with Ph_2CN_2 (37 mg. 0.19 mmol) and stirred for 5 min at room temperature. After removal of the solvent. the residue was dissolved in 5 mL of acetone. Et_3NHCl (39 mg. 0.29 mmol) was added. and the mixture was stirred for 30 min at room temperature. The solvent was removed. the green residue was extracted with 2 mL of toluene. and the solution was chromatographed on Al_2O_3 (neutral. activity grade V. length of column 4 cm). With toluene. a green fraction was eluted. from which after careful removal of the solvent a green solid (**2**) was isolated: yield 74 mg (62%): mp 102 °C dec. For **3** (mp 100 °C dec). **4** (mp 138 °C dec). and **5** (mp 118 °C dec). the yields were 72%. 62%. and 29%. respectively.

(5) A complete set of the analytical and spectroscopic data for the complexes **2−9** has been provided as supporting information.

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(8) A typical procedure is as follows. A suspension of **2** (146 mg. 0.23 mmol) in 5 mL of benzene was treated with a 0.75 M solution of CH_2=CHMgBr (0.62 mL. 0.47 mmol) in THF and stirred for 45 min at room temperature. A change of color from green to yellow occurred. After the solvent was removed. the residue was extracted with 6 mL of pentane/toluene (2:1). and the extract was brought to dryness in vacuo. The yellow solid (**6a.b**) obtained was washed with 2 mL of pentane and dried: yield 91 mg (63%): mp 82 °C dec. The ratio of the *exo*/*endo* isomers **6a/b** was determined to be 1.9:1 by ^1H NMR spectroscopy. For **7a.b** (mp 91 °C dec) and **8a.b** (mp 80 °C dec). the yields were 45% and 57%. respectively.

(9) Crystal data for **6a**: monoclinic. $P2_1/c$ (No. 14). $a = 10.915(5)$ Å. $b = 11.897(3)$ Å. $c = 23.574(11)$ Å. $\beta = 102.46(2)°$. $V = 2989(2)$ Å^3. $Z = 4$. $D_{calc} = 1.382$ g cm^{-3}. $T = 293$ K. μ(Mo Kα) = 5.95 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer using ω/θ-scan mode ($2\theta_{max} = 49.9°$). Of the 5234 reflections measured. 4938 were unique and 4926 had $I > 2\sigma(I)$: 361 variables were refined to give $R = 5.4\%$ and $R_w = 8.5\%$ with a reflex−parameter ratio of 13.6 and a residual electron density of +0.681/−0.860 e Å^{-3}.

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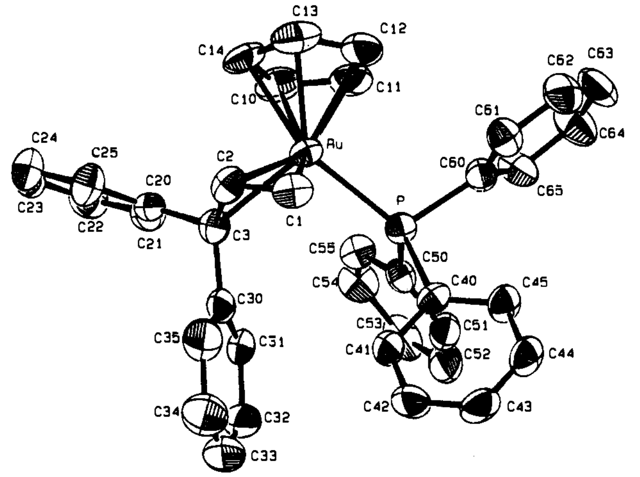

Figure 1. ORTEP diagram for the molecular structure of complex **6a** (thermal ellipsoids with 50% probability). Principal bond lengths (Å) and interbond angles (deg): Ru–C1 2.184(7), Ru–C2 2.085(6), Ru–C3 2.243(6), Ru–P 2.329(2), C1–C2 1.399(9), C2–C3 1.420(9), C1–C2–C3 121.7(7), C2–Ru–C1 38.2(3), C2–Ru–C3 38.1(2), Ru–C1–C2 67.1(4), Ru–C3–C2 64.9(3), Ru–C2–C1 74.7(4), Ru–C2–C3 77.0(4).

CpRu precursors and allyl Grignard reagents, the obvious difference is that the bond lengths between the metal and the terminal carbon atoms of the allyl unit in **6a** are unequal. As far as we know, the only other transition-metal complex containing Ph_2CCHCH_2 as a π-bonded allyl ligand is the platinum(II) compound $[Pt(\eta^3\text{-}Ph_2CCHCH_2)Cl]_n$, the structure of which, however, is unknown.[12]

To find out whether the chloro ligand in **2** can be displaced not only by a vinyl but also by an alkyl group, the reaction of **2** with methyllithium has been studied. Treatment of a solution of **2** in toluene with a solution of CH_3Li in ether at room temperature, followed (after 30 min) by addition of 5 mL of acetone, gave a yellow-brown reaction mixture, from which upon chromatographic workup yellow crystals of **9** were isolated in 65% yield. The ^1H NMR spectrum displays a high-field resonance at δ −9.79 (d, J(PH) = 35 Hz) for the hydridic as well as two well-separated signals at δ 3.87 and 1.77 for the olefinic protons. These data, together with those of the ^{13}C and ^{31}P NMR spectra,[5] leave no doubt that the proposed structure of **9** shown in Scheme 2 is correct. It seems conceivable that the initial product of the reaction of **2** with CH_3Li is the carbene(methyl) compound $[C_5H_5RuCH_3(=CPh_2)(PPh_3)]$, which by migratory insertion yields the 16-electron intermediate $[C_5H_5Ru(CMePh_2)(PPh_3)]$ and finally by β-H shift the hydrido(olefin) complex. In this context, it should be noted that the coupling of surface-bound methylene and alkyl groups has been postulated as a key step in Fischer–Tropsch synthesis,[13] which like the reaction of **2** with methyllithium leads to olefins as the main products.

The cleavage of the allyl–ruthenium bonds in **6a,b**–**8a,b** by acetic acid in benzene proceeds slowly at room temperature and gives the olefins **10**–**12** in virtually quantitative yield. They have been identified by comparison of their ^1H NMR data with those of authentic samples.[14] Since compound **1** is the second product of the reaction of **6a,b**–**8a,b** with CH_3CO_2H, a cyclic process can be created which proves that the trisubstituted ethene derivatives **10**–**12** can be built up from a carbene, a vinyl unit, and a proton in the coordination sphere of Ru(II).

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Supporting Information Available: Analytical and spectroscopic data for complexes **2**–**9**, details of the X-ray analysis of **6a**, and tables of bond lengths and bond angles, and atomic positional and anisotropic thermal parameters for **6a** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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