Organometallics **2001,** *20,* 3851−3853 3851

Facile Rearrangement of Metallacyclopentatrienes to Butadienyl Carbenes by a 1,2-Hydrogen Shift

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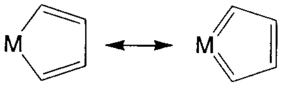
Received May 17, 2001

Summary: Cationic metallacyclopentatriene complexes having an α-alkyl substituent undergo facile 1,2-hydrogen shift to give butadienyl carbenes. This is exemplified by the reaction of $[RuCp(L)(CH_3CN)_2]PF_6$, where L = $SbPh_3$, $SbBu^n{}_3$, and $AsPh_3$, with 2,8-decadiyne, 1-hexyne, and benzylacetylene. There is an interesting mechanistic changeover on going to L = PR_3, in which case PR_3 migrates with an allyl carbene complex being formed.

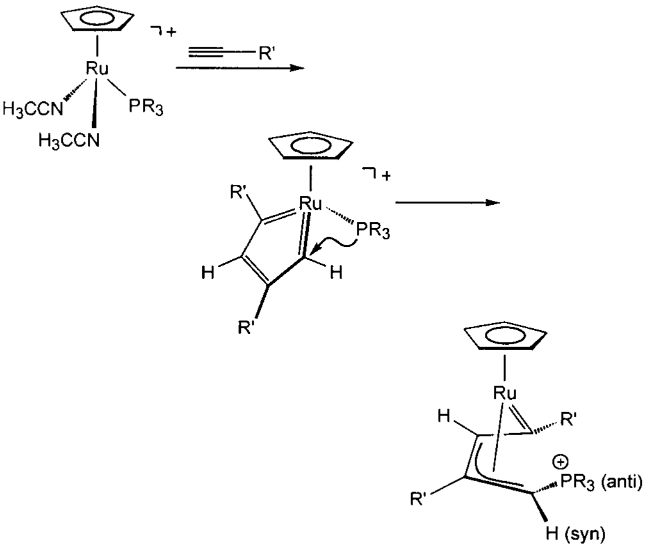
Transition metal complexes with vacant coordination sites, or bearing weakly coordinating ligands, are known to undergo oxidative coupling reactions with alkynes to give metallacyclopentadienes **I**.[1] Such species have attracted considerable interest, because they are considered to be important intermediates in alkyne cyclotrimerization.[2] In recent years, metallacyclopentatriene complexes **II**, a resonance form of **I** with a biscarbene functionality incorporated into the five-membered metallacycle, have been isolated[3] or invoked as key intermediates in several catalytic reactions involving alkynes, e.g., in the double cyclopropanation of 1,6-diynes with strained cyclic olefins, in the reaction of two alkyne molecules with carboxylic acids, and in the linear cotrimerization between two alkyne molecules and acrylonitrile.[1,4]



I **II**

We have recently shown[5] that the labile complex $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = e.g., Me, Ph, Cy), which serves as synthetic equivalent for the 14-electron fragment $[RuCp(PR_3)]^+$, reacts with terminal alkynes to give ruthenium allyl carbene complexes (Scheme 1).[6] This conversion is a very complex one involving oxidative coupling of two alkynes and an unusual PR_3 migration, with an electrophilic cationic metallacyclopentatriene complex as a conceivable intermediate. Here we change the conditions in order to make the surmised intermediate species observable, or hopefully isolable. For this purpose we replaced the terminal alkyne with an internal alkyne, and furthermore, we replaced the phosphine co-ligand with the larger and presumably less nucleophilic group 15 ligands SbR_3 (R = Ph, Bu^n) and $AsPh_3$. The intention was that, due to a size mismatch with carbon, nucleophilic attack at the α-carbon of the metallacycle is impeded. Along these lines, in fact, some evidence has been obtained in favor of the expected intermediate, which, however, proved to be unstable, giving rise to a novel rearrangement. The purpose of the present communication is to describe this.

Scheme 1



Treatment of $[RuCp(SbPh_3)(CH_3CN)_2]PF_6$ (**1a**) with 2,8-decadiyne (1 equiv) resulted in the formation of the

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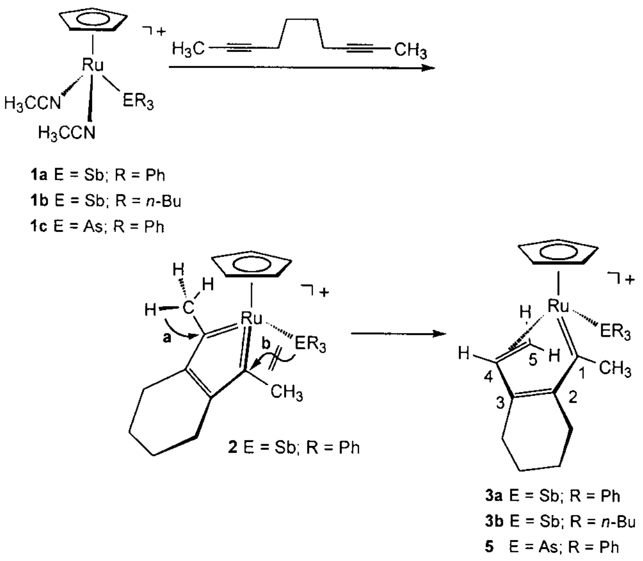
Scheme 2



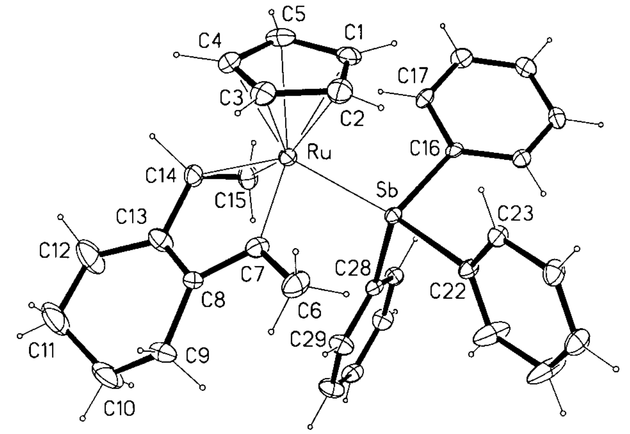


Figure 1. Structural view of **3a** showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ 2.239(6), Ru−C(7) 1.946(7), Ru−C(14) 2.175(7), Ru−C(15) 2.222(7), Ru−Sb 2.575(1), C(7)−C(8) 1.435(9), C(8)−C(13) 1.33(1), C(13)−C(14) 1.48(1), C(14)−C(15) 1.41(1), C(7)−C(8)−C(13) 113.2(6), C(8)−C(13)−C(14) 118.9(5), C(13)−C(14)−C(15) 120.9(7), Sb−Ru−C(7) 89.7(2).

butadienyl carbene complex $[CpRu({=}C(CH_3)C(CH_2)_4C\text{-}\eta^2\text{-}CH{=}CH_2)(SbPh_3)]PF_6$ (**3a**) in 81% isolated yield (Scheme 2). Monitoring this reaction by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy revealed the transient appearance of an intermediate consistent with the cationic metallacyclopentatriene structure $[CpRu({=}C(CH_3)_2C_2(CH_2)_4)(SbPh_3)]^+$ (**2**), depicted in Scheme 2.[7,8] Thus, the resonances in the $^{13}C\{^1H\}$ NMR spectrum at 330.3 and 171.3 ppm can be associated with the C_α and C_β ring carbons, respectively. Further, the unusual downfield shift of the C_α carbon resonance is in agreement with an unsaturated bis-carbene ligand (cf. $RuCp({=}C_2(Ph)_2\text{-}CH_2)Br$, for which the resonances of the C_α and C_β atoms, respectively, are found at 271.1 and 156.0 ppm[3a]). Finally, the signal at 53.5 ppm is relevant to the methyl carbon atoms.

Similar results were obtained when $SbBu^n_3$ was used instead of $SbPh_3$, giving the reaction of **1b** to **3b** in Scheme 2, and likewise when $AsPh_3$ was used instead of the stibine; that is, $[RuCp(AsPh_3)(CH_3CN)_2]PF_6$ (**1c**) converted with 2,8-decadiyne to the butadienyl carbene complex$[CpRu({=}C(CH_3)C(CH_2)_4C\text{-}\eta^2\text{-}CH{=}CH_2)(AsPh_3)]\text{-}PF_6$ (**5**). In the following we shall concentrate the discussion on **3a**.

The step from **2** to **3** in Scheme 2 is intriguing, since it involves activation of an α-substituent by an electrophilic carbene (path a), which is unprecedented for a metallacyclopentatriene. Hitherto, a 1,2-hydrogen shift is known only for electrophilic alkylidenes and Fischer-type carbenes.[9] There is only one more example of a butadienyl carbene as encountered recently in the reaction of an osmacyclopentatriene complex with *tert*-butylamine.[10] As anticipated, there was no evidence of path b, i.e., stibine or arsine migration, in sharp contrast to the phosphine analogues.

The ^1H NMR spectroscopic data for **3a** include characteristic resonances at 5.30 (dd, H,[4] $^3J_{HH} = 10.7$ Hz, $^3J_{HH} = 10.1$ Hz), 3.80 (d, H^{5cis}, $^3J_{HH} = 10.1$ Hz), and 1.85 ppm (d, H^{5trans}, $^3J_{HH} = 10.7$ Hz), assignable to the vinyl protons of the coordinated double bond. In the $^{13}C\{^1H\}$ NMR spectrum the characteristic resonance of the carbene carbon occurs as a doublet centered at 337.0 ppm. The uncoordinated and coordinated sp^2 carbon atoms C^2, C^3, C^4, and C^5 of the butadienyl unit exhibit resonances at 190.0, 160.1, 76.1, and 50.7 ppm, respectively, while the resonance of the methyl carbon atom is observed at 44.6 ppm. In addition to full NMR spectroscopic and analytical characterization, the solid state structure of **3a** was determined by single-crystal X-ray diffraction.[11] An ORTEP diagram is depicted in Figure 1 with important bond distances reported in the caption. Accordingly, **3a** adopts a three-legged piano stool conformation with $SbPh_3$ and the two C=C bonds and the carbene carbon atom of the butadienyl moiety

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(7) Reaction of **1a** with 2,8-decadiyne in acetone-d_6: A 5 mm NMR tube was charged with a solution of **1a** (45 mg, 0.060 mmol) in acetone-d_6 (0.5 mL) and was capped with a septum. 2,8-Decadiyne (8.9 μL, 0.060 mmol) was added by syringe, and the sample was transferred to a NMR probe. ^1H and $^{13}C\{^1H\}$ NMR spectra were immediately recorded. The formation and disappearance of $[CpRu({=}C_2(CH_3)_2C_2\text{-}(CH_2)_4)(SbPh_3)]PF_6$ (**2**) was observed. ^1H NMR (δ, acetone-d_6, 20 °C): 7.66−7.16 (m, 15H, Ph), 6.08 (s, 5H, Cp), 2.15−2.05 (m, 4H, CH_2), 1.60 (s, 6H, CH_3), 1.37−0.92 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 330.3 (2C, C_α, $C_{\alpha'}$), 171.3 (2C, C_β, $C_{\beta'}$), 136.2 (6C, $Ph^{2,6}$), 131.9 (3C, Ph^1), 130.7 (6C, $Ph^{3,5}$), 130.3 (3C, Ph^4), 93.7 (5C, Cp), 53.5 (2C, CH_2), 27.0 (2C, CH_2), 21.6 (2C, CH_3). Additional resonances due to the formation of **3a** were observed after 1 h.

(8) Preparation and data for **3a**: A solution of **1a** (100 mg, 0.134 mmol) in CH_2Cl_2 (5 mL) was treated with 2,8-decadiyne (21.9 μL, 0.147 mmol) and was stirred for 45 min, whereupon the color of the solution turned red. After that the volume of the solution was reduced to about 1 mL, Et_2O was slowly added, and a red microcrystalline precipitate was formed. The supernatant was decanted, and the solid was washed twice with Et_2O and dried under vacuum. Yield: 85 mg (81%). Anal. Calcd for $C_{33}H_{34}F_6PRuSb$: C, 49.64; H, 4.29. Found: C, 49.59; H, 4.32. ^1H NMR (δ, acetone-d_6, 20 °C): 7.77−7.29 (m, 15H, Ph), 5.56 (s, 5H, Cp), 5.30 (dd, $^3J_{HH} = 10.7$ Hz, $^3J_{HH} = 10.1$ Hz, 1H, H^4), 3.63 (d, $^3J_{HHis} = 10.1$ Hz, 1H, H^{5trans}), 2.84 (3H, CH_3), 2.57−1.40 (m, 8H, CH_2), 1.86 (d, $^3J_{HH} = 10.7$ Hz, 1H, H^{5cis}). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 337.0 (1C, C^1), 190.0 (1C, C^2), 160.1 (1C, C^3), 136.5 (6C, $Ph^{2,6}$), 132.5 (3C, Ph^4), 131.2 (6C, $Ph^{3,5}$), 130.7 (3C, Ph^1), 89.3 (5C, Cp), 76.1 (1C, C^4), 50.7 (1C, C^5), 44.6 (CH_3), 36.9, 26.7 (2C, CH_2), 22.9 (2C, CH_2).

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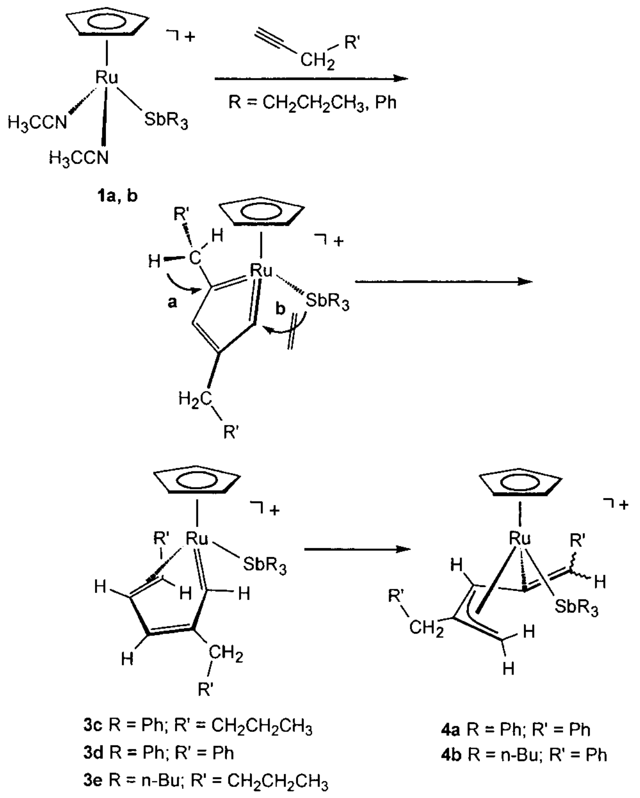
(11) X-ray crystal structure analysis of **3a**: $C_{33}H_{34}F_6PRuSb$, $M_r = 798.39$, monoclinic, space group $P2_1$, $T = 223(2)$ K, $a = 9.873(5)$ Å, $b = 15.377(7)$ Å, $c = 10.230(5)$ Å, $\beta = 93.39(2)$, $V = 1550(1)$ Å^3, $Z = 2$, $\mu = 1.468$ mm^{-1}. Of 22 188 reflections collected with a Bruker Smart CCD diffractometer and Mo Kα radiation, 6427 were independent; $R_{int} = 0.039$; final R indices: $R_1 = 0.044$ (all data), $wR_1 = 0.102$ (all data).

Scheme 3



$3c$ R = Ph; R' = $CH_2CH_2CH_3$
$3d$ R = Ph; R' = Ph
$3e$ R = n-Bu; R' = $CH_2CH_2CH_3$

$4a$ R = Ph; R' = Ph
$4b$ R = n-Bu; R' = Ph

as the legs. The most notable feature is the short Ru−C(7) bond distances of 1.946(7) Å, which is in line with a metal carbon double bond. Furthermore, the butadienyl C−C bonds C(8)−C(13), C(13)−C(14), and C(14)−C(15) show the expected short−long−short pattern (1.33(1), 1.48(1), and 1.41(1) Å, in the same order).

Scheme 2 is enlarged by an additional rearrangement step when instead of the diyne a terminal alkyne is used having CH bonds adjacent to the C−C triple bond capable of 1,2-hydrogen shift reactions in metallacyclopentatriene complexes. This is depicted in Scheme 3. At first **1a** or **1b** reacts with $HC{\equiv}CCH_2R'$ (R′ = $CH_2CH_2CH_3$, Ph) (2 equiv) to afford the butadienyl complexes [CpRu(=CHC(*n*-R′)CH-η^2-CH=CH-*n*-R′)(SbR_3)]PF_6 (**3c**−**e**) in high yields.[12] In this reaction the initial oxidative coupling step takes place selectively in a head-to-tail fashion, putting the substituents in the metallacyclopentatriene intermediate exclusively in the α- and β′-position. The NMR spectra of **3c**−**e** are very similar to those of **3a**. It is interesting, however, that in the conversion of **1b** with $HC{\equiv}CCH_2Ph$ no butadienyl carbene but rather the allyl vinyl complex **4b** is observed. In fact, the analogous complex **4a** is obtained quantitatively when a solution of **3d** in acetone is kept overnight at room temperature. Both rearrangement reactions involve 1,4-hydrogen migration.

In conclusion, we have shown for the first time that cationic metallacyclopentatriene complexes having an α-alkyl substituent are quite reactive, undergoing a facile 1,2-hydrogen shift to give butadienyl carbenes. The definite absence of migration of SbR_3 and AsR_3, in contrast to that of PR_3, points to distinct differences between these ligands. Unfortunately, quantitative data on pertinent σ donor and π acceptor strengths are not available.[13,14] In our opinion, as remarked above, the size mismatch between As and Sb on one hand and C on the other may have a say in the unwillingness to change places.

Acknowledgment. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project No. P14681-CHE) is gratefully acknowledged.

Supporting Information Available: Text giving full experimental details and spectroscopic and analytical data for complexes **3b**, **3d**, **3e**, **4a**, **4b**, and **5** and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complex **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Preparation and data for **3c**: This complex has been prepared analogously to **3a** with **1a** (400 mg, 0.536 mmol) and 1-hexyne (135.8 μL, 1.180 mmol) as the starting materials. Yield: 380 mg (86%). Anal. Calcd for $C_{35}H_{40}F_6PRuSb$: C, 50.74; H, 4.87. Found: C, 50.69; H, 4.82. ^1H NMR (δ, acetone-d_6, 20 °C): 15.63 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H^1), 7.93−7.20 (m, 15H, Ph), 6.84 (t, $^4J_{HH}$ = 2.5 Hz, 1H, H^3), 5.78 (s, 5H, Cp), 5.39 (td, ?J_{HH} = 10.9 Hz, $^4J_{HH}$ = 3.0 Hz, 1H, H^5), 4.88 (dd, $^3J_{HH}$ = 10.1 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, H^4), 2.65−2.50 (m, 1H, CH_2), 2.34−2.02 (m, 2H, CH_2), 1.84−1.02 (m, 6H, CH_2), 1.00−0.84 (m, 1H, CH_2), 0.83−0.69 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 304.0 (1C, C^1), 169.0 (1C, C^2), 151.8 (1C, C^3), 136.3 (6C, $Ph^{2,6}$), 131.9 (3C, Ph^4), 130.6 (6C, $Ph^{3,5}$), 129.3 (3C, Ph^1), 92.0 (5C, Cp), 86.7 (1C, C^4 or C^5), 85.0 (1C, C^4 or C^5), 37.9, 32.4, 32.2, 29.2, 22.8 (5C, CH_2), 14.0 (1C, CH_3), 13.8 (1C, CH_3).

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