Reactions of ruthenium cyclopropenyl complexes with trimethylsilyl azide

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Treatment of three cyclopropenyl complexes [Ru]–C=C(Ph)CHR {[Ru] = (η^5-C_5H_5)$(PPh_3)_2$Ru; R = Ph 1a, CN 1b, CH=CH_2 1c} with Me_3SiN_3 afforded the nitrile complex 3a, the zwitterionic tetrazolate complex 6, and 7, respectively; for 1c, the triazole 8 was also obtained.

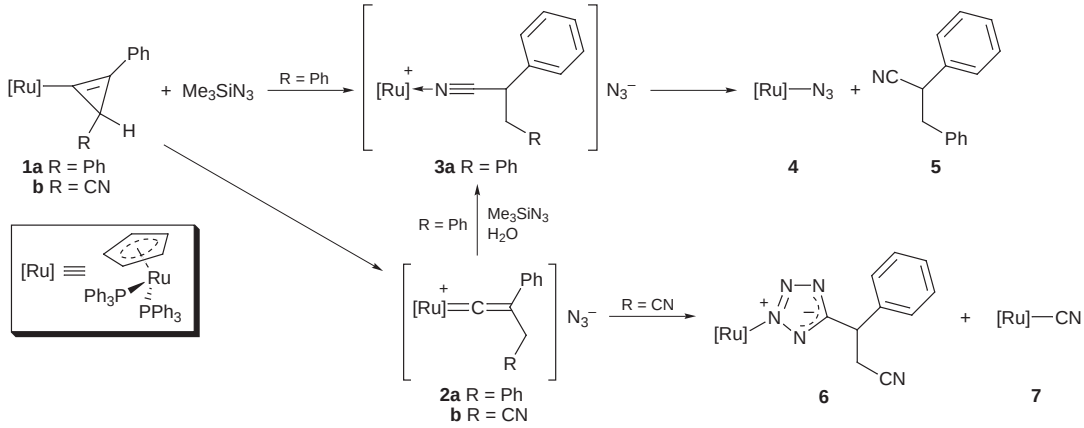
Organic cyclopropene is highly strained and its estimated strain energy is > 50 kcal mol^{-1} (1 cal = 4.184 J).[1] This molecule has played a crucial role in the development of important concepts such as aromaticity and chemical reactivities.[2] A few recent papers focused on applications of various cyclopropenes in organic synthesis.[3] In organometallic systems, deprotonation of a number of vinylidene complexes {[Ru]=C=C(Ph)CH_2R}I {[Ru] = (η^5-C_5H_5)$(PPh_3)_2$Ru; R = CN, Ph, CH=CH_2} readily afforded ruthenium cyclopropenyl complexes.[4] Protonation opens the three-membered rings of these Ru complexes to give back the vinylidene moiety. Nevertheless, in the ruthenium system, the cyclopropenyl and the vinylidene complexes display distinctive reactivities. We carried out reactions of cyclopropenyl complexes with various organic substrates. Herein we report the reaction of Me_3SiN_3 ($TMSN_3$) with a number of ruthenium cyclopropenyl complexes containing different substituents at the cyclopropenyl ring to yield various products.

Upon addition of a fivefold excess of $TMSN_3$ to **1a** in THF at room temperature, the solution displayed color changes during the course of the reaction. The light yellow solution of **1a** turned to deep red at the initial stage then became light orange in *ca.* 3 h and, after 5 h, turned yellow again. We thus carried out the reaction at −10 °C and, while the solution was deep red, isolated **2a**‡ as the major product and the N-coordinated nitrile complex **3a**‡ as the minor product, Scheme 1. From the light orange solution of the same reaction at room temperature, **3a** could be isolated in high yield. Finally with a 5 h reaction time the reaction gave **4**[5] and **5**.[6]‡ As a precursor of **3a**, **2a** is unstable at room temperature.

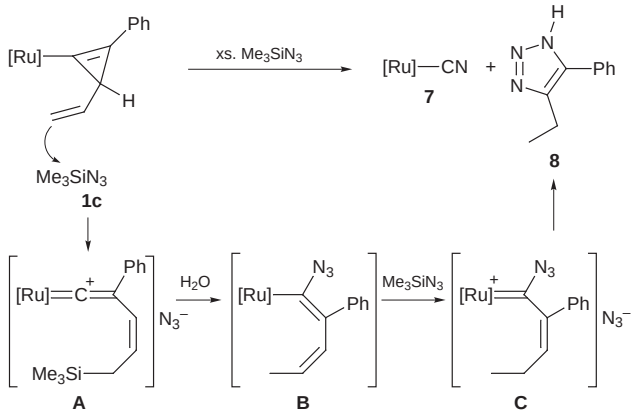
Complex **3a** is also unstable and decomposes to give **4** and **5**. Exchange of the N_3^- counter anion with PF_6^- made **2a** and **3a** more stable. In the ^{1}H NMR spectrum of **2a**, a singlet resonance at δ 3.50 is assigned to the CH_2 group. The ^{31}P NMR spectrum displays a singlet resonance at δ 42.5. However, in the ^{31}P NMR spectrum of **3a** two doublet resonances at δ 41.7 and 41.2 with J_{PP} 35.3 Hz indicate the presence of a diastereotopic center in the N-coordinated nitrile ligand and, in the ^{1}H NMR spectrum, two resonances at 3.15 (J_{HH} 16.6, 6.5 Hz) and 3.00 (J_{HH} 16.6, 10.0 Hz) are assigned to the CH_2 group. The parent peak of the mass spectrum of **3a** clearly indicates addition of one nitrogen atom to **2a**.

Treatment of **1b** with $TMSN_3$ at room temperature caused addition of four nitrogen atoms to **1b** and afforded the yellow tetrazolate complex **6**‡ in high yield and **7**‡ in *ca.* 5% yield, Scheme 1. Complex **6** is stable at room temperature, and in the course of the reaction only a deep red color attributed to a vinylidene intermediate **2b** was observed. The intermediate **2b** could be isolated at 0 °C. In the ^{1}H NMR spectrum of **6**, a dd resonance at δ 4.32 (J_{HH} 7.4, 7.7 Hz) is assigned to the methyne proton and two multiplet resonances displaying doublets of an AB pattern at δ 2.66 (J_{HH} 16.6, 7.4 Hz) and 2.44 (J_{HH} 16.6, 7.7 Hz) are assigned to two methylene protons. In the ^{31}P NMR spectrum of **6**, two doublet resonances at δ 43.8 and 41.7 with J_{PP} 38.0 Hz are assigned to the two PPh_3 ligands owing to the presence of a diastereotopic center. The proton source of the reactions of **1a** and **1b** is believed to come from water in $TMSN_3$ (no attempt was made to dry $TMSN_3$ due to potential hazards) and protons are incorporated into the product through hydrolysis of the TMS substituents. TMSOH was distilled off with THF solvent from the reaction mixture and identified by mass spectrometry. In both reactions, addition of D_2O to THF led to incorporation of two deuterium atoms at two vicinal carbon atoms of both **5** and **6**. No reaction was observed between {[Ru]=C=C(Ph)CH_2CH}PF_6 and $TMSN_3$ possibly owing to the covalent character of the Si–N bond in $TMSN_3$ and weak nucleophilicity of the cationic vinylidene complex to cleave the Si–N bond.

The reaction of **1a** with $TMSN_3$ may proceed by an electrophilic addition of a TMS group followed by hydrolysis to afford **2a**. Further nucleophilic addition of N_3^- at C_α and electrophilic addition of a second TMS group at C_β followed by loss of N_2 gives the N-coordinated nitrile complex **3a**,[5] Scheme 1. In the reaction of **1b** with $TMSN_3$, formation of **6** is



Scheme 1



Scheme 2

rationalized by a [3 + 2] cycloaddition of the CN bond with a second N_3^-.[7] As early as 1958, formation of tetrazolate ring structure has been observed in the [3 + 2] cycloaddition reaction of a nitrile group with azide.[8] Metal-coordinated azide ligands undergo 1,3-dipolar cycloaddition reactions with carbon–carbon and carbon–heteroatom multiple bonds. Among others, this chemistry has been investigated by the group of Beck. The metals involved are most often palladium(II),[9] platinum(II)[10] and cobalt(III)[11] although a whole range of other transition metals[12] has been used. These metal azido complexes react with nitrile to give various tetrazolate complexes.[13] Formation of the tetrazolate ring in **6** is derived from the reaction of nitrile with [Ru]–N_3 since under our mild reaction condition, no such reaction was observed. The reaction of the acetylide complex [Ru]–C≡CPh with an excess of $TMSN_3$ afforded **4** and $PhCH_2CN$, identified by elemental analysis and high resolution mass spectroscopy. Conversion of a vinylidene precursor to N-coordinated nitrile by hydrazine, an organometallic Beckmann rearrangement, has been reported in an iron system.[14]

Interestingly, treatment of **1c** with an excess of $TMSN_3$ afforded **7** and **8**,‡ Scheme 2. The organic product is identified by elemental analysis and high resolution mass spectrometry. Formation of **7** and **8** by cleavage of the C=C double bond of the cyclopropenyl ring and transformation of the vinyl to an ethyl group could be explained as followed. Addition of a TMS group to the terminal carbon atom of the vinyl group accompanied by opening of the three-membered ring resulted in formation of **A**, Scheme 2. We previously reported that the reaction of TCNQ with **1c** gave similar addition at the terminal carbon of the vinyl group.[4] Subsequent nucleophilic addition of N_3^- at C_α followed by hydrolysis gave **B**. Further addition of $TMSN_3$ at C_δ followed by hydrolysis led to the formation of **C**. The single bond character of the C_α–C_β in **C** facilitates its cleavage, which is accompanied by a [3 + 2] cycloaddition of the C_β–C_γ double bond with N_3^- to give the triazole compound **8** and **7**. The fact that **7** is isolated in this reaction as the only organometallic product suggests that it is not likely to have an intermediate with a terminal N-coordinated nitrile ligand. Formation of **7** as a minor product in the reaction of **1b** with $TMSN_3$ could proceed through the same pathway. A detailed mechanism for these processes is currently under investigation.

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Notes and References

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‡ *Selected spectroscopic data*: ^{1}H and ^{13}C-{^{1}H} NMR were recorded in $CDCl_3$ relative to $SiMe_4$ and ^{31}P NMR data with H_3PO_4 as external standard in $CDCl_3$. **2a**: ^{1}H NMR, δ 7.41–6.80 (m, 45 H, Ph), 5.21 (s, 5 H, Cp), 3.56 (s, 2 H, CH_2); ^{31}P NMR, δ 42.5 (s). FAB MS: *m*/*z* 883 (M^+), 691 (M^+ − $CCPhCH_2Ph$). **2b**: ^{1}H NMR, δ 7.50–6.96 (m, 35 H, Ph), 5.21 (s, 5 H, Cp), 3.22 (s, 2 H, CH_2). **3a**: ^{1}H NMR (253 K), δ 7.43–6.85 (m, 45 H, Ph), 4.50 (t, J_{HH} 10.0, 6.5 Hz, 1 H, CH), 4.33 (s, 5 H, Cp), 3.15, (J_{HH} 16.6, 6.5 Hz, 1 H, CH_2), 3.00 (J_{HH} 16.6, 10.0 Hz, 1 H, CH_2). ^{13}C NMR (253 K), δ 136.4–127.2 (Ph), 83.6 (Cp), 41.3 (CH), 40.0 (CH_2). ^{31}P NMR, δ 41.7, 41.2 (two d, J_{PP} 35.3 Hz). FAB MS: *m*/*z* 898 (M^+), 691 (M^+ − $NCCHPhCH_2Ph$). **4**: ^{1}H NMR, δ 7.68–7.07 (m, 30 H, Ph), 4.18 (s, 5 H, Cp); ^{13}C NMR, δ 138.4–127.4 (Ph), 81.3 (Cp); ^{31}P NMR, δ 41.8 (s). FAB MS: *m*/*z* 733.1 (M^+); 705.0 (M^+ − N_2). Anal. Calc. for $C_{41}H_{35}N_3P_2Ru$: C, 67.20; H, 4.81; N, 5.73. Found: C, 67.92; H, 4.95; N, 4.91%. **5**: ^{1}H NMR, δ 7.43–7.09 (m, 10 H, Ph), 3.98 (dd, J_{HH} 8.4, 6.7 Hz, 1 H, CH), 3.17, (dd, J_{HH} 13.7, 6.7 Hz, 1 H, CH_2) 3.11 (dd, J_{HH} 13.7, 8.4 Hz, 1 H, CH_2). HRMS: *m*/*z* 207.1050 (M^+). Anal. Calc. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C. 87.01; H, 6.30; N, 6.65%. **6**: ^{1}H NMR (C_6D_6), δ 7.59–6.81 (m, 35 H, Ph), 4.45 (dd, J_{HH} 7.4, 7.7 Hz, 1 H, CH), 4.30 (s, 5 H, Cp), 2.66, (J_{HH} 16.6, 7.4 Hz, 1 H, CH), 2.44 (J_{HH} 16.6, 7.7 Hz, 1 H, CH_2); ^{13}C NMR, δ 164.1 (CNN, C_α), 140.2 (C_{ipso}), 138.3–127.1 (Ph), 118.6 (CN), 83.1 (Cp), 39.9 (CH), 23.5 (CH_2). ^{31}P NMR, δ 43.8, 41.7 (two d, J_{PP} 38.0 Hz). FABMS: *m*/*z* 889.2 (M^+ + 1, Ru = 104), 691 (M^+ − $N_4C_2HPhCH_2CN$), 429 (M^+ − PPh_3, $N_4C_2HPhCH_2CN$). Anal. Calc. for $C_{51}H_{43}N_5P_2Ru$: C, 68.91; H, 4.88; N, 7.88. Found: C, 69.20; H, 4.96; N, 7.96%. **7**: ^{1}H NMR, δ 7.69–6.95 (m, 30 H, Ph, 4.36 (s, 5 H, Cp); ^{13}C NMR, δ 138.2–127.3 (Ph), 85.0 (Cp); ^{31}P NMR, δ 50.3 (s). FABMS: *m*/*z* 717.0 (M^+); 691.0 (M^+ − CN). Anal. Calc. for $C_{42}H_{35}NP_2Ru$: C, 70.38; H, 4.92; N, 1.95. Found: C, 69.94; H, 4.85; N, 2.06%. **8**: ^{1}H NMR, δ 7.31–7.19 (m, 5 H, Ph), 2.89 (q, J_{HH} 7.6 Hz, 2 H, CH_2), 1.30 (t, J_{HH} 7.6 Hz, 3 H, CH_3). HRMS: *m*/*z* 173.0952 (M^+). Anal. Calc. for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.53; H, 6.21; N, 23.98%.

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