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[7] Correct analytical data are available for **3**–**6** and **8**.

[8] Crystal data for **2**: $C_{35}H_{32}N_4Ru \cdot C_4H_8O$, $M_r = 681.82$, triclinic, space group $P\bar{1}$, $a = 11.414(14)$ Å, $b = 14.297(12)$ Å, $c = 11.332(8)$ Å, $\alpha = 108.77(6)$, $\beta = 104.29(10)$, $\gamma = 105.25(11)^\circ$, $Z = 2$, $V = 1574(3)$ Å^3, $\rho_{calcd} = 1.439$ g cm^3, $\mu(Mo_{K\alpha}) = 5.37$ cm^{-1}, final $R1$, $wR2$, and S are 0.0878, 0.2225, and 1.030 for 410 parameters and 5831 unique observed reflections with $I > 2\sigma(I)$. **7**: $C_{32}H_{30}N_4O_3Ru \cdot 1.5\,C_7H_8$, $M_r = 757.37$, monoclinic, space group $P2_1/c$, $a = 11.269(4)$ Å, $b = 9.445(2)$ Å, $c = 33.854(12)$ Å, $\beta = 91.63(3)^\circ$, $Z = 4$, $V = 3602(2)$ Å^3, $\rho_{calcd} = 1.397$ g cm^3, $\mu(Mo_{K\alpha}) = 0.481$ mm^{-1}, final $R1$, $wR2$, and S are 0.0365, 0.1117, and 1.896 for 467 parameters and 4986 unique observed reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-177. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (44) 1223-336 033; e-mail: deposit@ccdc.cam.ac.uk).

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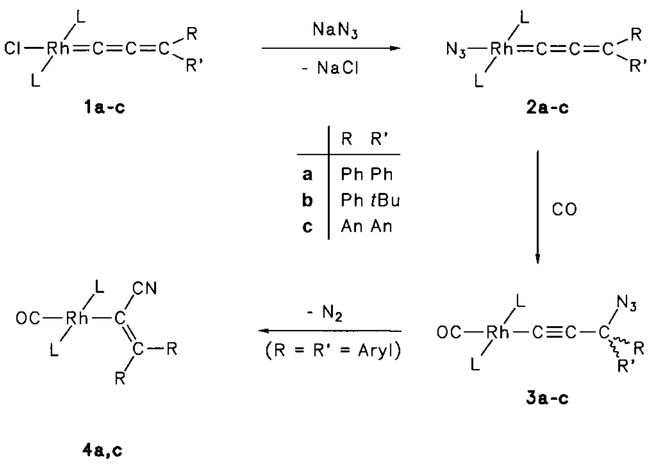
Unprecedented C—N Coupling Following Migration of an Azido Ligand to a C=C=CRR′ Unit**

Matthias Laubender and Helmut Werner*

Dedicated to Professor Lord Lewis
on the occasion of his 70th birthday

Migratory insertion of CO into metal–carbon bonds represents one of the most important reactions in organometallic chemistry and homogeneous catalysis.[1, 2] In the course of our investigations on the reactivity of metallaallenes [L$_n$M=C=CRR′] and metallabutatrienes [L$_n$M=C=C=CRR′],[3] we found that not only compounds such as *trans*-[Rh(CH=CH$_2$)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$]—generated in situ from **1a** and CH$_2$=CHMgBr—but also those of the general composition *trans*-[Rh(OR)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (R = Ph, COCH$_3$) easily undergo insertion of the C$_3$Ph$_2$ unit into the Rh—C or Rh—O bond on treatment with CO.[4] This prompted us to prepare the structurally related complexes *trans*-[Rh(X)(=C=C=CRR′)(P*i*Pr$_3$)$_2$], where X is a N-bonded ligand, to find out whether a formal insertion of the allenylidene unit into the Rh—N bond also takes place in the presence of CO. Here we report that for X = N$_3$ such a reaction occurs and, more noteworthy, that the migration of the azide is followed by an unprecedented C—N coupling to generate a substituted acrylonitrile ligand.

The chlororhodium(I) complexes **1a**–**c** react with excess NaN$_3$ in acetone/THF (1/1) at room temperature to give, after recrystallization from acetone, deeply colored **2a**–**c** as crystalline solids in practically quantitative yields (Scheme 1; **2a**: red, **2b**: green, **2c**: violet). The most characteristic features of the spectroscopic data of **2a**–**c** (Table 1) are the three low-field signals between $\delta = 255$ and 140 for the allenylidene



Scheme 1. L = P*i*Pr$_3$, An = *p*-C$_6$H$_4$OMe.

Table 1. Selected spectroscopic data for **2a**–**c**, **3b**, **4a**, **c**, and **5** (without data for phosphane ligands or *tert*-butyl and aryl groups).

2a: IR (C$_6$H$_6$): $\tilde{\nu} = 2060$ (N=N=N), 1870 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 244.6$ (dt, ^2J(Rh,C) = 15.1, ^3J(P,C) = 6.0 Hz, Rh=C=*C*=C), 233.7 (dt, ^1J(Rh,C) = 62.4, ^2J(P,C) = 17.1 Hz, Rh=*C*=C=C), 140.5 (s, Rh=C=C=*C*)

2b: IR (C$_6$H$_6$): $\tilde{\nu} = 2050$ (N=N=N), 1885 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 255.0$ (dt, ^1J(Rh,C) = 62.4, ^2J(P,C) = 17.1 Hz, Rh=*C*=C=C), 230.3 (dt, ^2J(Rh,C) = 16.1, ^3J(P,C) = 6.0 Hz, Rh=C=*C*=C), 162.0 (br s, Rh=C=C=*C*)

2c: IR (C$_6$H$_6$): $\tilde{\nu} = 2050$ (N=N=N), 1885 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 235.0$ (dt, ^1J(Rh,C) = 61.4, ^2J(P,C) = 17.1 Hz, Rh=*C*=C=C), 228.4 (dt, ^2J(Rh,C) = 15.1, ^3J(P,C) = 6.0 Hz, Rh=C=*C*=C), 142.0 (s, Rh=C=C=*C*)

3b: IR (C$_6$H$_6$): $\tilde{\nu} = 2100$ (N=N=N), 2065 (C≡C), 1945 cm^{-1} (CO); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): $\delta = 195.4$ (m, RhCO), 121.5 (dt, ^1J(Rh,C) = 44.3, ^2J(P,C) = 19.1 Hz, Rh*C*≡C), 112.8 (dt, ^2J(Rh,C) = 12.1, ^3J(P,C) = 2.0 Hz, RhC≡*C*), 77.7 (br s, RhC≡C*C*)

4a: IR (C$_6$H$_6$): $\tilde{\nu} = 2145$ (C≡N), 1945 cm^{-1} (CO); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): $\delta = 195.3$ (dt, ^1J(Rh,C) = 56.3, ^2J(P,C) = 15.6 Hz, RhCO), 160.3 (br t, ^3J(P,C) = 4.5 Hz, C=*C*Ph$_2$), 143.0 (dt, ^1J(Rh,C) = 31.2, ^2J(P,C) = 14.6 Hz, RhC), 125.2 (t, ^3J(P,C) = 2.0 Hz, C≡N)

4c: IR (C$_6$H$_6$): $\tilde{\nu} = 2145$ (C≡N), 1947 cm^{-1} (CO); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): $\delta = 194.4$ (dt, ^1J(Rh,C) = 57.3, ^2J(P,C) = 15.1 Hz, RhCO), 160.4 (t, ^3J(P,C) = 5.0 Hz, C=*C*(*p*-MeOC$_6$H$_4$)$_2$), 136.9 (dt, ^1J(Rh,C) = 31.2, ^2J(P,C) = 15.1 Hz, RhC), 126.3 (br s, C≡N)

5: IR (C$_6$H$_6$): $\tilde{\nu} = 2213$ (NCO), 1892 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): $\delta = 255.2$ (dt, ^1J(Rh,C) = 60.4, ^2J(P,C) = 17.1 Hz, Rh=*C*=C=C), 233.5 (dt, ^2J(Rh,C) = 15.1, ^3J(P,C) = 6.0 Hz, Rh=C=*C*=C), 159.9 (br s, Rh=C=C=*C*)

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[*] Prof. Dr. H. Werner, Dipl.-Chem. M. Laubender
Institut für Anorganische Chemie der Universität
Am Hubland, D-97074 Würzburg (Germany)
Fax: Int. code + (49) 931-888 4605
e-mail: helmut.werner@mail.uni-wuerzburg.de

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carbon atoms in the ^{13}C NMR spectra and the strong N=N=N stretching frequency at 2050 – 2060 cm^{-1} in the IR spectra. As the X-ray crystal structure analysis of **2b** (Figure 1) reveals,[5] the Rh-C1-C2-C3 chain is almost linear—as in the related chloro derivative *trans*-[RhCl{=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$][6]—whereas the *trans*-disposed Rh-N1-N2-N3 unit is bent. The bending of 143.7(5)° is more significant than in the analogous carbonyl compound *trans*-[Rh(N$_3$)(CO)(PPh$_3$)$_2$], in which the angle Rh-N1-N2 is 132(1)°.[7]

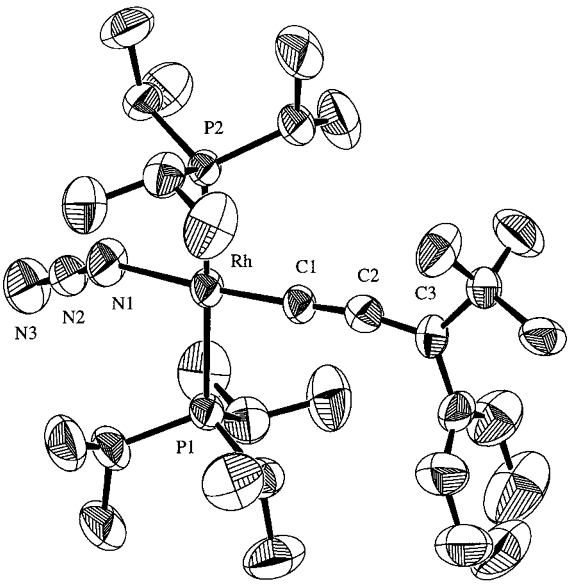


Figure 1. Molecular structure of **2b** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Rh–P1 2.348(2), Rh–P2 2.347(1), Rh–C1 1.849(5), Rh–N1 2.057(5), N1–N2 1.177(7), N2–N3 1.161(7), C1–C2 1.269(7), C2–C3 1.348(7); P1-Rh-P2 175.59(6), C1-Rh-N1 175.7(2), P1-Rh-C1 89.4(2), P1-Rh-N1 93.5(2), P2-Rh-C1 89.9(2), P2-Rh-N1 87.4(2), Rh-C1-C2 177.6(5), Rh-N1-N2 143.7(5), N1-N2-N3 175.8(7), C1-C2-C3 169.1(6).

Like the phenolato- and acetatorhodium(I) derivatives *trans*-[Rh(OR)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$], the azido complexes **2a–c** are highly reactive toward CO. When CO was passed through a solution of **2a–c** in toluene at −60 °C for 30 s and the temperature then slowly raised to 20 °C, yellow crystalline solids were obtained in yields of about 90 %. For R = Ph and R′ = *t*Bu the analytical composition of the isolated product corresponded to that of **3b** (see Scheme 1). In analogy to the related complexes *trans*-[Rh{C≡CC(OPh)Ph$_2$}(CO)(P*i*Pr$_3$)$_2$],[4b] the ^{13}C NMR spectrum of **3b** displays two doublets of triplets at δ = 121.5 and 112.8 for the carbon atoms of the C–C triple bond, and the IR spectrum two absorptions at 2100 and 2065 cm^{-1}, which are assigned to the N=N=N and C≡C stretching frequencies. Owing to these data, there is no doubt that treatment of **2b** with CO results in a migration of the N$_3$ ligand to the allenylidene unit and that the intact azido group in the product is linked to the γ-carbon atom of the C$_3$ chain.

Quite unexpectedly, the compounds obtained from **2a**, **c** and CO possess a different composition than **3b** (although they have the same color). The IR spectra display only *one* sharp absorption between 2000 and 2200 cm^{-1} (Table 1), and the ^{13}C NMR spectra *three* resonances at δ = 160 – 125, which all show P–C coupling. These data, together with the stability of the solids toward air and moisture, indicate that the final products of the reaction of **2a** and **2c** with CO are the carbonyl(vinyl)rhodium complexes **4a** and **4c**, respectively. The assumption that they are formed via **3a** and **3c** as intermediates is consistent with the ^{31}P NMR (δ = 54.1 (d, J(Rh,P) = 125.3 Hz)) and the ^{13}C NMR spectra of the species (δ = 127.4 (dt, J(Rh,C) = 43.0, J(P,C) = 21.3 Hz, Rh–*C*≡C), 113.8 (br d, J(Rh,C) = 12.9 Hz, Rh–C≡*C*), 72.1 (s, C≡C–*C*)) generated by passing CO through a solution of **2a** in [D$_8$]THF at −55 °C. Upon warming to room temperature, this species is rapidly converted into **4a** by elimination of N$_2$. Theoretical work on the reactivity of unsaturated carbon chains C$_n$ linked to a transition metal suggests that for $n = 3$ the α- and γ-carbon atoms are electron poor.[8] Therefore, it is conceivable that the supposed intermediates **3a** or **3c** rearrange to an isomer with a C(N$_3$)=C=CRR′ moiety. This would then eliminate N$_2$ to give the final product.

The X-ray crystal structure of **4c** is shown in Figure 2. The four-coordinated metal center possesses a slightly distorted square-planar configuration with Rh–C1, Rh–C3, Rh–P1, and Rh–P2 distances that are quite similar to those of the butadienyl complex *trans*-[Rh{C(CH=CH$_2$)=CHPh}(CO)(P*i*Pr$_3$)$_2$].[9] The C1-Rh-C3 axis is nearly linear, whereas the P1-Rh-P2 axis is somewhat bent; the bending of 167.10(4)° is more pronounced than in **2b** (175.59(6)°). The plane including C2, C3, and C4 is almost perpendicular (86.8(1)°) to that formed by Rh, C1, C3, P1, and P2, which probably minimizes the repulsive interactions between the six isopropyl groups and the substituents at the C–C double bond.

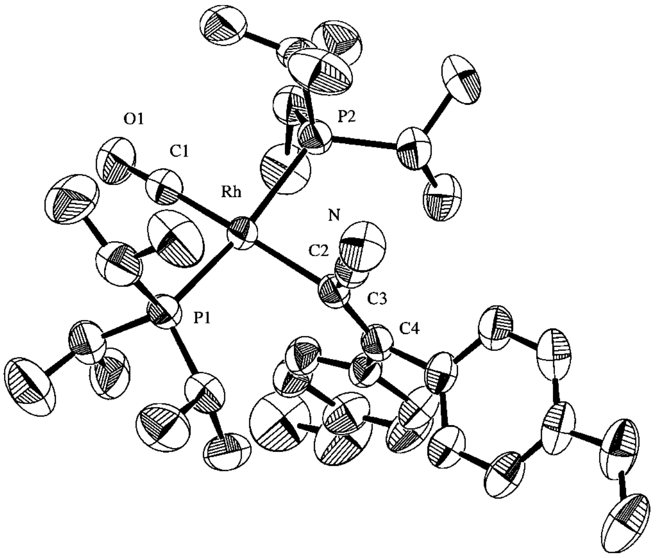
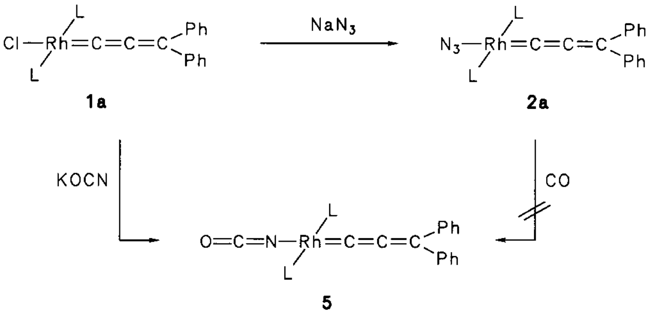


Figure 2. Molecular structure of **4c** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Rh–P1 2.338(1), Rh–P2 2.340(1), Rh–C1 1.834(5), Rh–C3 2.106(4), C1–O1 1.146(5), C2–C3 1.428(6), C2–N 1.144(5), C3–C4 1.367(3); P1-Rh-P2 167.10(4), C1-Rh-C3 174.6(2), P1-Rh-C1 89.7(2), P1-Rh-C3 91.9(1), P2-Rh-C1 88.5(1), P2-Rh-C3 91.2(1), Rh-C1-O1 175.1(4), Rh-C3-C2 109.8(3), Rh-C3-C4 133.2(3), C3-C2-N 174.9(5), C2-C3-C4 117.0(4).

In contrast to several azidometal complexes,[10] the allenylidene derivatives **2a–c** do not react with CO to give the corresponding isocyanato compounds *trans*-[Rh(NCO)-

$(=C=C=CRR')(PiPr_3)_2]$. Therefore, one representative of this type of species was prepared by a different route (Scheme 2). Treatment of **1a** with excess KOCN in acetone/THF (1/1) at room temperature gives complex **5** as a red solid in 95% yield. Under the conditions used to form **3a**, **c** (in situ) and **3b**, **5** is completely inert toward CO. As far as N-bonded ligands are concerned, the reactivity of the Rh-bonded azido group in **2a**–**c** toward CO is unique. To the best of our knowledge, there is also no precedence for the type of C–N coupling which occurs during the conversion of **2a** and **2c** into **4a** and **4c**. With regard to the lability of the intermediate observed during the formation of **4a**, it is rather surprising that the related substituted alkynyl complex **3b** is completely inert and does not react either thermally or photochemically to afford *trans*-$[Rh\{C(CN)=C(Ph)tBu\}(CO)(PiPr_3)_2]$. Treatment of **4a** and **4c** with trifluoracetic acid results in cleavage of the Rh–C σ bond, leading to formation of the corresponding acrylonitrile derivatives $R_2C=CHCN$ (R = Ph, An) in quantitative yields.



Scheme 2. L = P*i*Pr$_3$.

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[5] Data for the X-ray structure analyses: **2b**: crystals from pentane (−20 °C), $C_{31}H_{56}N_3P_2Rh$ (635.7); crystal dimensions $0.3 \times 0.3 \times 0.5$ mm; triclinic; space group $P\bar{1}$ (no. 2); $a = 9.0808(6)$, $b = 11.7579(6)$, $c = 16.886(2)$ Å, $\alpha = 98.035(8)$, $\beta = 90.944(8)$, $\gamma = 102.408(5)°$, $Z = 2$, $V = 1741.5(3)$ Å^3, $\rho_{calcd} = 1.212$ g cm^{-3}; $T = 293(2)$ K; $2\Theta_{max.} = 46°$; of 4465 reflections measured, 4105 were unique ($R_{int.} = 0.0173$) and 3247 observed ($I > 2\sigma(I)$); Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated, zirconium filter (factor 15.4); Lp and empirical absorption corrections (Ψ scan, min. transmission 96.83%). The structure was solved by direct methods and refined with the full matrix, least-squares method; $R_1 = 0.0399$, $wR_2 = 0.0839$ (for 3247 reflections with $I > 2\sigma(I)$), $R_1 = 0.0612$, $wR_2 = 0.1069$ (for all 4105 data); data-to-parameter ratio 10.98; residual electron density $+0.753/-0.484$ e Å^{-3}. **4c**: crystals from diethyl ether (−20 °C), $C_{36}H_{56}NO_3P_2Rh$ (715.7); crystal dimensions $0.3 \times 0.3 \times 0.4$ mm; monoclinic; space group $P2_1/c$ (no. 14); $a = 11.560(1)$, $b = 16.790(1)$, $c = 19.253(1)$ Å, $\beta = 93.48(1)°$, $Z = 4$, $V = 3730.1(4)$ Å^3; $\rho_{calcd} = 1.274$ g cm^{-3}; $T = 293(2)$ K; $2\Theta_{max.} = 46°$; of 4984 reflections measured, 4238 were unique ($R_{int.} = 0.0174$) and 3431 observed ($I > 2\sigma(I)$); Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated, zirconium filter (factor 15.4); Lp and empirical absorption corrections (Ψ scan, min. transmission 93.72%). The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0340$, $wR_2 = 0.0703$ (for 3431 reflections with $I > 2\sigma(I)$), $R_1 = 0.0492$, $wR_2 = 0.0792$ (for all 4238 data); data-to-parameter ratio 10.53; residual electron density $+0.343/-0.223$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100601. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Three-Component Coupling Reactions of Alkyl Iodides, 1,3-Dienes, and Carbonyl Compounds by Sequential Generation of Radical and Anionic Species with $CrCl_2$[**]

Kazuhiko Takai,* Naoto Matsukawa, Akira Takahashi, and Takafumi Fujii

Although conjugated dienes are good radical-trapping agents,[1] their use in organic synthesis is quite limited because further radical addition leading to polymerization occurs. Such radical chain reactions stem from the similar reactivity of the formed allylic radicals and the starting alkyl radicals. One way to prevent the undesirable side reactions is to reduce the allylic radicals to the corresponding anions (Scheme 1). However, a strong reductant such as samarium(II) readily reduces alkyl radicals, formed from alkyl halides, to furnish alkyl anions; the lifetime of the alkyl radicals is so short that intermolecular C–C bond formation cannot occur.[2, 3] We

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[*] Prof. Dr. K. Takai, N. Matsukawa, A. Takahashi, T. Fujii
Department of Applied Chemistry, Faculty of Engineering
Okayama University
Tsushima, Okayama 700 (Japan)
Fax: Int. code + (81) 86-251-8021
e-mail: ktakai@cc.okayama-u.ac.jp

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