Ruthenium Carbenes Bonded to a Macrocycle: Carbon Monoxide Induced Carbene Migration Pathways from the Metal to the Ligand**

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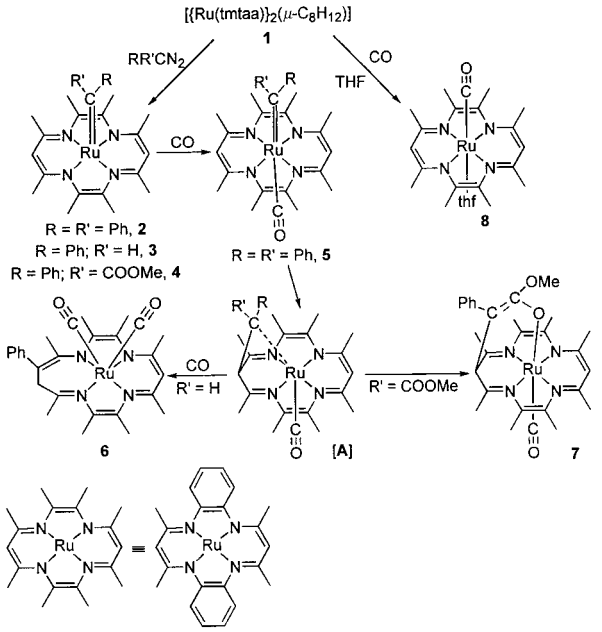
The potential of the metal–carbene functionality[1] bonded to a macrocyclic structure is still largely unexplored, except for some remarkable exceptions in metal–porphyrin chemistry, particularly in the case of the iron[2] and ruthenium[3] couple. This fact is rather surprising in the case of ruthenium, because recently the ruthenium–carbene functionality bonded to conventional ancillary ligands has had a large impact in catalysis of metathesis reactions.[4]

The present paper shows some aspects of the ruthenium–carbene unit when bonded to the easily accessible tetramethyldibenzotetraazaannulene [tmtaaH$_2$].[5] The chemistry of [Ru(tmtaa)] has so far been almost unexplored. Our starting material is not the stable [Ru(tmtaa)(PR$_3$)$_2$],[6] but the labile olefin complex **1** (Scheme 1).



Scheme 1. Synthesis of **2**–**8**. In the routes to **6** and **7** a ruthenium-to-macrocycle migration of the carbene functionality is indicated.

Reaction of **1** with diazoalkanes led to the corresponding carbene derivatives **2**–**4**,[7] which have been fully characterized. The X-ray analysis on **2**[8] is the first X-ray structure of a Ru–carbene bonded to a macrocyclic structure.

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The coordination environment of the ruthenium center is a distorted tetragonal pyramid, unlike in carbene–Fe[2a] and carbene–Os porphyrins,[9] where the metal is always hexacoordinate. The metal is displaced by 0.374(3) Å from the average N$_4$ plane towards the carbene carbon. The Ru–C23 vector is perpendicular to the N$_4$ core. The carbene C23,C24,C30 plane is almost parallel to the N1–N3 vector (torsional angles: C30,C23,Ru,N3 −6.6(6) and C24,C23,Ru,N2 −91.0(6)°). The Ru=C bond length [1.874(8) Å], which does not have any counterpart in Ru–porphyrin or macrocyclic chemistry, is rather close to those found in Ru–phosphane derivatives.[4a, e, f] The question

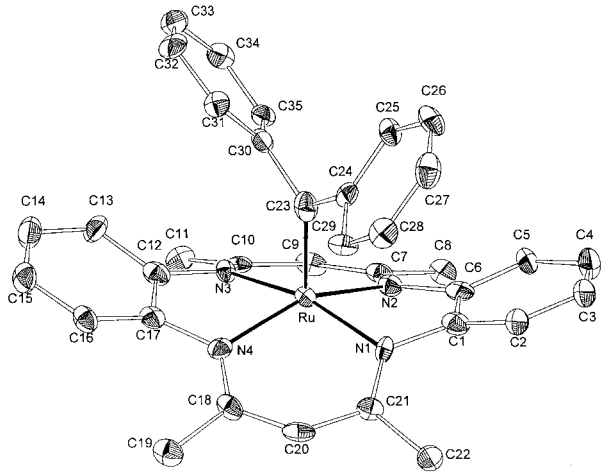

Figure 1. ORTEP drawing of **2** (thermal ellipsoids at 50% probability). Selected bond lengths [Å]: Ru–C23, 1.874(3); Ru–N1, 2.044(6); Ru–N2, 2.024(6); Ru–N3, 2.034(6); Ru–N4, 2.028(7). Bond angles [°]: Ru-C23-C24, 122.5(5); Ru-C23-C30, 122.3(5); C24-C23-C30, 116.4(6).

whether the oxidation state of Ru in **2** is II or IV can be reasonably answered by considering the Ru distance from the N$_4$ plane.[10] The value found in the present case [0.347(3) Å)] is expected for a low-spin diamagnetic d^6 center [compare with 0.216(5) Å in [Ru(tmtaa)(CO)(thf)] (**8**)].[7, 11] A much longer distance would be expected for a d^4 configuration. The tmtaa ligand has the usual saddle-shaped conformation.[5]

The carbene derivatives **2**–**4** are remarkably stable. However, when THF solutions of **2**–**4** are treated with carbon monoxide (1 atm), depending on the substituents at the carbene carbon, three different reaction pathways are observed. In the case of **2** we isolated **5**, which corresponds to the first common step of the reaction with the simple coordination of carbon monoxide *trans* to the diphenylcarbene fragment. In the case of **3** and **4**, carbon monoxide labilizes the carbene causing its migration to the *meso* carbon of the macrocycle.[5f] The reaction of the resulting free radical (intermediate A in Scheme 1) depends on the substituent R′. If R′ = H, the free radical causes the enlargement of the macrocycle to form the bent *cis*-dicarbonyl derivative **6**, whose structure has been confirmed by an X-ray analysis.[11] For R′ = COOMe (**4**), the free radical intermediate **A** delocalizes the free radical center on the COOMe substituent, which then undergoes a one-electron reduction and rearranges to form a Ru–O alkoxo bond (**7**, Figure 2).[8] The transfer of the carbene carbon to C9

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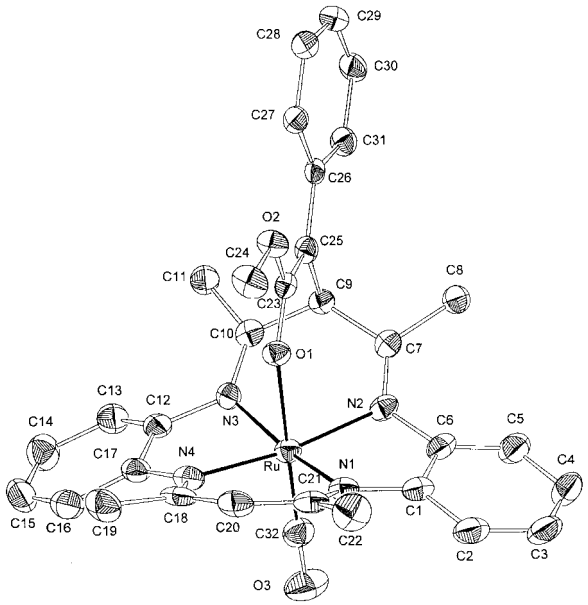

Figure 2. ORTEP drawing of **7** (thermal ellipsoids at 50% probability). Selected bond lengths [Å]: Ru–O1, 2.134(3); Ru–N1, 2.011(3); Ru–N2, 2.024(3); Ru–N3, 2.006(6); Ru–N4, 2.027(3); C7–C9, 1.518(5); C9–C10, 1.529(6); C9–C25, 1.538(5); C23–C25, 1.387(5); C23–O1, 1.260(4); C23–O2, 1.368(4).

removes the aromaticity and the planarity of the six-membered metallacycle Ru,N2,C7,C9,C10,N3; C9 is displaced 0.315(4) Å out of the N2,C7,C10,N3 plane. Consequently, C7–N2 [1.270(5) Å] and C10–N3 [1.278(5) Å] become imino groups, and the *meso*-alkylated tmtaa functions now as a monoanionic ligand. The assumption that C9 and Ru are bridged as shown in Scheme 1 is supported by a) the C23–C25 [1.390(5) Å] double bond character; b) the planarity of the bridge [torsional angle for C23-C25-C26-C27 is $-7.8(6)^\circ$]; c) some lengthening of the C23–O1 bond [1.260(4) Å], which is in agreement with a charge delocalization over the O1-C23-C25 fragment that functions as a monoanionic oxoallyl moiety.

The formation of **5**–**7**, on reaction of **2**–**4** with carbon monoxide, is extremely informative not only on the specific chemical behavior of the Ru–carbene in a macrocyclic environment, but in general on how such a functionality reacts. The Ru–carbene labilization by an incoming π acid is, in fact, the key step in the Ru–carbene assisted metathesis reaction,[4] though in the latter case the *cis*-geometrical proximity led to the reaction between the labilized carbene and the external substrate. The present investigation can serve as a model for the migration of carbene from the metal to the porphyrin in the iron systems.[2] Further applications of the present results are the use of this unconventional carbene bonded to a metal–macrocycle as a potential metathesis catalyst or as a precursor to high-valent ruthenium complexes.

Experimental Section

2: To a suspension of **1**·THF (3.77 g, 7.06 mmol) in THF (150 mL) was added a solution of diphenyldiazomethane (1.38 g, 7.10 mmol) in THF (50 mL). The mixture was stirred for 36 h, during which time it slowly became soluble with the concomitant evolution of nitrogen gas, and then concentrated to 10 mL. *n*-Hexane (30 mL) was added, and the microcrystalline material filtered off and dried in vacuo (3.55 g, 74%). Crystals suitable for X-ray analysis were grown in THF/hexane. Elemental analysis calcd for **2** ($C_{39}H_{40}N_4ORu$) (found): C 68.70 (68.78), H 5.91 (5.99), N 8.22 (8.52). ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): $\delta = 6.92-6.88$ (m, 4H, Ar); 6.73–6.69 (m, 4H, Ar); 6.45 (m, 10H, Ph); 4.91 (s, 2H, CH); 3.56 (m, 4H, THF); 2.13 (s, 12H, CH_3); 1.40 (m, 4H, THF). ^{13}C NMR (C_6D_6, 50.3 MHz, 298 K): $\delta = 291.8$ (C carbene). Crystals contain a THF molecule of crystallization.

7: An orange solution of **4** (0.58 g, 0.98 mmol) in THF (100 mL) was cooled (0°C) and then saturated with CO. The solution immediately became red and was kept overnight under CO. The solvent was removed in vacuo, and the product treated with hexane (30 mL), filtered, and the resulting solid dried in vacuo (0.39 g, 64%). Crystals suitable for X-ray analysis were grown in toluene/hexane (1/1). Elemental analysis calcd for **7** ($C_{32}H_{30}N_4O_3Ru$) (found): C 62.02 (61.50), H 4.88 (5.10), N 9.04 (8.92). IR (nujol, $\tilde{\nu} = 1905$ (s, CO), 1732 (m, COO) cm^{-1}. ^{1}H NMR ([D$_6$]benzene, 400 MHz, 298 K): $\delta = 7.87-6.51$ (m, 13H, Ar); 4.65 (s, 1H, HC=C); 4.48 (s, 1H, CH); 3.59 (s, 3H, OCH_3); 2.01 (s, 6H, CH_3); 1.88 (s, 6H, CH_3). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): $\delta = 211.9$ (CO), 164.6, 161.7, 157.2, 150.9, 145.7, 142.4, 128.8, 126.9, 125.2, 122.0, 121.0, 120.6, 120.3, 109.1, 71.4, 63.7, 50.4, 23.7, 20.2.

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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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[10] A correlation in tmtaa complexes has been established between the out of plane of the metal and its d^n configuration.[5d]

[11] C. Floriani, unpublished results.

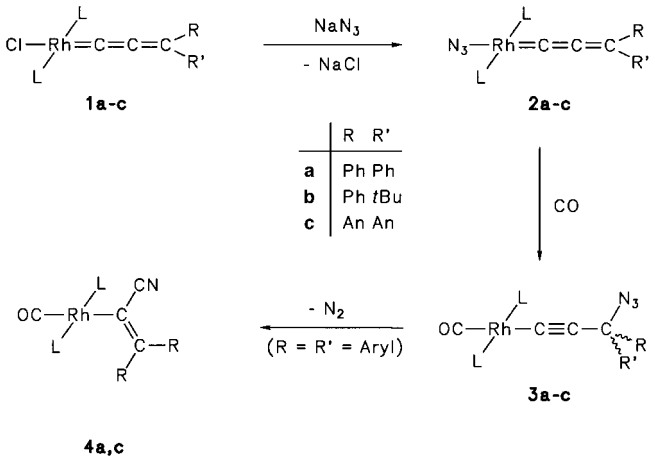
Unprecedented C–N Coupling Following Migration of an Azido Ligand to a C=C=CRR′ Unit**

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_nM=C=CRR′] and metallabutatrienes [L_nM=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;



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

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

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_6H_6): $\tilde{\nu} = 2060$ (N=N=N), 1870 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, CD_2Cl_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_6H_6): $\tilde{\nu} = 2050$ (N=N=N), 1885 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, CD_2Cl_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_6H_6): $\tilde{\nu} = 2050$ (N=N=N), 1885 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, CD_2Cl_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_6H_6): $\tilde{\nu} = 2100$ (N=N=N), 2065 (C≡C), 1945 cm^{-1} (CO); ^{13}C NMR (100.6 MHz, C_6D_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_6H_6): $\tilde{\nu} = 2145$ (C≡N), 1945 cm^{-1} (CO); ^{13}C NMR (100.6 MHz, C_6D_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_6H_6): $\tilde{\nu} = 2145$ (C≡N), 1947 cm^{-1} (CO); ^{13}C NMR (100.6 MHz, C_6D_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_6H_6): $\tilde{\nu} = 2213$ (NCO), 1892 cm^{-1} (C=C=C); ^{13}C NMR (100.6 MHz, C_6D_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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