[9] a) X-ray crystal structure analysis of $[Zn(\mathbf{1b})]\cdot C_{14}H_{10}(C_{65}H_{43}N_5Zn)$: Red block, crystal size $0.23 \times 0.14 \times 0.12$ mm, monoclinic, space group $C2/c$, $a = 25.410(5)$, $b = 13.114(4)$, $c = 28.920(6)$ Å, $\beta = 107.54(4)^\circ$, $V = 9189(4)$ Å^3, $Z = 8$, $\rho_{calc} = 1.378$ g cm^{-3}, $\mu = 0.698$ mm^{-1}, $T = 293(2)$ K; Enraf-Nonius CAD4 diffractometer; MoKα radiation ($\lambda = 0.71073$ Å), scan method ω; 5761 data measured; 5607 independent reflections, $R(\text{int}) = 0.2001$. The structure was solved by direct methods and refined by a full-matrix least-squares procedure against F^2 (all non-hydrogen atoms anisotropic), with SHELXL-97.[10] $R = 0.0643$, $wR^2 = 0.1459$ for the 1218 reflections with $F_o > 4\sigma(F_o)$, GOF = 0.867. Max./min. residual electron densities 0.323/ −0.618 e Å^{-3}. No absorption correction. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, as supplementary publication CCDC-100641. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: Int. code + (44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Well-Defined Surface-Bonded Ruthenium Complexes with Molecular Nitrogen[**]

Hans Miessner[*] and Klaus Richter

Ruthenium is considered to possess great potential in the development of new catalysts for the ammonia synthesis. Indeed, recently a number of papers have reported the adsorption and the activation of nitrogen on ruthenium catalysts.[1]

The interaction of molecular nitrogen with supported transition metal catalysts is usually weak. By IR spectroscopy it was possible to confirm the adsorption of N_2 on ruthenium catalysts only at low temperatures (123 K),[2] or on certain supports (Al_2O_3, MgO).[3] Depending on the support, the promoter, and the pretreatment, the N_2 stretching vibrations were found in a wide range between 2214 and 1910 cm^{-1}.

Some reports have also covered the formation of dinitrogen–metal complexes in zeolites. For instance, monodinitrogen complexes with Cu^I ions have been identified in mordenite[4] and in ZSM-5.[5] We recently reported on the formation of well-defined surface-bonded rhodium complexes in dealuminated Y-zeolite (DAY),[6] which are stable up to 523 K in a nitrogen stream. The compounds were identified as the bis(dinitrogen) rhodium complex $[Rh^I(N_2)_2]^+$ and the mixed carbonyldinitrogen rhodium complex $[Rh^I(CO)N_2]^+$ and are probably located on cationic sites in the zeolite. In the present paper we show that ruthenium centers in zeolites also form defined surface-bonded compounds with molecular nitrogen. The chemistry of these compounds appears to be considerably more varied than that of the rhodium complexes.

The IR difference spectra obtained from a monocarbonyl ruthenium complex bonded to the DAY zeolite after treatment with a N_2/Ar gas mixture at 523 K are shown in Figure 1.

The complex was obtained by partial decarbonylation of a dicarbonyl ruthenium complex on the DAY zeolite, in a manner similar to that for the reactive monocarbonyl rhodium complex in Rh/DAY.[6] The negative band in the difference spectra at 2036 cm^{-1} and the positive bands in the carbonyl stretching region at 2083, 2023, 2016, 1997, and 1970 cm^{-1} clearly indicate that the monocarbonyl compound (2036 cm^{-1}) is replaced by other surface-bonded carbonyls, one of which is the starting dicarbonyl ruthenium reagent (2083 and 2016 cm^{-1}). At the same time, IR bands are clearly observed in the N_2 vibrational region at 2218, 2207, and 2173 cm^{-1}.

An analysis of the integrated band intensities from several experiments between 423 and 523 K and partial nitrogen pressures of 100–500 kPa indicated a correlation between the bands at 2218 and 2023 cm^{-1} on one hand, and between those at 2207 and 2173 cm^{-1} on the other (see Figure 1). Analogous to the results obtained with the Rh/DAY system,[6] the first band pair can be attributed to a carbonyldinitrogen ruthenium complex, and the second band pair to a bis(dinitrogen) ruthenium complex. The composition and the structure of the dinitrogen complexes were verified—similar to the manner employed in the Rh/DAY system[6]—from IR spectra recorded in the presence of ^{13}CO and $^{15}N_2$, and by force-field calculations. The formation of the dinitrogen complexes is reversible; the monocarbonyl is formed once again in the presence of hydrogen or in a pure argon stream at 523 K.

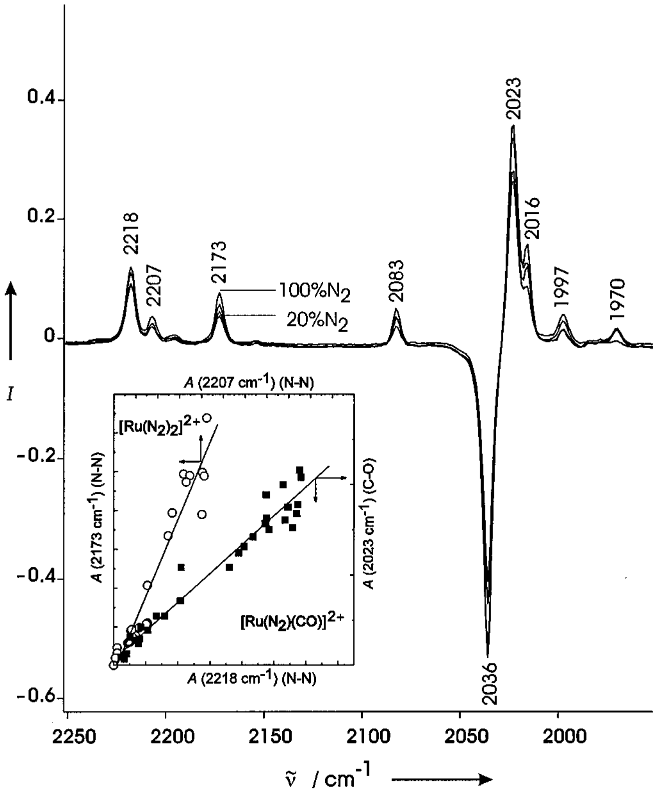

Figure 1. IR difference spectra (CO and N_2 vibration regions), recorded from the DAY-bonded monocarbonyl ruthenium complex after reaction with N_2/Ar at 523 K. The insert shows the correlation between the integrated intensities of the N_2 vibrations at 2207 and 2173 cm^{-1} (correlation coefficient $R^2 = 0.934$, $N = 25$) and the N_2 vibration at 2218 cm^{-1} and the CO vibration at 2023 cm^{-1} ($R^2 = 0.957$, $N = 30$). N = number of measurement values, A = absorption (arbitrary units).

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

As is the case for the pure carbonyl complexes on Ru/DAY, the carbonyl and dinitrogen bands of the dinitrogen ruthenium complexes occur at lower wavenumbers than those of the corresponding rhodium complexes. This indicates that stronger bonds are formed between the ruthenium centers and the ligands as a result of stronger π back bonding, but also that the nitrogen molecules are more strongly activated.

In contrast to the dinitrogen rhodium complexes, the IR spectra of the ruthenium complexes change significantly at low temperatures. Below 400 K new bands are observed at 2257, 2239, 2231, and 2205 cm^{-1}. The intensities of these bands increase at the expense of the bands at 2218, 2207, and 2173 cm^{-1}. The band at 2257 cm^{-1} correlates with a new carbonyl band at 2039 cm^{-1}, and studies performed with ^{13}CO and $^{15}N_2$ confirm the formation of a further monocarbonyldinitrogen compound. The structure of the complex evidently changes with temperature, due to, for example, differences in the bonding to the zeolite framework.

An additional significant difference to the rhodium system may also be related to the higher stability of the ruthenium–nitrogen bond. The dinitrogen rhodium complexes are very sensitive to traces of CO in the gas stream and are irreversibly transformed into the stable dicarbonyl rhodium compounds.[6] In contrast, the dinitrogen ruthenium complexes react with CO in the gas phase at temperatures below 350 K to form a further stable dinitrogen compound with an intense N_2 vibration band at 2231 cm^{-1}. Figure 2 shows the changes in the IR spectra in the regions of the N_2 and CO vibrations. In addition to a broad band at approximately 2130 cm^{-1} from physisorbed CO and carbonyl bands at 2152, 2081, and 2049 cm^{-1}, which may be attributed to a tricarbonyl ruthenium complex, there is an intense band at 2061 cm^{-1} and a weak band at 2129 cm^{-1}. The intensities of these bands change with that of the N_2 band at 2231 cm^{-1}, and we assigned them to a *trans*-dicarbonyldinitrogen ruthenium complex. A ligand exchange reaction with $^{15}N_2$ and ^{13}CO confirmed this assignment.

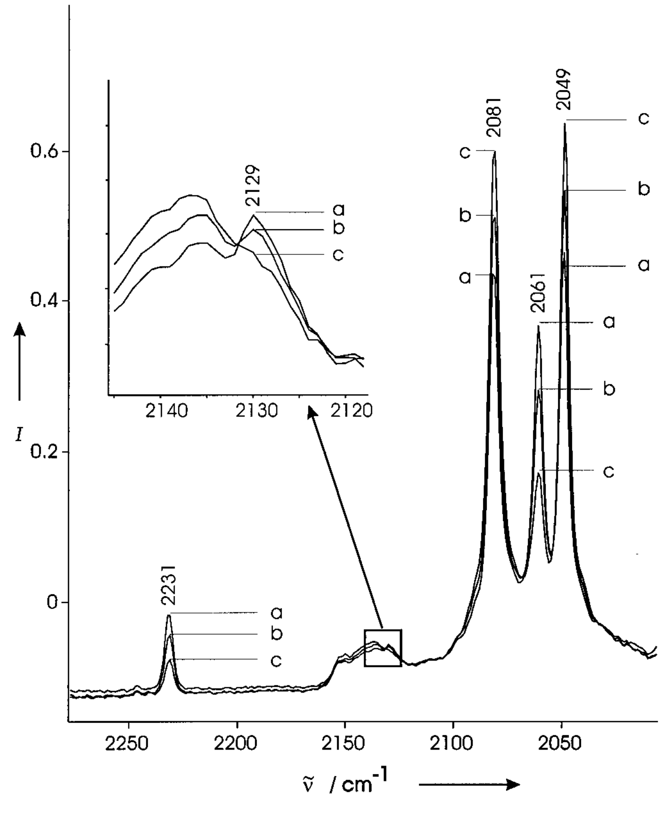

Figure 2. IR spectra in the CO and N_2 vibration regions in the presence of CO in the gas stream (5% CO/Ar:N_2 = 1:1) at 323 K (a), 343 K (b), and 363 K (c).

Table 1 provides an overview of the dinitrogen ruthenium complexes identified on the dealuminated DAY zeolite. As far as is presently known, the chemistry of molecular nitrogen and ruthenium compounds in dealuminated zeolites is considerably more diverse than that of rhodium compounds. Particularly remarkable is the higher bond strength of the molecular nitrogen to the ruthenium complexes compared to the rhodium complexes, and the associated weakening of the N≡N bond. Additional studies are required in order to show whether the nitrogen molecule can thus be sufficiently activated for further reactions such as, for example, protonation—the first step in a possible ammonia synthesis.

Table 1. N–N and C–O vibrational frequencies of the dinitrogen ruthenium complexes of the Ru/DAY system.

Species	T[K]	$\tilde{\nu}$[cm^{-1}]	
		(N_2)	(CO)
$[Ru^{II}(N_2)(CO)]^{2+}$	523	2218	2023
$[Ru^{II}(N_2)_2]^{2+}$	523	2207	
		2173	
$[Ru^{II}(N_2)(CO)]^{2+}$	323	2257	2039
$[Ru^{II}(N_2)(CO)_2]^{2+}$	323	2231	2129
			2061

Experimental Section

The DAY support used (Degussa, Germany) is a dealuminated Y zeolite with a Si:Al ratio ≥ 100:1. The sample Ru/DAY (1 wt.% Ru) was prepared by impregnation of the support with the necessary amount of $RuCl_3$ in ethanolic solution and then dried in air at 353 K. The remaining pretreatment was carried out in the IR cell and involved a carbonylation in a CO/Ar stream (5% CO) at 523 K and a partial decarbonylation in a H_2 stream at 523 K.

In order to study the effect of the residual chlorine still present after this treatment, a control experiment was carried out with $Ru_3(CO)_{12}$ as the ruthenium source. Identical results were obtained with the dinitrogen ruthenium complexes obtained this way.

The IR transmission studies were carried out with pressed samples made from the pure substance (self-supported wafers) in a special steel cell in which in situ measurements up to 673 K and 5000 kPa are possible. The small dead volume coupled with a suitable gas supply and mass flow-rate controllers (MKS) allowed rapid changes in gas composition. The high purity gases used (AGA Gas GmbH) were additionally purified with OXYSORB (Messer Griesheim GmbH). ^{13}CO (99%; Linde AG) and $^{15}N_2$ (98%; Chemotrade) were used for the isotope exchange reactions.

The IR spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrometer at a resolution of 2 cm^{-1}.

Received August 1, 1997 [Z10765]
German version: *Angew. Chem.* **1998**, *110*, 125–127

Keywords: dinitrogen complexes · nitrogen fixation · surface chemistry · ruthenium · zeolites

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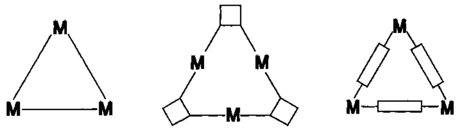
Molecular Triangle from enPt^{II} and 2,2′-Bipyrazine[**]

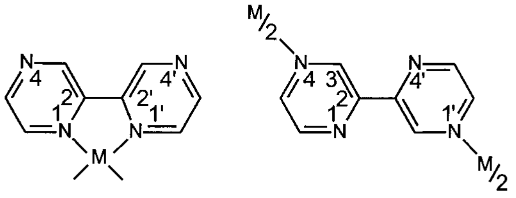
Ralf-Dieter Schnebeck, Lucio Randaccio,* Ennio Zangrando, and Bernhard Lippert*

Cyclic trimetallic complexes with metal–metal bonds[1] or bridging ligands[2,3] are known in large numbers (Scheme 1), but examples containing bridging heterocycles arranged approximately perpendicular to the metal triangle are relatively rare.[3] Here we report on a trinuclear Pt^{II} complex containing 2,2′-bipyrazine ligands (bpz) which fulfills the latter requirement and forms spontaneously in a self-assembly process. The compound is of interest with respect to the formation and stability of "molecular squares"[4] from 4,4′-bipyridine ligands and rectangular, square-planar metal units. However, the impression that combining these building blocks always leads to squares and rectangles is misleading. As first indicated by Fujita and co-workers,[5] *cis*-Pd^{II}en (en = ethylenediamine) can be used with 4,4′-bipy to form both molecular squares and triangles or both in a concentration-dependent equilibrium.



Scheme 1.

As demonstrated here, the heterocyclic ligand 2,2′-bipyrazine reacts with square-planar enM^{II} units (M = Pd or Pt) either with chelate or bridge formation (Scheme 2). In the first case bpz is practically coplanar with the coordination plane of M, whereas in the second case, following cyclization to the trinuclear complex, it is virtually perpendicular to the metal triangle. Compound **1** forms in 40% yield upon reaction of [(en)Pd$(H_2O)_2$]$(NO_3)_2$ with bpz[6] and recrystallization of the crude product from water in the presence of $NaClO_4$. Figure 1 depicts the cation of **1**. The results of the X-ray structure determination[7–9] reveal that the N(1)-Pd-N(1′) angle of 80.7(1)° deviates markedly from 90° and is in the range found for related complexes containing 2,2′-bipyridine[10] or *o*-phenanthroline.[11] In the case of a Ru^{II} compound containing a chelating bpz ligand, this value is 78.92(6)°.[12] The geometry of the Pd(en) unit is normal.[13] Attempts to use cation **1** as a corner stone in the preparation of a molecular square in the true sense[14]—that is, cyclization through the 4 and 4′ positions via linear metal units—have been unsuccessful as yet. We assume that the low basicity[15] of these positions rather than the nonideal N(4)-Pd-N(4′) angle



Scheme 2.

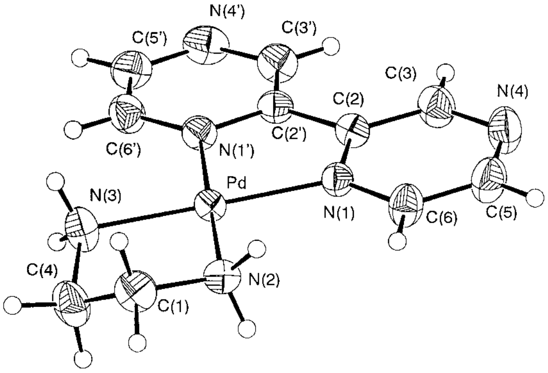


Figure 1. Structure of cation of **1**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 2.034(3), Pd–N(1′) 2.025(3), Pd–N(2) 2.026(3), Pd–N(3) 2.023(3); N(1)-Pd-N(1′) 80.7(1), N(1)-Pd-N(2) 98.8(1), N(1)-Pd-N(3) 178.2(1), N(1′)-Pd-N(2) 179.4(1), N(1′)-Pd-N(3) 97.6(1), N(2)-Pd-N(3) 83.0(1), N(4)-Pd-N(4′) 73.0(1).

[(en)Pd(bpz)]$(ClO_4)_2$ **1**

[(en)Pt(bpz)]$(NO_3)_2$ **1′**

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[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and MURST, Rome. It was part of a COST D1 project. en = ethylenediamine