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# Controlling the Structure of Supramolecular Porphyrin Arrays**

Anthony K. Burrell,* David L. Officer,*
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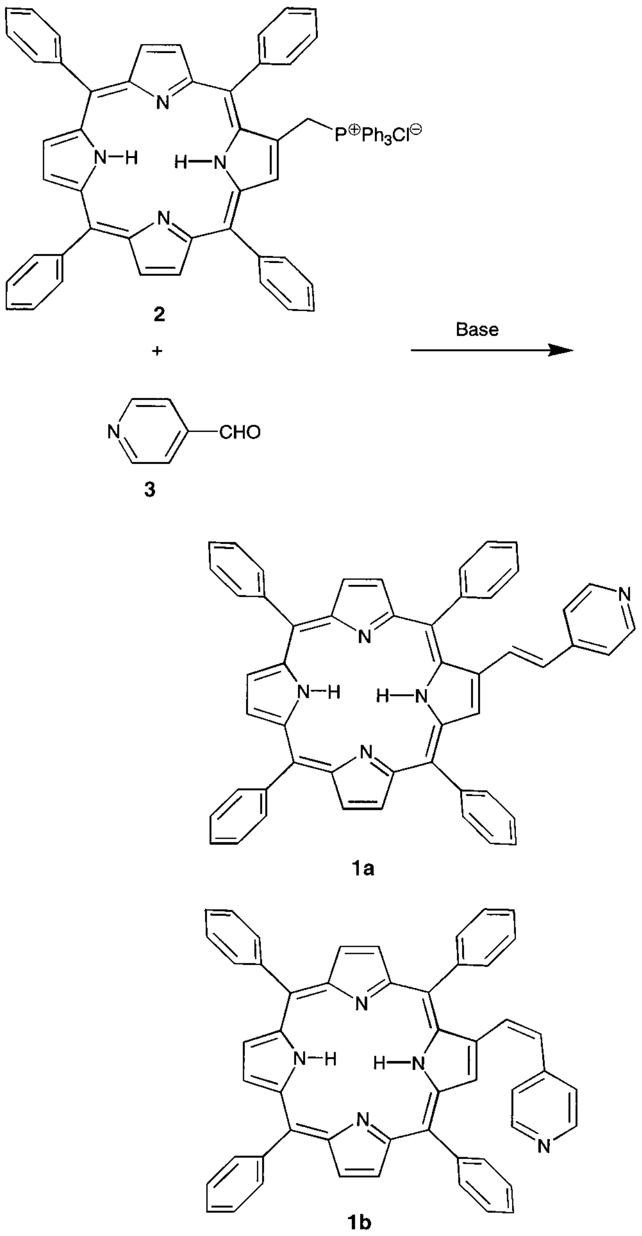
The importance of multichlorin assemblies in photosynthetic reaction centers and light-harvesting antenna complexes has inspired considerable interest in the synthesis of porphyrin arrays. Several synthetic strategies are employed for the assembly of multiporphyrin systems. A wide variety of porphyrin arrays of ever-increasing size have been constructed by the traditional methodology of covalently linking porphyrins.[1] More recently the incorporation of porphyrins into supramolecular assemblies has proven to be an attractive method for array formation. With careful choice of materials, the supramolecular structure of the array can be engineered. However, there is currently no porphyrin array system that can be "switched" from one ordered assembly to another. Here we report the first porphyrin system where the structure of the supramolecular assembly can be altered by a non-invasive technique such as photolysis.

With some notable exceptions,[2] the majority of the self-assembling porphyrin arrays are based upon metal–ligand interactions.[3] To a large extent this work has concentrated upon the coordination chemistry of *meso*-pyridyl porphyrins. Porphyrin assemblies prepared from *meso*-pyridyl porphyrins range from dimeric through to polymeric complexes.[3] Of particular interest are the ordered structures formed by a single component interacting with itself. The most common motif in this area is the use of pyridyl-functionalized metalloporphyrins; for example, the metal center of a zinc porphyrin will readily coordinate another ligand, such as pyridine. If the zinc porphyrin is also functionalized by a pyridine, the possibility for zinc–pyridine (inter-[4] or intramolecular[5]) interactions exist. The orientation of the pyridine functionality on the porphyrin macrocycle has a profound influence on the resulting superstructure, providing either dimeric[4f, 6] or oligomeric and polymeric[3j–l, 4] compounds. We have recently become interested in the formation of porphyrin arrays using coordination chemistry as a construction technique and the possibility that simple geometric changes, such as *cis/trans* alkene isomerization, would provide a method to control array superstructure.

As an introduction to this area we prepared the β-vinylpyridine functionalized porphyrin **1**. This compound can be obtained in 82% yield from the reaction of **2**[7] with 4-pyridinecarboxaldehyde (**3;** Scheme 1). The product isolated is an isomeric mixture of *trans* **1a** (62%) and *cis* **1b** (20%) that can be separated by careful chromatography. The $^1$H NMR spectra for both **1a** and **1b** are consistent with the structures reported. As expected **1a** is the more favored isomer, and solutions of **1b** convert into **1a** when heated in chloroform or if left exposed to light. Based on the X-ray



Scheme 1. Synthesis of **1a** and **1b**.

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structure of a related compound,[1a] the porphyrin core, the olefin, and the pyridine ring of **1a** are presumed to be essentially planar, whereas simple molecular models indicate that it is not possible for the *cis* isomer **1b** to adopt a planar conformation. The effect the geometry of the alkene has on the reactivity of these porphyrins is most apparent when they are treated with $Zn^{II}$.

The reaction of **1a** with $Zn(OAc)_2$ results in the rapid insertion of $Zn^{II}$ into the porphyrin core. Thin layer chromatography (TLC) of [Zn(**1a**)] did not yield a single spot as normally observed for metalloporphyrins. Instead [Zn(**1a**)] smears over a large portion of the TLC plate with almost every common eluent. The $^1H$ NMR spectrum of [Zn(**1a**)] is significantly changed from the spectrum observed for **1a**. The resonances of the pyridyl hydrogen atoms have shifted from $\delta = 7.11$ and 8.55 to 5.20 and 2.37, respectively, which is consistent with the coordination of the pyridine to a zinc porphyrin.[4] As it is not possible for this coordination to occur in an intramolecular fashion, the coordination must be intermolecular. This was confirmed by a single crystal X-ray analysis. The structure of [Zn(**1a**)] (Figure 1) consists of an infinite chain of porphyrins.[8] The pyridine is tilted 30.2(4)° from the plane of the zinc porphyrin core. The nitrogen atom of each pyridine group is coordinated, as an axial ligand, to the zinc in an adjacent molecule, resulting in an infinite solid-state polymer. The axial pyridine is not completely orthogonal to the plane of the zinc porphyrin, but tilted at 64.6(6)°. In the solid state, a second structural feature is also present. Each of the porphyrin chains is stacked on another at an average porphyrin–porphyrin distance of 3.8 Å, to give sheets of corrugated chains.

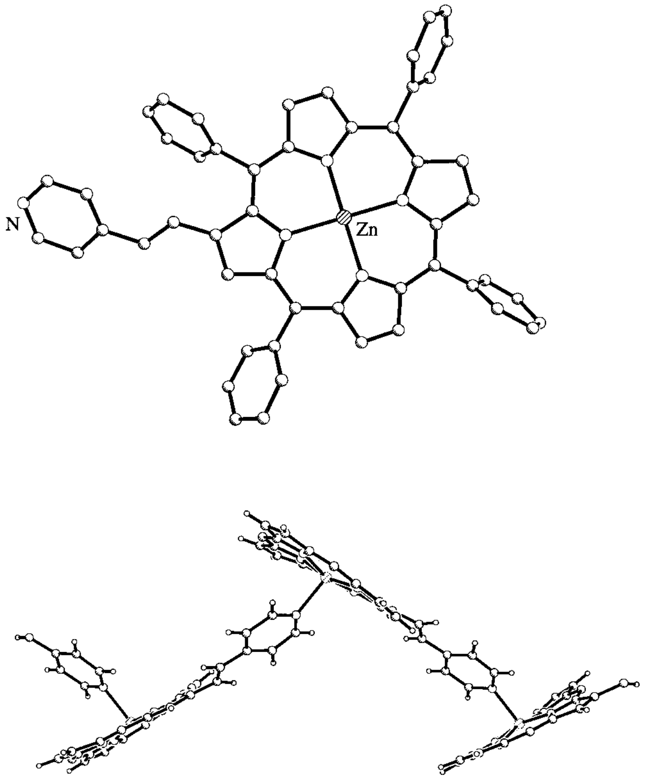


Figure 1. Molecular structure of a single molecule of [Zn(**1a**)] (top) and a section of the chain-like structure (bottom). The phenyl rings have been omitted from the second view for clarity.

The reaction of **1b** with $Zn(OAc)_2$ also results in the insertion of $Zn^{II}$ into the macrocycle, but the nature of [Zn(**1b**)] is completely different from that of [Zn(**1a**)]. [Zn(**1b**)] runs as a single spot on TLC and is significantly less polar than either **1b** or [Zn(**1a**)]. The $^1H$ NMR spectrum indicates that the pyridine group is coordinated to a porphyrin-bound zinc[4] as the pyridyl protons have shifted from $\delta = 7.07$ and 8.24 in **1b** to 5.18 and 2.06, respectively, in [Zn(**1b**)]. Once again these large chemical shift changes can only be explained by the coordination of the pyridine moiety to the zinc center in a porphyrin core. Fast atom bombardment (FAB) mass spectrometry provided a molecular ion peak corresponding to the dimeric complex [{Zn(**1b**)}$_2$]. X-ray diffraction grade crystals were difficult to obtain, but crystallizations that included small amounts of anthracene resulted in crystals suitable for analysis. The complex [{Zn(**1b**)}$_2$] crystallizes in the space group $C2/c$[9] and the structure, shown in Figure 2, clearly illustrates the dimeric nature. Each pyridine is coordinated to the zinc of the other porphyrin. The two porphyrin planes are tilted with respect to each other by 32(1)°. Presumably this distortion is to accommodate the geometrical requirements of the *cis* alkene linkage.

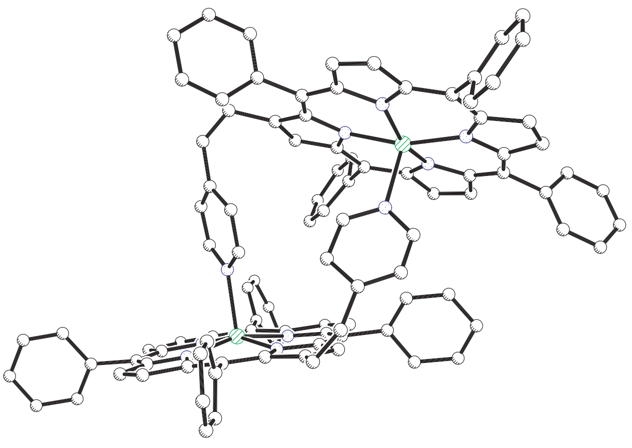
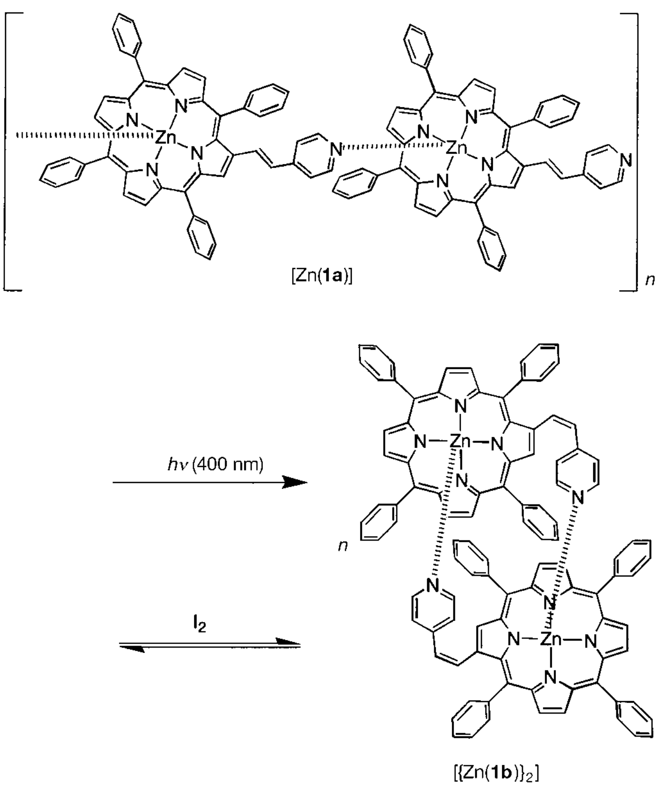


Figure 2. Molecular structure of [{Zn(**1b**)}$_2$].

The chelation-like binding of the [{Zn(**1b**)}$_2$] complex appears to result in a very stable complex, which is apparent from the strong molecular ion peak in the FAB mass spectrum. There is no evidence to indicate the presence of monomers. In contrast, the polymeric [Zn(**1a**)] appears to be quite dynamic in solution giving rise to an oligomeric mixture. The stability of the [{Zn(**1b**)}$_2$] complex can be further demonstrated by the conversion of [Zn(**1a**)] (*trans*) into [{Zn(**1b**)}$_2$] (*cis*) by irradiation with UV light, (Scheme 2). Other methods of isomerization have variable success. Thus, a mixture containing [Zn(**1a**)] and [{Zn(**1b**)}$_2$] can be generated by treating pure solutions of either [Zn(**1a**)] or [{Zn(**1b**)}$_2$] with iodine.

The alkene linkage in compounds **1a** and **1b** allows us to exert a control over the supramolecular structure of their derivatives. This is achieved by either beginning with the



Scheme 2. Conversion of [Zn(**1a**)] into [{Zn(**1b**)}$_2$].

appropriate *cis* or *trans* alkene as in traditional supramolecular chemistry or, more significantly, by converting the alkene, in the supramolecular complex, from *trans* to *cis* (or vice versa) and effectively switching from one supramolecular array to another. With this methodology it should be possible to control the molecular architecture of these supramolecular structures and thereby switch properties on or off as desired.

## *Experimental Section*

**1a** and **1b**: A solution of **2** (135 mg, 0.146 mmol) and **3** (16 µL, 0.168 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature before 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (67 µL, 0.448 mmol) was added. After 15 min, the reaction mixture was subjected to chromatography (silica, $CH_2Cl_2$/ethyl acetate 19/1) to give a *cis/trans* mixture (about 1:3 by $^1$H NMR) of products. A second careful separation on a flash column with the same eluent gave two major fractions. The first fraction can be recrystallized from $CH_2Cl_2$/methanol to give **1b** as a purple solid (21 mg, 20%): $^1$H NMR (270 MHz, $CDCl_3$): $\delta = -2.70$ (br s, 2H; NH), 6.23 and 6.67 (2 d, both 1H, $^3J = 12.1$ Hz; $H_{alkene}$), 7.07 (d, 2H, $^3J = 5.8$ Hz; $H_{pyridyl}$), 7.58–7.82 (m, 12H; $H_{m,pPh}$), 8.09 (d, 2H, $^3J = 7.5$ Hz; $H_{oPh}$), 8.16 (d, 2H, $^3J = 7.5$ Hz; $H_{oPh}$), 8.21–8.27 (m, 6H; $H_{oPh}$, $H_{pyridyl}$), 8.47 (s, 1H; $H_{pyrrole}$), 8.77–8.85 (m, 6H; $H_{pyrrole}$); UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 428$, 523, 563, 600, 657 nm. The second fraction contains **1a**, which is obtained as a purple solid after recrystallization from $CH_2Cl_2$/methanol (65 mg, 62%): $^1$H NMR (270 MHz, $CDCl_3$): $\delta = -2.59$ (br s, 2H; NH), 7.11 (d, 2H, $^3J = 6.1$ Hz; $H_{pyridyl}$), 7.19 (s, 2H, $H_{alkene}$), 7.74–7.85 (m, 12H; $H_{m,pPh}$), 8.19–8.28 (m, 8H; $H_{oPh}$), 8.55 (d, 2H, $^3J = 6.1$ Hz; $H_{pyridyl}$), 8.74–8.85 (m, 6H; $H_{pyrrole}$), 9.02 (s, 1H; $H_{pyrrole}$); UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 428$, 523, 563, 600, 657 nm. HR-MS calcd for $C_{51}H_{36}N_5$ ($MH^+$): 718.2971; found: 718.2947.

[Zn(**1a**)]: $^1$H NMR (270 MHz, $CDCl_3$): $\delta = 2.37$ (br s, 2H; $H_{pyridyl}$), 5.20 (br s, 2H; $H_{pyridyl}$), 6.09 and 6.31 (2 d, both 1H, $^3J = 16.1$ Hz; $H_{alkene}$), 7.21–7.27 (m, 3H; $H_{m,pPh}$), 7.68–7.79 (m, 11H; $H_{o,m,pPh}$), 8.08–8.24 (m, 6H; $H_{oPh}$), 8.57–8.60 (m, 2H; $H_{pyrrole}$), 8.79–8.83 (m, 5H; $H_{pyrrole}$); UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 433$, 558, 563, 621, 758 nm; HR-MS: calcd for $C_{51}H_{34}N_5{}^{64}Zn$ ($M+H)^+$: 780.2106; found: 780.2095 (monomeric fragment).

[{Zn(**1b**)}$_2$]: $^1$H NMR (270 MHz, $CDCl_3$): $\delta = 2.06$ (d, 2H, $^3J = 6.1$ Hz; $H_{pyridyl}$), 5.18 (d, 2H, $^3J = 6.1$ Hz; $H_{pyridyl}$), 5.28 and 6.28 (2 d, both 1H, $^3J = 11.8$ Hz; $H_{alkene}$), 7.31–7.43 (m, 6H; $H_{m,pPh}$), 7.71–7.93 (m, 10H; $H_{o,m,pPh}$), 8.10–8.36 (m, 4H; $H_{oPh}$), 8.44 (d, 1H; $^3J = 4.6$ Hz; $H_{pyrrole}$), 8.67–8.81 (m, 2H; $H_{pyrrole}$), 8.94 and 8.99 (m(AB), 4H, $^3J = 4.6$ Hz; $H_{pyrrole}$); UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 429$, 527, 564, 603 nm. HR-MS calcd for $C_{102}H_{70}N_{10}{}^{64}Zn_2$ ($M+4H)^+$: 1562.4368; found: 1562.4329.

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**Keywords:** isomerizations • porphyrin array • porphyrinoids • supramolecular chemistry • zinc

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[8] X-ray crystal structure analysis of [Zn(**1a**)]·2MeOH·$H_2O$ $C_{53}H_{43}N_5O_3Zn$: Red block, crystal size 0.23 × 0.3 × 0.25 mm, monoclinic, space group *C*2/*c*, $a = 28.063(6)$, $b = 18.737(4)$, $c = 19.028(4)$ Å, $\beta = 118.65(3)°$, $V = 8780(3)$ Å$^3$, $Z = 8$, $\rho_{calc} = 1.305$ g cm$^{-3}$, $\mu = 0.610$ mm$^{-1}$, $T = 293(2)$ K; Enraf-Nonius CAD4 diffractometer; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), scan method $\omega$; 4191 data measured; 4083 independent reflections, $R$(int) = 0.0277. 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] $R = 0.0626$, $wR^2 = 0.1736$ for the 1942 reflections with $F_o > 4\sigma(F_o)$, GOF = 0.962. Max./min. residual electron densities 0.948/−0.282 e Å$^{-3}$. No absorption correction. See also [9b].

[9] a) X-ray crystal structure analysis of [Zn(**1b**)] $\cdot C_{14}H_{10}(C_{65}H_{43}N_5Zn)$: Red block, crystal size 0.23 × 0.14 × 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; MoK$\alpha$ radiation ($\lambda = 0.71073$ Å), scan method $\omega$; 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.

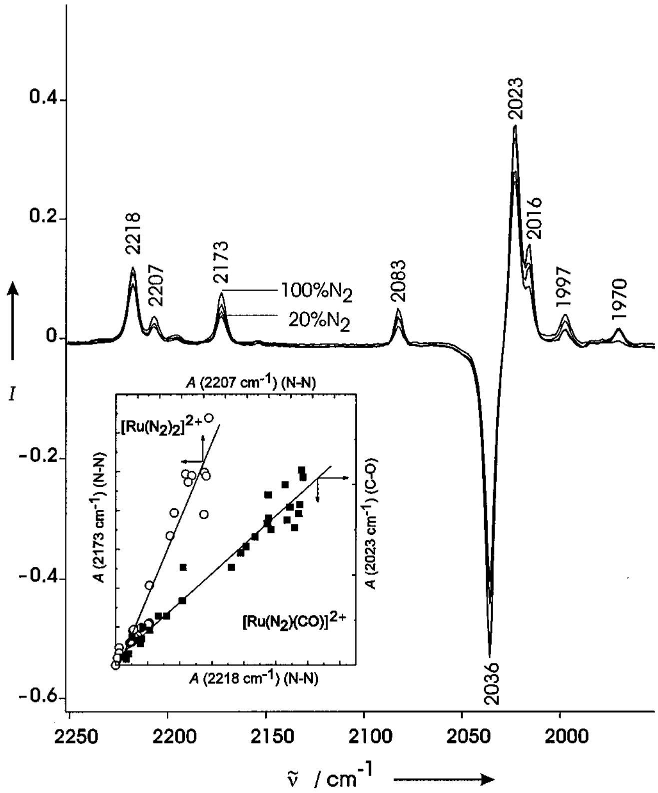

Figure 1. IR difference spectra (CO and $N_2$ vibration regions), recorded from the DAY-bonded monocarbonyl ruthenium complex after reaction with $N_2$/Ar at 523 K. The insert shows the correlation between the integrated intensities of the $N_2$ vibrations at 2207 and 2173 cm$^{-1}$ (correlation coefficient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