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**Supporting information for article:**

# Photocrystallography and IR-spectroscopy of light-induced linkage NO isomers in [RuBr(NO)2(PCyp3)2]BF4

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## S1. Structural data

Single crystal diffraction data have been collected at 10K in the ground state (GS) and in the photo-irradiated state after irradiation of the sample with a diode laser at 405nm (P=70mW) during 45min in the dark, until the photo-stationary state is reached.

### S1.1. Ground state structural refinement

Diffraction data were first collected at 10K in the ground state (GS). The corresponding structure was solved in the P-1 space group by direct methods with the SHELXS97 program and refined on $F^2$ by weighted full matrix least-squares methods using the SHELXL97 program. All non-hydrogen atoms were refined anisotropically ; hydrogen atoms were located in difference Fourier maps and treated using a riding model, constraining the isotropic displacement parameters to be 1.2 times those of the attached C atom. The refinement converged to agreement factors of R1=0.0527 and wR2=0.1084. The corresponding ORTEP plot is given in figure 1 of the manuscript.

### S1.2. Photo-irradiated state structural refinement

Based on infra-red spectroscopy measurements, the photo-irradiation conditions should lead to a sufficient conversion ratio. Photo-difference maps (Fig. 3) and Fobs Fourier electron density map (Fig. S1) reveal pronounced structural reorganisation around the N2-O2 nitrosyl ligand, with clear indications for the presence of only two molecular species GS and PLI. In their neutron diffraction studies of the MS1 and MS2 metastable states of sodium nitroprusside, Schaniel and coworkers measured the transmitted light intensity through the single crystal sample to fix *a priori* the population of metastable state during their structural refinements (Schaniel et al., 2005; Schaniel et al., 2006). In the present work, the population of PLI could not be determined precisely in the diffraction experimental conditions through the measurement of the transmitted light; the respective population of GS ($P_{GS}$) and PLI ($P_{PLI}$) are thus necessary parameters of the structural refinement (with the constraint $P_{GS} + P_{PLI} = 1$).

The photo-Wilson plot $\ln(I_{GS+PLI}/I_{GS})=K-2\Delta B*(\sin(\theta)/\lambda)^2$ has been calculated (Fig. S2). $I_{GS}$ and $I_{GS+PLI}$ are the Bragg intensities of the GS and photo-irradiated state respectively, normalized to a common scale, and $\Delta B$ is the GS to photo-irradiated state difference in average atomic displacement parameters. The obtained positive value of the fitted $\Delta B=0.038 Å^2$ indicates a systematic increase in atomic displacement parameters in the photo-irradiated structure, resulting from increased thermal vibration effects, or overall disorder generated by the light irradiation. It is unlikely that the increase in $\Delta B$ results from an increase in temperature of the sample, as is often the case for time-resolved photo-crystallographic experiments (Schmokel et al., 2010; Vorontsov et al., 2005), since our diffraction data collection was not performed with a permanent laser irradiation.

In order to identify the bonding mode (nitrosyl, isonitrosyl or side bonded) of the two nistrosyl groups in the PLI state, several refinement strategies corresponding to different structural models were applied.

### S1.3. Average + 2 nitrosyl N2-O2 model

In a first step, two initial configurations were introduced for the N2-O2 nitrosyl group based on the positions of the diffraction peaks in the calculated photo-difference map (Fig. 3), one corresponding to the GS molecular species with Ru-N2A-O2A nitrosyl configuration, the other one corresponding to the PLI species, assuming a Ru-N2B-O2B nitrosyl configuration. The initial positions for N2B and O2B were defined according to the two largest peaks in the photo-difference map, and corresponding to an MS2 side-bonded state. The other atoms of the molecule were freely refined anisotropically; their position corresponds therefore to the average position between the GS and PLI, weighted by the respective populations $P_{GS}$ and $P_{PLI}$. The N1-O1 group was considered in the nitrosyl configuration for this model. The two N2-O2 groups were refined separately and isotropically using constraints such that Uiso(N2A)=Uiso(N2B) and Uiso(O2A)=Uiso(O2B). For the least-squares refinement, a random spatial distribution of the PLI species was considered with the formalism $F_{photo\text{-}irradiated}(hkl)=P_{GS}*F_{GS}(hkl)+P_{PLI}*F_{PLI}(hkl)$ with the constraint $P_{GS} + P_{PLI} = 1$ (Vorontsov *et al.*, 2005). The refined population of PLI is 0.312(3).

The resulting agreement factors R1 and wR2 are 0.0551 and 0.1107 respectively, which is only slightly worse than the refinement of the ground state crystal structure (0.0533 and 0.1084), showing the consistency of this model. The refined atomic displacement parameters are much higher for N1-O1 compared to N2-O2 as shown on the ORTEP plot (Fig. S4), and given in table S1. This is due to the fact that N1-O1 undergoes a significant displacement in the PLI state as shown by the positive and negative electron density peaks near the N1 position in the photo-difference map (Fig. 3). This split position is wrongly taken into account by the atomic displacement parameters of N1, as revealed by the excessively enlarged thermal ellipsoid in the ORTEP plot. On the contrary, the atomic displacement parameters for N2B and O2B are very reasonable (Uiso(O1B)= 0.0115(4)Å$^2$, Uiso(N1B)= 0.0089(5)Å$^2$), and close to the values obtained for the GS. The displacement is higher for the terminal O2B atom with respect to the N2B atom, which is in the correct order for a Ru-N2B-O2B libration around the heavy pivot atom Ru.

### S1.4. GS-rigid group + PLI-rigid group model

In a second model, the complete molecular structure of the ground state, corrected for the change of lattice parameters on irradiation, was introduced and refined as a rigid group (rigid group 1). The atomic displacement parameters are fixed at the GS structure values for all the atoms. For the PLI species, the Ru and Br atoms are freely refined isotropically with a Ru-N2B-O2B nitrosyl configuration. A split position is considered for N1 (N1A and N1B). The remaining atoms of the PLI molecule including N2A-O2A are treated as a rigid group (rigid group 2) using the GS structure. The atomic displacement parameters of the PLI N2B and O2B were constrained to have the same values than the refined ones of the GS N2A and O2A. The refined population of PLI is 28.1(13)%, which is close to the value obtained for the previous refinement. The agreement statistic factors for this model are R1=0.0840, and wR2=0.0786. This model is much more constrained than the previous one, the number of refined parameters is reduced drastically (from 385 to 75!). The refinement results in unrealistic negative atomic displacement parameters for both Ru (-0.00496(16)Å$^2$) and Br (-0.0015(3)Å$^2$) atoms of the PLI state (Fig. S5). The difficulty in the refinement of such a split model with two rigid groups is highlighted in figure S6, on which we can see that the GS and PLI state are located at pretty much the same position in the crystal, which prevents a good deconvolution between the two species to be reached. As a matter of fact, in the photo-difference maps, significant positive and negative electron densities are located in the region

corresponding to N2-O2, Ru, Br and N1 only; no contribution can be detected in the neighbourhood of the two phosphorus atoms, which indicates that P1 and P2 are located at roughly the same position in the GS and PLI state. This is very different from our published refinement on the related $[RuCl(NO)_2(PPh_3)_2]BF_4$ compound for which such a refinement strategy was successful. (Casaretto et al., 2015). As a conclusion, we can say that according to the present data, it may be not possible to split the atomic positions of Ru and Br, the position contrast between GS and PLI state is not enough to be resolved in our photo-crystallographic experiment.

#### S1.5. N1-O1 split nitrosyl + 2 nitrosyl N2-O2 model

Since the previous complete split model with GS and PLI rigid groups was unsuccessful, a third model was constructed with the hypothesis of two configurations of N1-O1, using the same strategy than for the first model (*Average + 2 nitrosyl N2-O2 model*). The N1-O1 group was split with a nitrosyl ground state Ru-N1A-O1A configuration with population $P_{GS}$, and a second nitrosyl Ru-N1B-O1B configuration with population $P_{PLI}$=1-$P_{GS}$.The results of the structural refinement leads to a refined population of PLI of 31.6(3)%, and agreement statistic factors of R1=0.0552, and wR2=0.1108, marginally higher than for the single nitrosyl N1-O1 configuration. This refinement leads furthermore to reasonable values for the atomic displacement parameters (Uiso(O1B)= 0.0090(4)$Å^2$, Uiso(N1B)= 0.0096(5)$Å^2$). The corresponding ORTEP plot is given in figure S7.

#### S1.6. N1-O1 isonitrosyl + 2 nitrosyl N2-O2 model

This model is very similar to the previous model, except that the PLI configuration for N1-O1 is considered as isonitrosyl Ru-O1B-N1B. The results of the structural refinement are very similar, with a refined population of PLI of 30.8(3)%, and agreement statistic factors of R1=0.0553, and wR2=0.1113. The refinement of N1-O1 as an isonitrosyl in the PLI state (Ru-O1B-N1B case), leads to atomic displacement parameters which are not reasonable with a much higher displacement for O1B which is linked to Ru than for the terminal N1B (Uiso(O1B)=0.0123(5)) $Å^2$, Uiso(N1B)=0.0066(4) $Å^2$). Accordingly, the assignment of N1-O1 in the PLI state as an isonitrosyl is most probably wrong.

#### S1.7. N1-O1 nitrosyl + N2-O2 isonitrosyl model

The fifth model considered two nitrosyl configurations for N1-O1 (as for model *N1-O1 split nitrosyl + 2 nitrosyl N2-O2 model)*, two configurations for N2-O2, the ground state Ru-N2A-O2A configuration, and the isonitrosyl Ru-O2B-N2B configuration. The refined population of PLI is 33.7(4)%, and the agreement statistic factors are R1=0.0555, and wR2=0.1120. The atomic displacement parameters for N2B and O2B are not reasonable with a much higher displacement for O2B which is linked to Ru than for the terminal N2B (Uiso(O2B)=0.0118(5)) $Å^2$, Uiso(N2B)= 0.0093(5)$Å^2$). Accordingly, the assignment of N2-O2 in the PLI state as an isonitrosyl is most probably wrong.

As a conclusion, the only structural model which is reasonable, according to the agreement statistics and atomic displacement parameters is model *N1-O1 split nitrosyl + 2 nitrosyl N2-O2.*

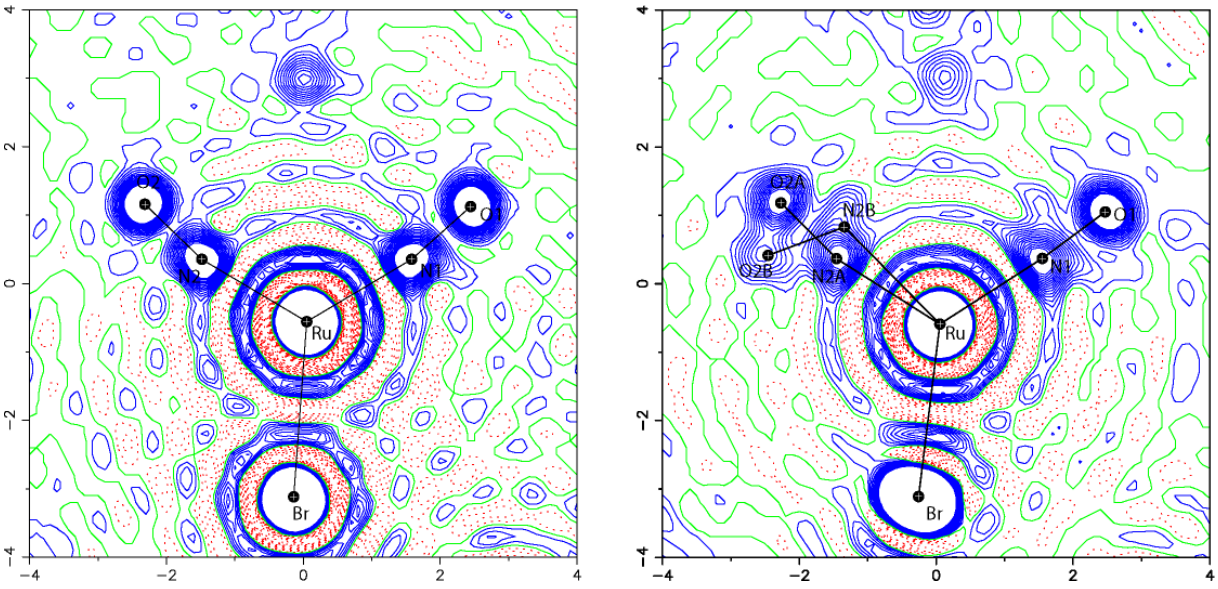


**Figure S1** Fobs Fourier electron density map calculated in the Ru-N1-N2 plane, with contours of ±1.00eÅ$^{-3}$ (red, negative; blue, positive) for the (left) ground state, and (right) PLI state.

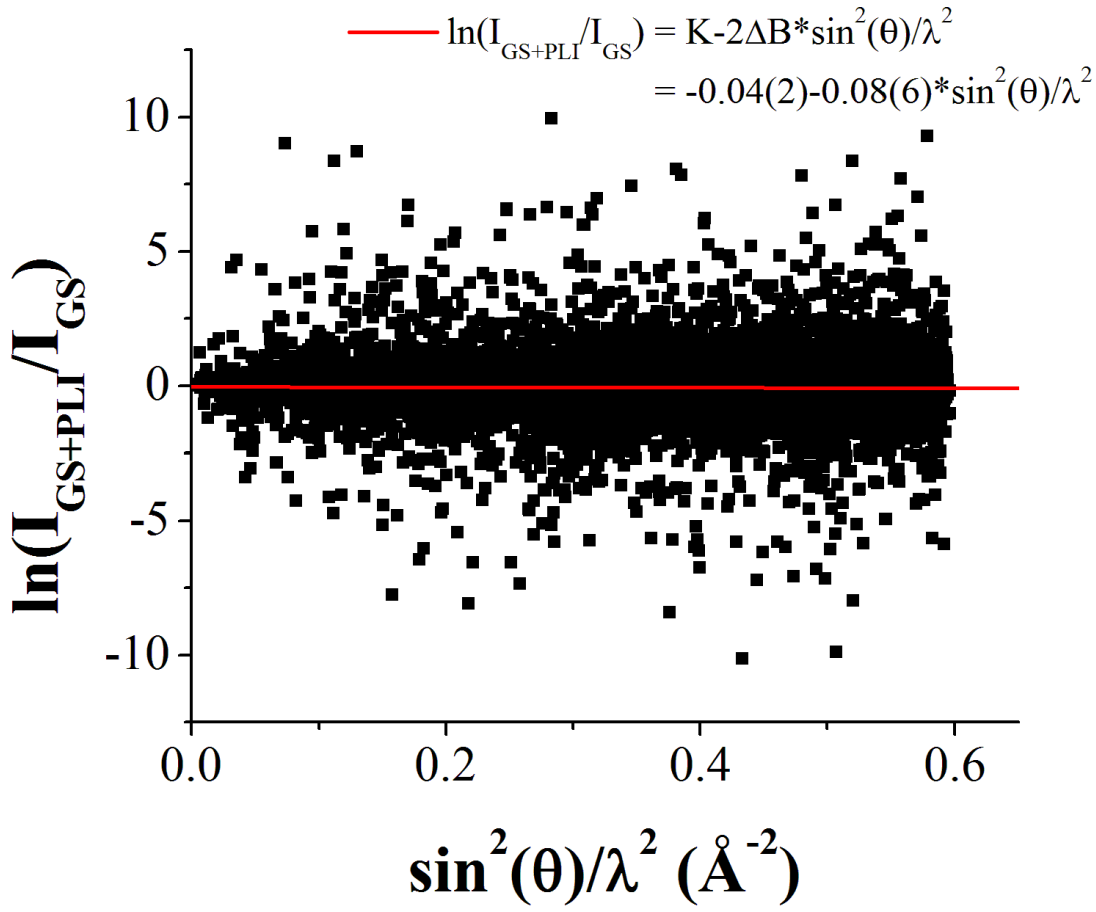


**Figure S2** Photo-Wilson plot in the form of $\ln(I_{GS+PLI}/I_{GS})$ as a function of $(\sin(\theta)/\lambda)^2$, where the Bragg intensities of the GS $I_{GS}$ and photo-irradiated state $I_{GS+PLI}$ have been normalized to a common scale using SHELXL. ΔB is the GS to photo-irradiated state difference in average atomic displacement parameters.

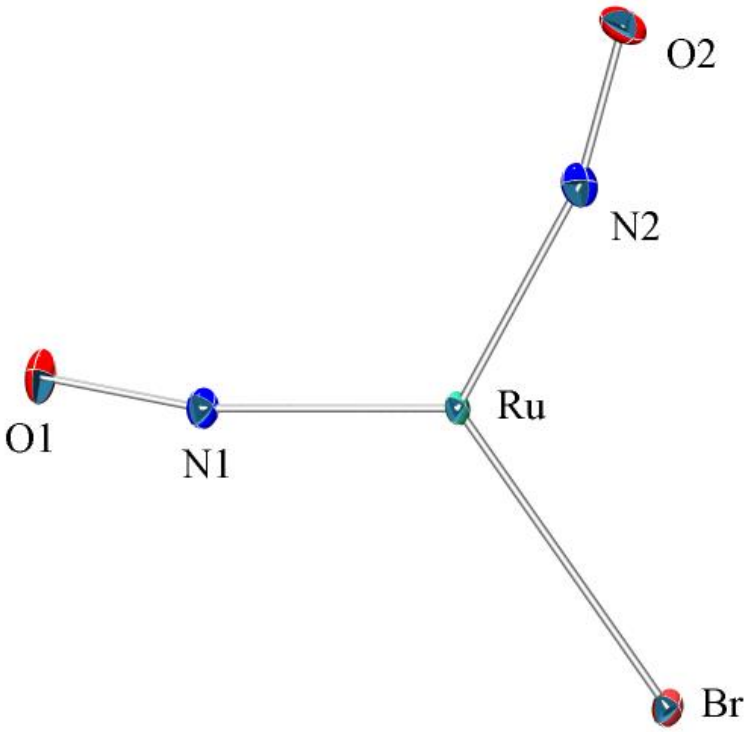


**Figure S3** ORTEP (Burnett & Johnson, 1996) view of the ground state in the Ru-N1-N2 plane. Ellipsoids are plotted at the 50% probability level.

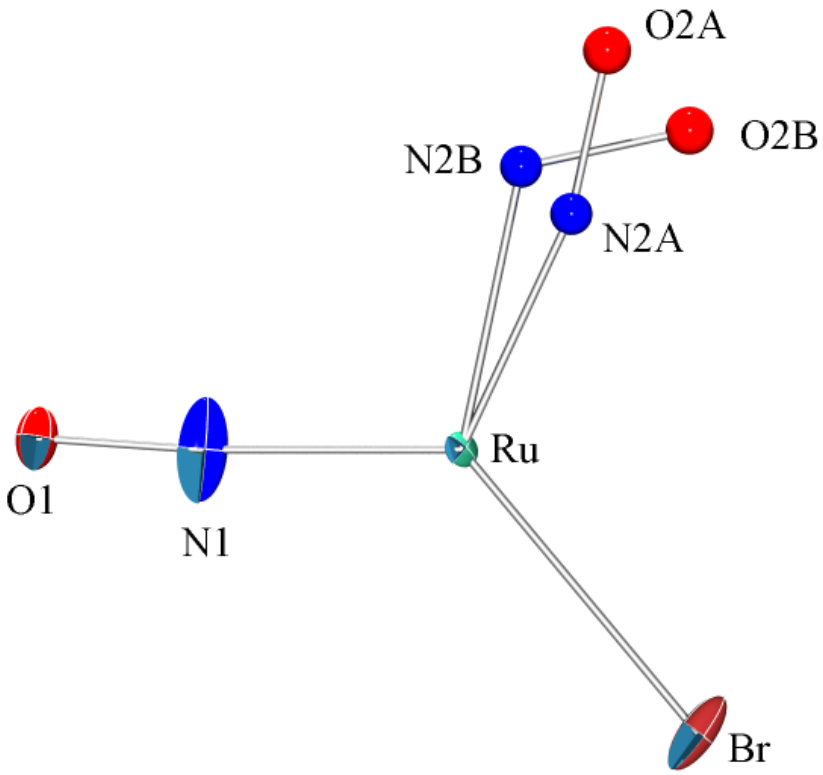


**Figure S4** ORTEP (Burnett & Johnson, 1996) view in the Ru-N1-N2 plane for the Average + 2 nitrosyl N2-O2 structural model. Ellipsoids are plotted at the 50% probability level.

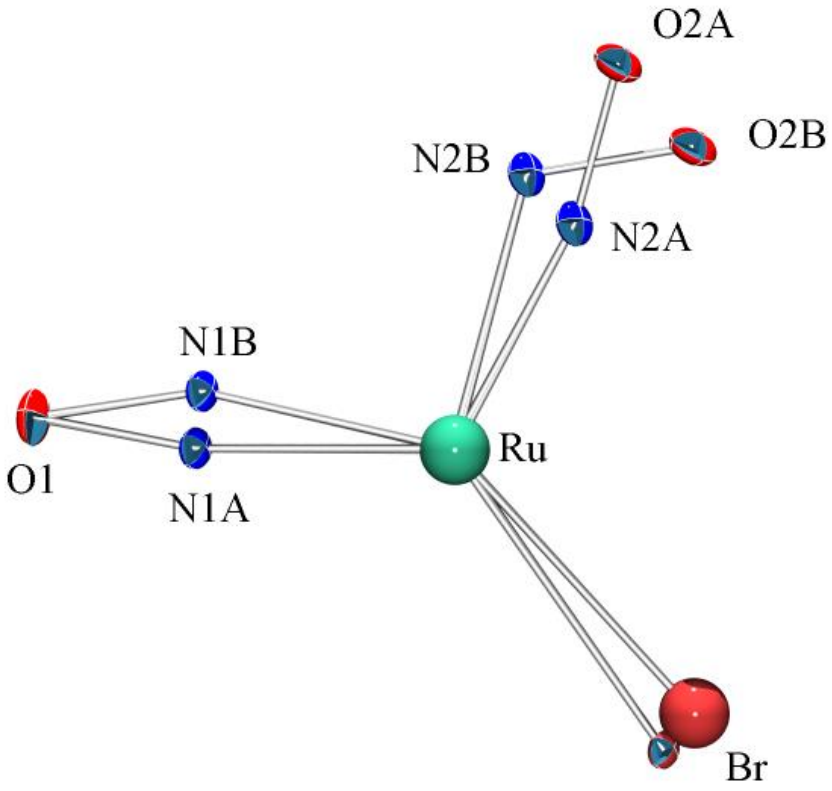


**Figure S5** ORTEP (Burnett & Johnson, 1996) view in the Ru-N1-N2 plane for the GS-rigid group + PLI-rigid group structural model. Ellipsoids are plotted at the 50% probability level. The isotropic displacement parameters for Ru and Br in the PLI state are wrongly negative.

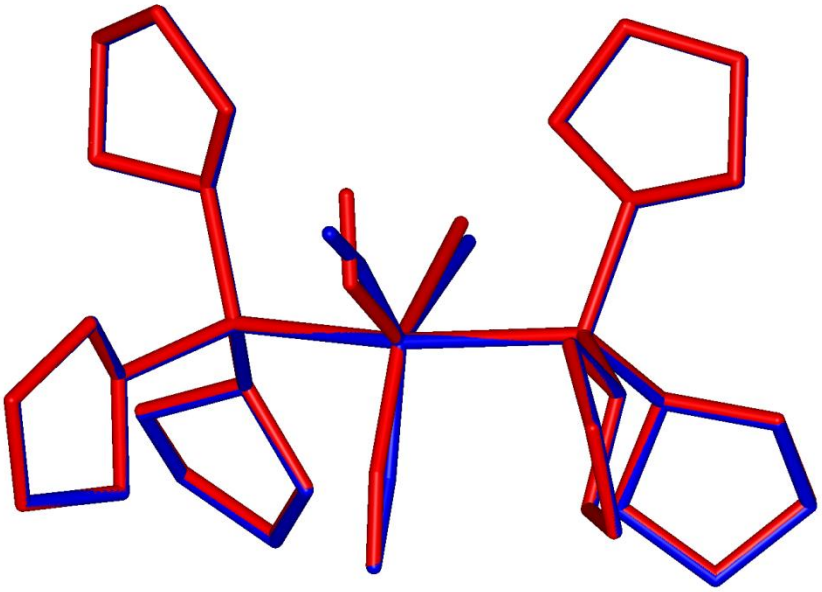

**Figure S6** Superposition of the GS (in blue) and PLI (in red) molecular structure in the GS-rigid group + PLI-rigid group structural model.

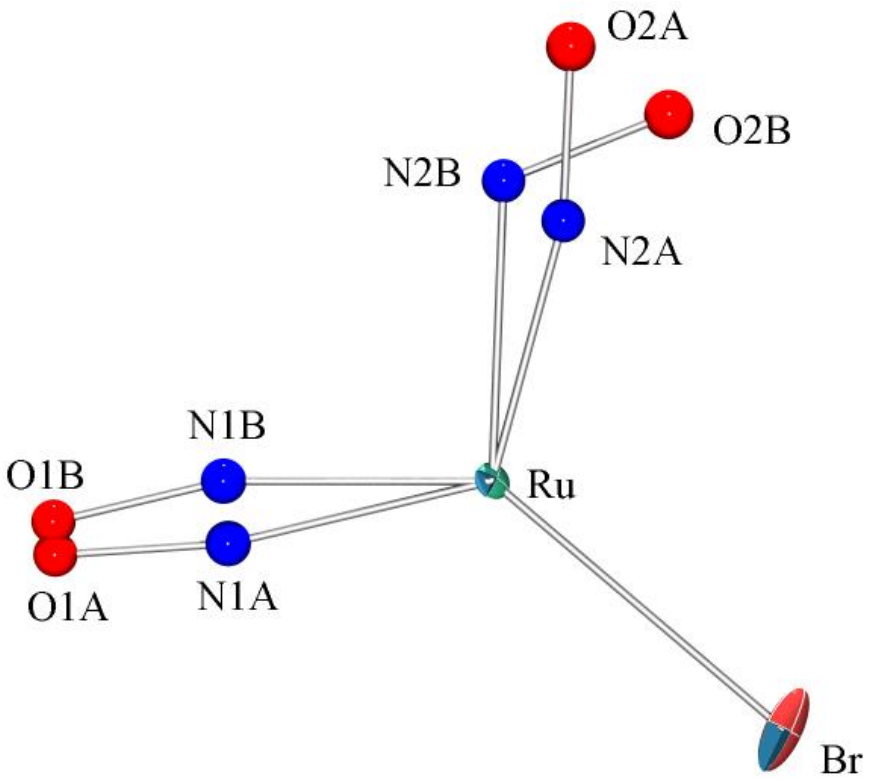


**Figure S7** ORTEP (Burnett & Johnson, 1996) view in the Ru-N1-N2 plane for the N1-O1 split nitrosyl + 2 nitrosyl N2-O2. Ellipsoids are plotted at the 50% probability level.

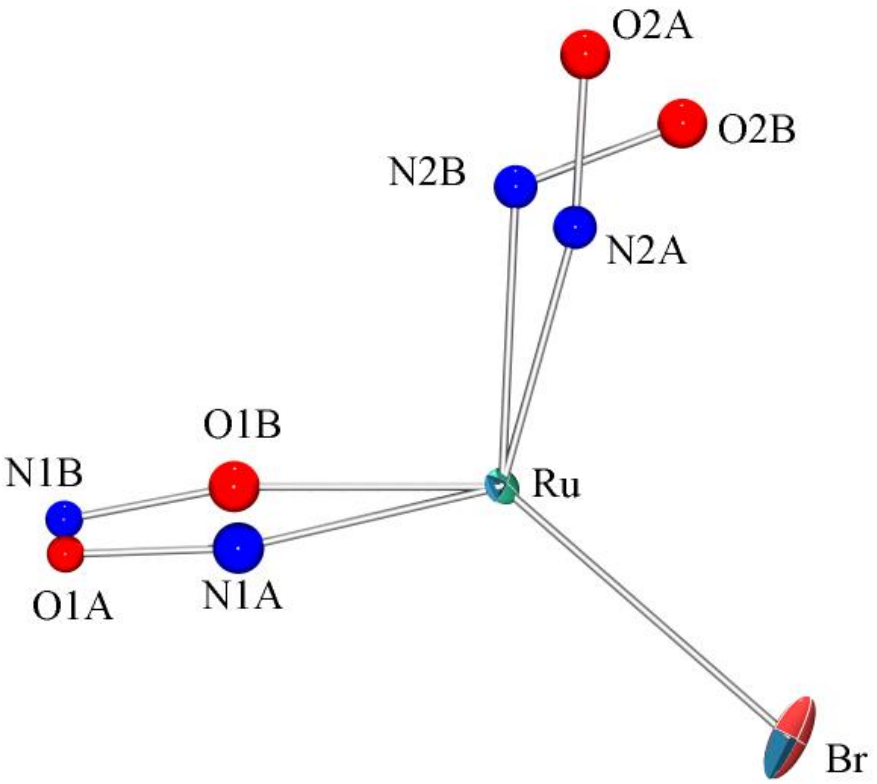


**Figure S8** ORTEP (Burnett & Johnson, 1996) view in the Ru-N1-N2 plane for the N1-O1 isonitrosyl + 2 nitrosyl N2-O2. Ellipsoids are plotted at the 50% probability level.

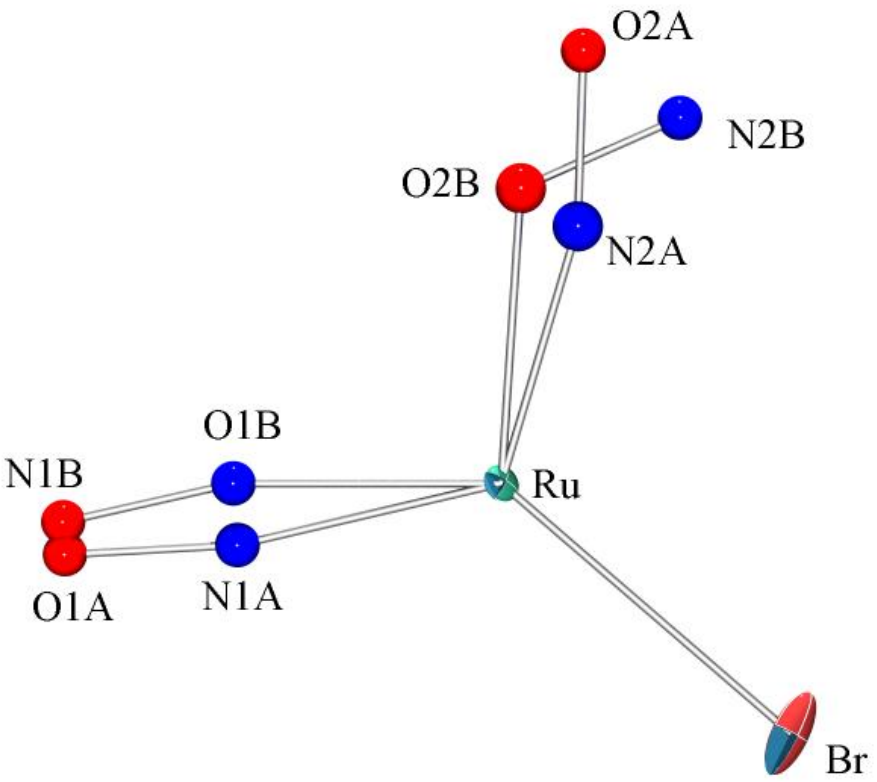


**Figure S9** ORTEP (Burnett & Johnson, 1996) view in the Ru-N1-N2 plane for the N1-O1 nitrosyl + N2-O2 isonitrosyl. Ellipsoids are plotted at the 50% probability level.

### S2. Infrared spectroscopy

Infrared measurements were performed at $T$ = 10 K using various diode lasers in the range 385-532nm for population of the PLI state (Fig. S10). The maximum population was reached with $\lambda$ = 405 nm up to 39(1) %.

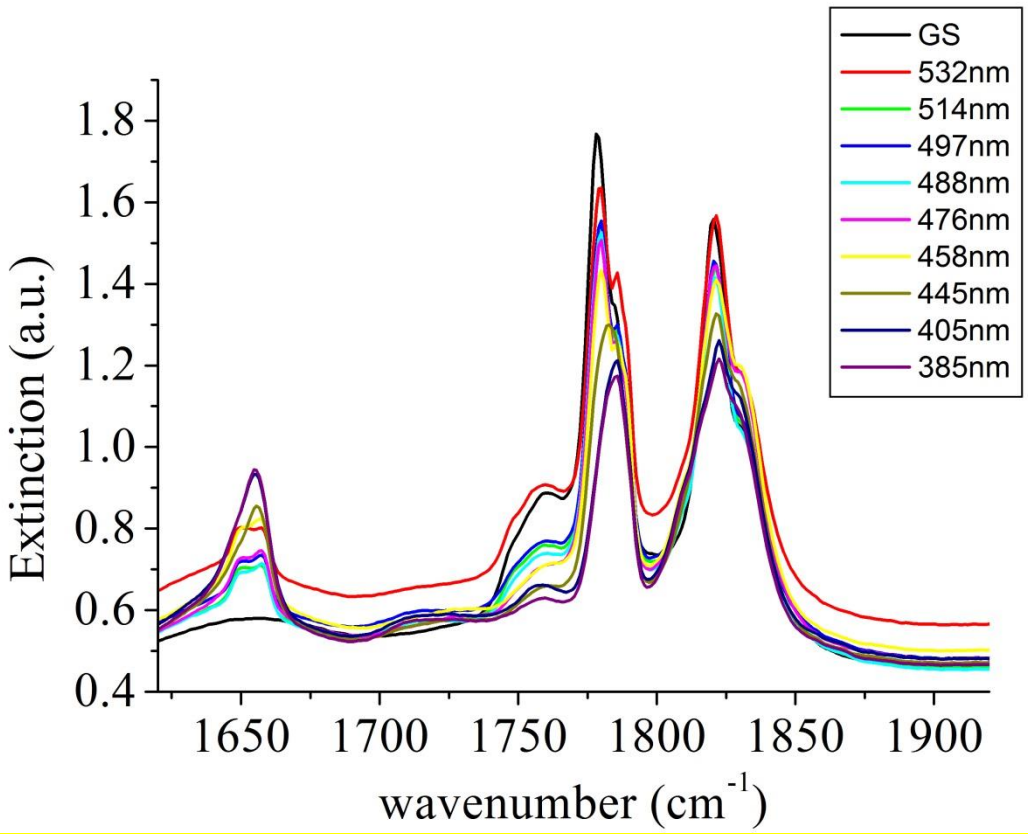


**Figure S10** Infrared spectrum of the ν(NO) stretching modes at 10 K in the GS (black line), and after illumination with diode lasers of various wavelength.

References

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Schaniel, D., Woike, T., Schefer, J., Petříček, V., Krämer, K. W. & Güdel, H. U. (2006). *Phys. Rev*. B **73**, 174108.

Schmokel, M. S., Kaminski, R., Benedict, J. & Coppens, P. (2010). *Acta Cryst*. **A66**, 632-636.

Vorontsov, I. I. & Coppens, P. (2005). *J. Synchrotron Rad*. **12**, 488-493.

**Table S1** Refinement details for $[RuBr(NO)_2(PCyp_3)_2)]BF_4$ (**1**) in the ground state (GS) and photo-irradiated state (GS+PLI).

| | Ground state | Photo-irradiated state | | | | |
|---|---|---|---|---|---|---|
| Refinement strategy | | Average + 2 nitrosyl N2-O2 | GS-rigid group + PLI-rigid group | N1-O1 split nitrosyl + 2 nitrosyl N2-O2 | N1-O1 isonitrosyl + 2 nitrosyl N2-O2 | N1-O1 split nitrosyl + N2-O2 isonitrosyl |
| N2A-O2A configuration | nitrosyl | nitrosyl | nitrosyl | nitrosyl | nitrosyl | nitrosyl |
| N2B-O2B configuration | | nitrosyl | nitrosyl | nitrosyl | nitrosyl | isonitrosyl |
| N1-O1 configuration | nitrosyl | nitrosyl | nitrosyl | isonitrosyl | isonitrosyl | nitrosyl |
| No. of variables | 388 | 385 | 75 | 381 | 381 | 381 |
| Refinement software | SHELXL | SHELXL | JANA2006 | SHELXL | SHELXL | SHELXL |
| [a,d]R1 [$F^2 > obs*\sigma(F^2)$] | 0.0527 [0.0408] | 0.0551 [0.0431] | 0.0840 [0.0669] | 0.0552 [0.0433] | 0.0553 [0.0434] | 0.0555 [0.0435] |
| [b,d]wR2 [$F^2 > obs*\sigma(F^2)$] | 0.1084 [0.0991] | 0.1107 [0.1026] | 0.0786 [0.0766] | 0.1108 [0.1028] | 0.1113 [0.1034] | 0.1120 [0.1038] |
| *GoF* | [c]1.044 | [c]1.048 | [e]2.41 | [c]1.049 | [c]1.054 | [c]1.038 |
| $\Delta\rho_{max,\ min}$ (eÅ$^{-3}$) | 2.665 / -2.369 | 2.317 / -2.287 | 7.55 / -2.19 | 2.307 / -2.280 | 2.304 / -2.281 | 2.301 / -2.286 |
| Refined population of PLI ($P_{PLI}$) | / | 31.2(3)% | 28.1(3)% | 31.6(3)% | 30.8(3)% | 33.7(4)% |
| Ueq(Ru) | 0.00487(4) | 0.00516(4) | 0.0049 | 0.00516(4) | 0.00517(5) | 0.00515(5) |
| Ueq(RuB) | / | / | -0.00496(16) | / | / | / |
| Ueq(Br) | 0.00636(4) | 0.01642(6) | 0.0064 | 0.01642(6) | 0.01643(6) | 0.01641(6) |
| Ueq(BrB) | / | / | -0.0015(3) | / | / | / |
| Ueq(N1A)<br>Ueq(O1A) | 0.0072(3)<br>0.0102(3) | 0.0240(5)<br>0.0125(3) | 0.0072<br>0.0102 | 0.0096(5)<br>0.0090(4) | 0.0123(5)<br>0.0066(4) | 0.0093(5)<br>0.0090(4) |
| Ueq(N1B)<br>Ueq(O1B) | / | / | / | 0.0096(5)<br>0.0090(4) | 0.0066(4)<br>0.0123(5) | 0.0093(5)<br>0.0090(4) |
| Ueq(N2A)<br>Ueq(O2A) | 0.0080(3)<br>0.0104(3) | 0.0089(5)<br>0.0115(4) | 0.0079<br>0.0104 | 0.0088(5)<br>0.0113(4) | 0.0089(5)<br>0.0116(4) | 0.0118(5)<br>0.0093(4) |
| Ueq(N2B)<br>Ueq(O2B) | / | 0.0089(5)<br>0.0115(4) | 0.0079<br>0.0104 | 0.0088(5)<br>0.0113(4) | 0.0089(5)<br>0.0116(4) | 0.0093(4)<br>0.0118(5) |

[a]R1 = $\sum|Fo-Fc|/Fo$. [b]wR2= $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c]GoF= $\{\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{var})\}^{1/2}$. [d]obs=2 for the SHELXL refinement and obs=3 for the JANA2006 refinement. [e]GoF= $\{\Sigma[w(F_o-F_c)^2]/(N_{obs}-N_{var})\}^{1/2}$.