

## Supplementary material

### Evidence for a photoinduced isonitrosyl isomer in ruthenium dinitrosyl compounds

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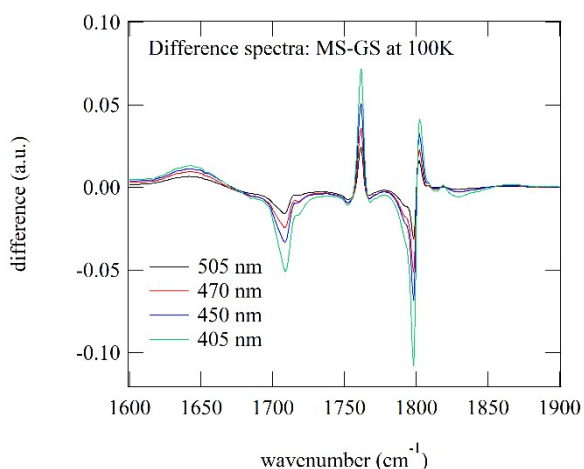


Fig. S1. Difference spectra at  $T = 100$  K showing the characteristic changes, decrease of GS bands at  $1710$  and  $1798$   $\text{cm}^{-1}$  and growth of new bands (PLI-2) at  $1761$   $\text{cm}^{-1}$  and  $1804$   $\text{cm}^{-1}$  as well as a broad band at  $1640$   $\text{cm}^{-1}$ .

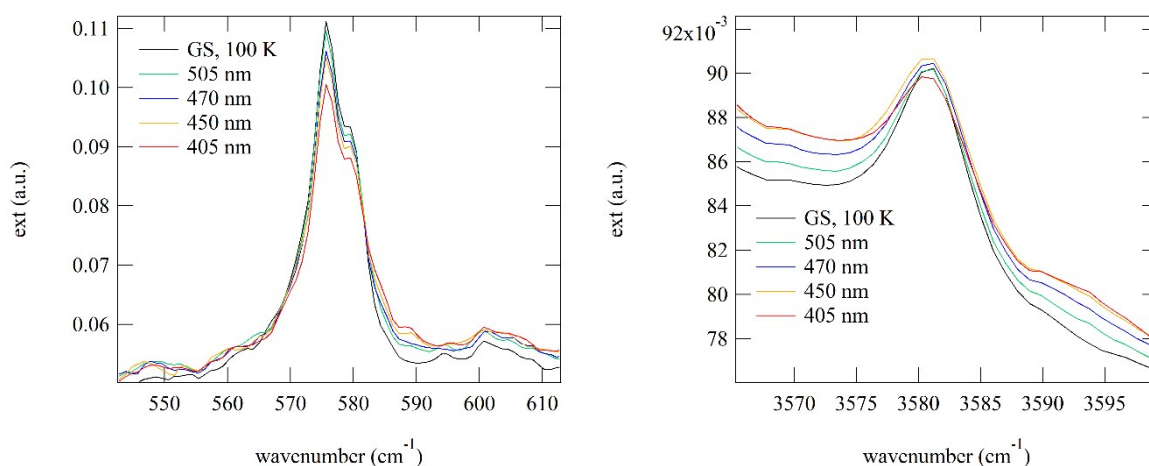


Fig. S2. Population of the photoinduced linkage isomer PLI-2 as a function of irradiation wavelength at  $100$  K. The GS  $\delta(\text{NO})$  band at  $576$   $\text{cm}^{-1}$  (left) and harmonic of  $\nu_{\text{sym}}(\text{NO})$  at  $3581$   $\text{cm}^{-1}$  (right) decrease. The population determined from the decrease of the area is  $15(5)\%$ .

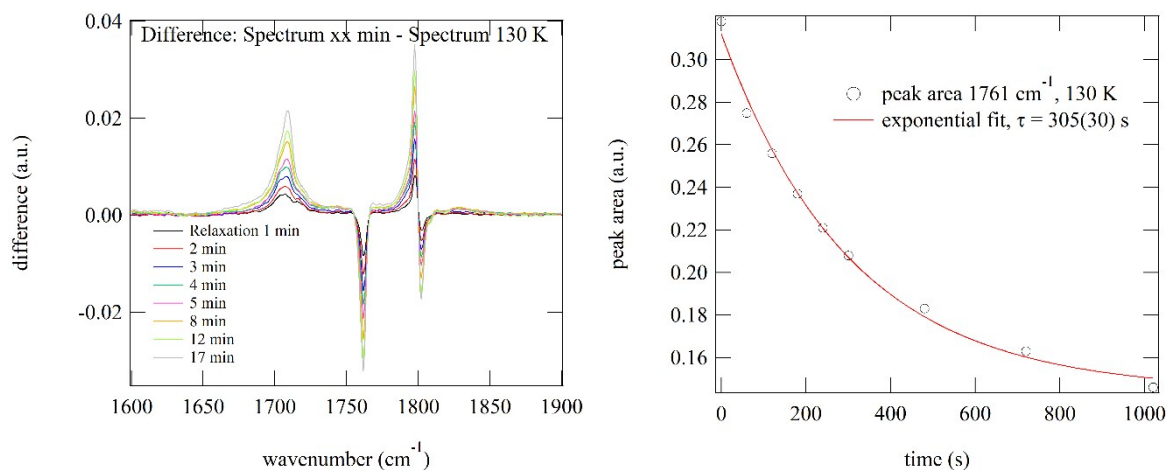


Fig. S3. (left) Difference spectra during relaxation at 130 K. Decrease of the characteristic bands at  $1761$  and  $1804$   $\text{cm}^{-1}$  of PLI-2 and corresponding increase of the GS bands at  $1710$  and  $1798$   $\text{cm}^{-1}$ . (right) Mono-exponential fit to the decrease of the peak area of the  $1761$   $\text{cm}^{-1}$  band at  $T = 130$  K, yielding a lifetime of  $305(30)$  s.

#### VISIBLE ABSORPTION SPECTROSCOPY

Visible absorption spectra were collected on KBr pellets as a function of temperature and photoexcitation. Fig. S4 shows the corresponding spectra in the ground state and upon photoexcitation at  $405$  nm. We can detect significant but weak changes in the spectrum, a decrease in absorption in the  $3.2$ - $2.6$  eV energy range, and an increase above  $2.6$  eV. The changes are much more obvious by plotting the difference absorption spectrum (Fig. S5). These changes in the absorption spectrum correspond to the population of PLI-1, PLI-2, and PLI-3.

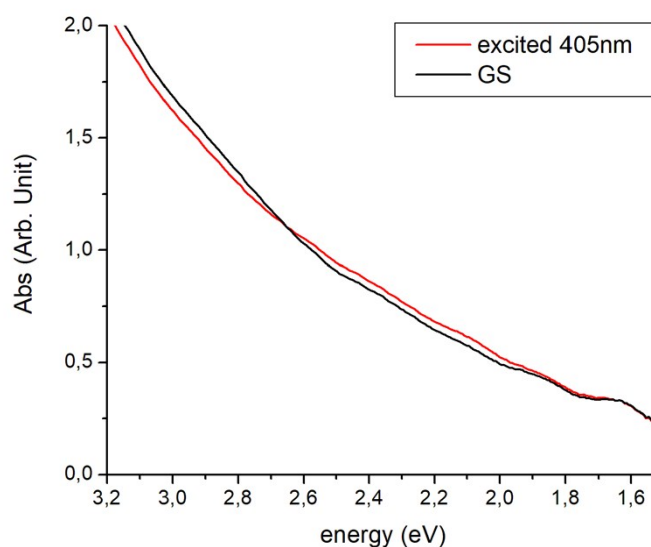


Fig. S4. Visible absorption spectra in the ground state (GS) at  $12$  K and after photoexcitation at  $405$  nm.

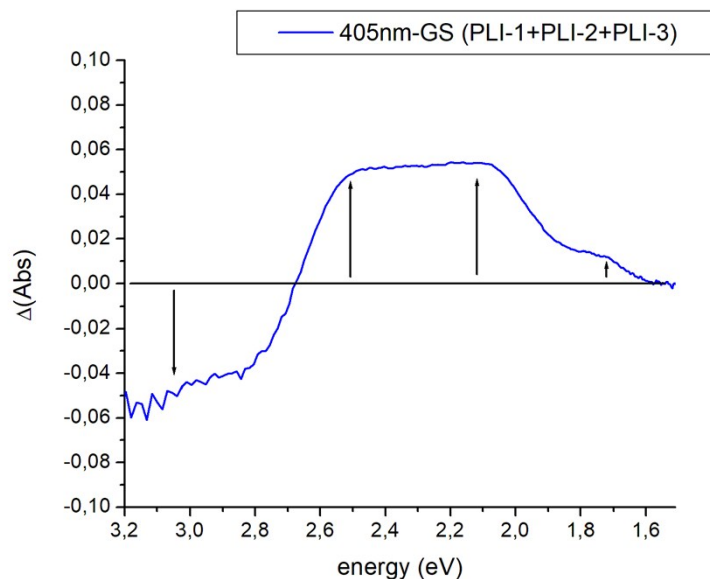


Fig. S5. Difference visible absorption spectrum during photoexcitation at 12 K. The photoexcited spectrum contains contributions from GS, PLI-1, PLI-2, and PLI-3.

According to the infrared spectroscopy results, the spectral signature of the three PLI states can be isolated by raising the temperature to appropriate values. Raising to 60 K allows to relax PLI-1, so that the difference spectrum between 60K and those collected at 12 K after photoexcitation corresponds directly to the contribution of PLI-1. Similarly, raising further to 90 K allows to relax PLI-3, and raising to 140 K allows to relax PLI-2 (see Fig. 6 in the manuscript).

It has been shown in the infrared analysis that photoexcitation at 10 K with 405 nm light and subsequent exposure to infrared light depopulates PLI-2. The corresponding sequence has been measured with visible optical spectroscopy, the results are given in Figure S6. The difference spectrum is very similar to the PLI-2 contribution isolated by temperature raising to 140 K (see Fig. 3 in the manuscript), which indicates that 980 nm photoexcitation could depopulate PLI-2.

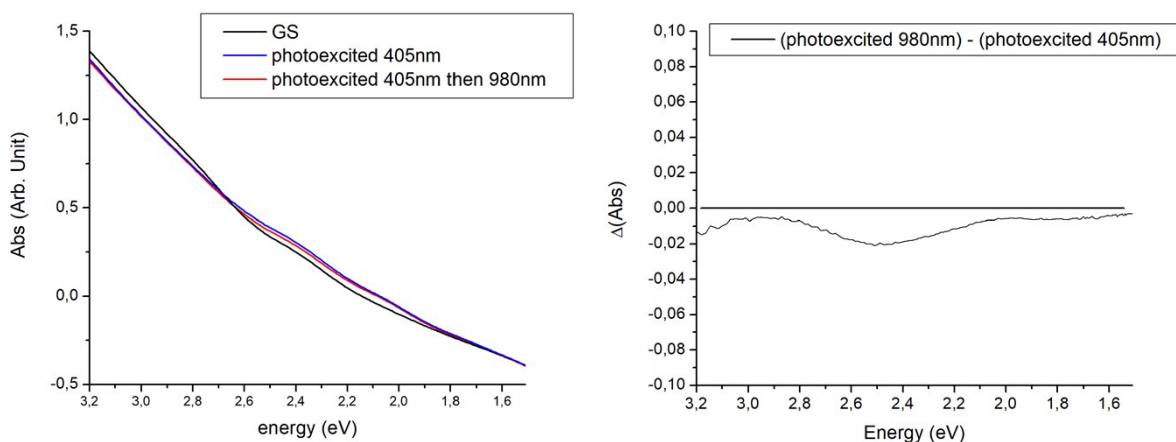


Fig. S6. (left) Visible absorption spectra in the ground state (GS) at 12 K, after photoexcitation at 405 nm, and photoexcitation at 405 nm with subsequent photoexcitation at 980 nm. (right) difference absorption spectrum highlighting the effect of 980 nm photoexcitation.

We have further followed the evolution of the spectrum as a function of time with constant 405 nm irradiance at 12 K starting from the sample in the GS state. Fig. S7 (left) shows the corresponding evolution of the difference absorption spectrum as a function of Q. Fig. S7 (right) shows the evolution at selected relevant energies corresponding to characteristics of the three different PLI states: 2.56 eV (pure PLI-2 state contribution), 2.12 eV (almost pure PLI-1 state), 1.74 eV (strong contribution of PLI-3 state), 3.1 eV (depopulation of GS). The evolution follows the same trend at the four energies, which indicates that the different PLI states are populated in parallel by 405nm photoexcitation at 12K We do not observe any successive population.

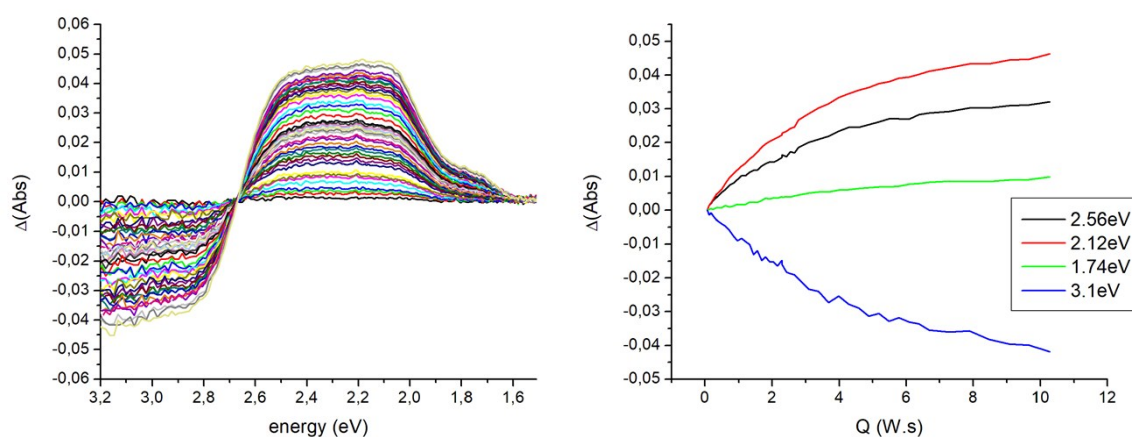


Fig. S7. (left) Difference absorption spectra upon 405 nm photoexcitation at 12 K. (right) evolution at selected relevant energies: 2.56 eV, 2.12 eV, 1.74 eV, and 3.1 eV.

## PHOTOCRYSTALLOGRAPHY

### Refinement of the ground state structure

The crystal structure of the ground state was refined using the SHELXL2014 software. All non-H atoms were refined anisotropically. The PCy<sub>3</sub> ligand exhibits a disorder on one of the cyclohexane rings, which was taken into account using two split orientations for that fragment (respective refined populations of 0.777(2) and 0.223(2)). The [BF<sub>4</sub>]<sup>-</sup> anion also exhibits disorder on two orientations (respective refined populations of 0.812(7) and 0.188(7)). Hydrogen atoms were generated at their ideal positions, and treated using a riding model, constraining the isotropic displacement parameters to 1.2 times those of the attached C atom.

### Refinement of the photo-excited structure

The single crystal sample was irradiated at 100 K with a diode laser of 405 nm ( $P = 90$  mW) for 60 min in the complete dark, until the photo-stationary state was reached. According to the infrared results, at this temperature and irradiation wavelength, the PLI-2 metastable state can be selectively populated with a sufficiently high population. We have indeed found that by raising the temperature slightly above 90 K, PLI-1 and PLI-3 completely relax to the ground state, so that the PLI-2 state may be isolated in the crystal by 405 nm irradiation. The corresponding photodifference map (Figure 3 in the manuscript) exhibits several specific features which provide evidences for the GS to PLI-2 state

structural reorganization, no evidence for PLI-1 is detected. The crystal in the photo-excited state therefore corresponds to a random distribution of GS and PLI-2 species. In a first step, a structural refinement has been tested considering the complete molecular structure of the ground state as a rigid group and the PLI-2 state as an additional molecular conformation. This is called a split model. Such a strategy was used successfully in our previous determination of the PLI-1 structure in  $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]\text{BF}_4$  (Casaretto et al., IUCr (2015). 2, 35-44). In the present case, this strategy does not converge to a satisfactory situation. A meaningful structural refinement was reached starting from the GS structural model, and splitting only the bent nitrosyl with N1A-O1A in the GS position, and N1B-O1B in the PLI-2 configuration.

From this point, different hypotheses concerning the possible configurations of the two nitrosyl groups in the PLI-2 state were tested. The results of these refinements can be estimated, based on the refinement agreement statistics, obtained structural parameters, and atomic displacement parameters (ADPs) for the nitrogen and oxygen atoms of the two nitrosyl groups. These results are summarized in table S1.

It is to be noted that the disorder characterized for the ground state (one of the cyclohexane ring, and the  $[\text{BF}_4]^-$ ) persists in the photo-excited state and was also treated using a split model. The obtained positions and refined populations for the split positions differ only marginally from the ground state. As a matter of fact, the values obtained at the convergence of our best refinement model are : 0.767(2) and 0.233(2) for the cyclohexane ring, and 0.805(7) and 0.195(7) for the tetrafluoroborate anion. This is furthermore consistent with the fact that the corresponding fragments do not show any contribution in the photo-difference map.

Table S1. Refinements details for the different hypotheses for PLI-2.

hypotheses	1 (MS1)	2 (MS1a)	3 (MS11)
Configuration of N1BO1B	Isonitrosyl	nitrosyl	Isonitrosyl
Configuration of N2BO2B	nitrosyl	Isonitrosyl	isonitrosyl
$^a\text{R}_1 [F^2 > 2*\sigma(F^2)]$	0.0428 [0.0351]	0.0427 [0.0350]	0.0453 [0.0376]
$^b\text{wR}_2 [F^2 > 2*\sigma(F^2)]$	0.0825 [0.0773]	0.0825 [0.0773]	0.0888 [0.839]
N1B-O1B	0.97(7)	1.161(2)	1.00(7)
N2-O2	1.161(2)	1.55(12)	1.40(9)
Ueq(N1B) / Ueq(O1B)	0.0230(6) / 0.0175(5)	0.0190(3) / 0.0257(3)	0.0230(6) / 0.0177(5)
Ueq(N2) / Ueq(O2)	0.0184(3) / 0.0276(3)	0.0264(4) / 0.0174(3)	0.0175(6) / 0.0244(4)
Population of MS in %	18(2)	2(1)	9(2)/8(3)

$$^a\text{R}_1 = \sum |F_o - F_c| / F_o. \quad ^b\text{wR}_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

- in the hypothesis (1), corresponding to MS1 of DFT, N1B-O1B is in an isonitrosyl configuration (Ru-O1B-N1B). The agreement statistics is close to the values obtained for the ground state refinement, the N1B-O1B bond distance is shorter than for the ground state, and the ADPs for N1B and O1B are consistent with a lower value for the O1B atom attached to Ru, and a larger value for the terminal N1B atom.

- in the hypothesis (2), corresponding to MS1a of DFT, N2B-O2B is in a isonitrosyl configuration. The refinement agreement statistics are almost identical to hypothesis (1), but the refinement yields a very

small population of the MS with a bent configuration of Ru-O2B-N2B, indicating rather a compensation for some residual density around the molecule than a PLI. This corresponds to more or less a ground state configuration, which we can therefore exclude as valuable hypothesis for PLI-2.

- in the hypothesis (3), corresponding to MS11 of DFT, both NO groups are considered as isonitrosyl configurations in the PLI-2 state. The refinement agreement statistics are higher than for hypothesis (1). The resulting ADPs for N2 and O2 are not consistent. As a matter of fact, the O2 atom being attached to the Ru atom leads to higher ADPs compared to the terminal N2 atom. The reverse situation would be expected (higher ADPs for the terminal atom). This corresponds to a wrong atom type assignment: Ru-O2-N2 should be Ru-N2-O2 instead. This conclusion is consistent with the calculated photodifference map (Fig. 4 in the manuscript) since for an isonitrosyl N2-O2 configuration, a strong positive electron density would be expected at the position of N2, and a strong negative electron density would be expected at the O2 position; this is not the observed case.

As a conclusion, we can firmly assert that the PLI-2 state corresponds to N1-O1 in an isonitrosyl configuration, and N2-O2 in a nitrosyl configuration: it consists of a single linkage isomerism of N1-O1 solely. Accordingly, the results of hypothesis (1) are discussed in the manuscript.