



Cite this: *Dalton Trans.*, 2015, **44**, 17189

Received 4th August 2015,
 Accepted 27th August 2015
 DOI: 10.1039/c5dt02994e
www.rsc.org/dalton

Syntheses and properties of phosphine-substituted ruthenium(II) polypyridine complexes with nitrogen oxides[†]

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Four novel phosphine-substituted ruthenium(II) polypyridine complexes with nitrogen oxides—*trans*-(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]PF₆ (**trans-NO₂**), *cis*(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]PF₆ (**cis-NO₂**), [Ru(trpy)(dppbz)-(NO₂)]PF₆ (**PP-NO₂**), and *cis*(P,NO)-[Ru(trpy)(Pqn)(NO)](PF₆)₃ (**cis-NO**)—were synthesised (trpy = 2,2':6',2"-terpyridine, Pqn = 8-(diphenylphosphanyl)quinoline, and dppbz = 1,2-bis(diphenylphosphanyl)benzene). The influence of the number and position of the phosphine group(s) on the electronic structure of these complexes was investigated using single-crystal X-ray structural analysis, UV-vis absorption spectroscopy, and electrochemical measurements. The substitution lability of the nitrogen oxide ligand of each complex is discussed in comparison with that of the corresponding acetonitrile complexes.

Introduction

Ruthenium(II) polypyridine complexes are widely studied materials because of their contributions to fundamental coordination chemistry, including electrochemistry, photochemistry, and photophysics,¹ and their potential applications in energy conversion,² luminescent sensors,³ electroluminescence displays,⁴ and biotechnology.⁵ Of particular interest are the Ru(II) complexes [Ru(TL)(BL)(L)]ⁿ⁺ (TL = tridentate polypyridine ligand, BL = bidentate polypyridine ligand, and L = monodentate labile ligand) given their catalytic activity for various reactions, such as oxidation,^{6,7} reduction,^{8–11} and photo-induced reactions.¹²

Phosphine-containing ruthenium(II) complexes are also attractive for potential applications in energy conversion systems¹³ and catalysis^{14–17} owing to the σ -donating and

π -accepting abilities of the phosphine ligands. Thus, it should be possible to develop ruthenium complexes that have novel and tunable properties and reactivity by designing mixed polypyridyl/phosphine complexes. There have been several reports on the syntheses of ruthenium(II) polypyridine complexes containing monodentate phosphine ligands^{16,18,19} and their catalytic activities.^{19d,20} However, ruthenium(II) polypyridine complexes of the type [Ru(TL)(BL)(L)]ⁿ⁺ bearing bidentate ligands with P and N donors have not been investigated.

In our previous report,²¹ we synthesised and structurally characterised for the first time a series of phosphine-containing ruthenium(II) polypyridine complexes of the type [Ru(TL)-(BL)(L)]ⁿ⁺, with L = acetonitrile, TL = 2,2':6',2"-terpyridine (trpy), and BL = 8-(diphenylphosphanyl)quinoline (Pqn) or 1,2-bis(diphenylphosphanyl)benzene (dppbz) (Scheme 1). The influence of the number and position of phosphine donors on the structures and electronic properties was characterised, and unique isomerisation behaviours of these complexes were observed. The coordinating phosphorus ligands played a crucial role in these isomerisation reactions, and the results encouraged us to investigate in more detail the influence of the P atom on the physical properties of Ru-based metal complexes.

In this study, we investigated the reaction of phosphine-containing ruthenium complexes with the nitrogen oxides, NO and NO₂[–], because of their biological roles as signalling molecules²² and reservoirs,²³ in addition to the fundamental interest in their coordination chemistry. Here, we show the syntheses, structural characterisation, and electrochemical and spectroscopic properties of a series of ruthenium(II)

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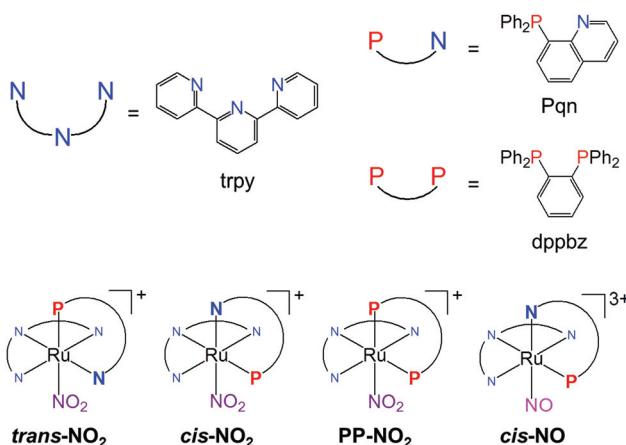
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[†] Electronic supplementary information (ESI) available. CCDC 1040452–1040454. For ESI and crystallographic data in CIF or other electronic format see DOI: [10.1039/c5dt02994e](https://doi.org/10.1039/c5dt02994e)





Scheme 1 Structures of a tridentate ligand (trpy), bidentate ligands (Pqn and dppbz), and metal complexes (**trans-NO₂**, **cis-NO₂**, **PP-NO₂**, and **cis-NO**) used in this study.

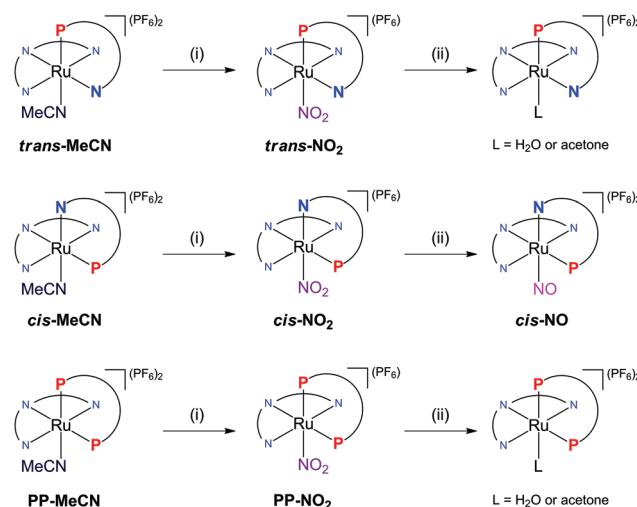
polypyridine complexes containing Pqn or dppbz with nitric oxides. Three novel nitrito- κN complexes—*trans*(P,NO₂)- and *cis*(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]PF₆ (**trans-NO₂** and **cis-NO₂**), and [Ru(trpy)(dppbz)(NO₂)]PF₆ (**PP-NO₂**)—were successfully synthesised. Described here are the single-crystal X-ray structural determinations, UV-vis absorption spectra, and electrochemical measurements for these complexes, and the preparation of the nitrosyl complex *cis*(P,NO)-[Ru(trpy)(Pqn)-(NO)][PF₆]₃ (**cis-NO**) from **cis-NO₂** and its properties are examined. The present study allows us to probe systematically the chemical and structural properties of phosphine-containing ruthenium complexes with nitrogen oxides by the use of the geometric isomers of the Pqn complex. Additionally, other reactivity properties and comparisons with those of the corresponding acetonitrile complexes are presented.

Results and discussion

Syntheses and characterisation

The synthetic procedures to obtain **trans-NO₂**, **cis-NO₂**, and **PP-NO₂** are shown in Scheme 2. The precursors, **trans-MeCN**, **cis-MeCN**, and **PP-MeCN**, were synthesised according to the method that we previously reported.²¹ The reaction of the respective acetonitrile complexes with excess NaNO₂ in a 1:1 mixture of ethanol:water at 100 °C gave the corresponding nitrito- κN complexes (**trans-NO₂**, **cis-NO₂**, and **PP-NO₂**).^{24,26b} The resulting products were characterised by ¹H NMR and ³¹P{¹H} NMR spectroscopy and elemental analysis.

The ³¹P{¹H} NMR spectra of **trans-NO₂** and **cis-NO₂** in CD₃CN displayed singlets at δ 53.10 and 54.06, respectively, showing upfield shifts ($\Delta\delta$ = 5.70 and 1.90) compared to the spectra of the corresponding acetonitrile complexes, **trans-MeCN** and **cis-MeCN** (δ 58.80 and 55.96). The ³¹P{¹H} NMR spectrum of **PP-NO₂** in CD₃CN afforded two doublets at δ 62.65 and 68.59 with coupling constants of 14.2 Hz, again



Scheme 2 Syntheses of **trans-NO₂**, **cis-NO₂**, **PP-NO₂**, and **cis-NO**. (i) NaNO₂ in a 1:1 mixture of ethanol:water at 100 °C. (ii) HPF₆ in acetone at 0 °C.

showing upfield shifts ($\Delta\delta$ = 5.85 and 1.18, respectively) compared with the spectrum of **PP-MeCN** (68.57 and 69.77, ²J_{P-P} = 20.2 Hz).

Conversions of the nitrito- κN complexes to the corresponding ruthenium nitrosyls were attempted by adding an excess of HPF₆ to acetone solutions of the nitrito- κN species at 0 °C. The preparations of **trans-NO** and **PP-NO** from **trans-NO₂** and **PP-NO₂**, respectively, were not successful because of the instability of the nitrosyl complex or of a reaction intermediate under acidic conditions (for details, see Fig. S1 and S2 in the ESI†). However, **cis-NO** was isolated in 85% yield and was characterised by ¹H and ³¹P{¹H} NMR spectroscopy and elemental analysis. The ³¹P{¹H} NMR spectrum of **cis-NO** in acetone-*d*₆ gave a singlet at δ 54.23. **cis-NO** immediately converted to a solvent-coordinated complex in acetonitrile (Fig. S3 in the ESI†) but was meta-stable in weaker-coordinating solvents, such as acetone, γ -butyrolactone and ethylene glycol (Fig. S4 in the ESI†). The difference in the stability of these nitrosyl complexes will be discussed in the “Substitution lability of nitrogen oxide” section.

Crystal structures

Single crystals of **trans-NO₂** and **PP-NO₂** suitable for structural determination were obtained by recrystallisation from diethyl ether/methanol/acetonitrile. Single crystals of the *cis*-nitrito- κN complex were obtained as the BPh₄⁻ salt, *cis*(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]BPh₄ (**cis-NO₂'**), by adding an excess of NaBPh₄, instead of NH₄PF₆, after the reaction. The molecular structures of **trans-NO₂**, **cis-NO₂'**, and **PP-NO₂** determined by single-crystal X-ray crystallography and the summary of crystallographic data are shown in Fig. 1 and Table 1, respectively. The asymmetric unit of the monoclinic *P2₁/n* crystal of **trans-NO₂** contained one cationic ruthenium complex, one PF₆ anion, and one acetonitrile molecule. The **cis-NO₂'** crystallised with



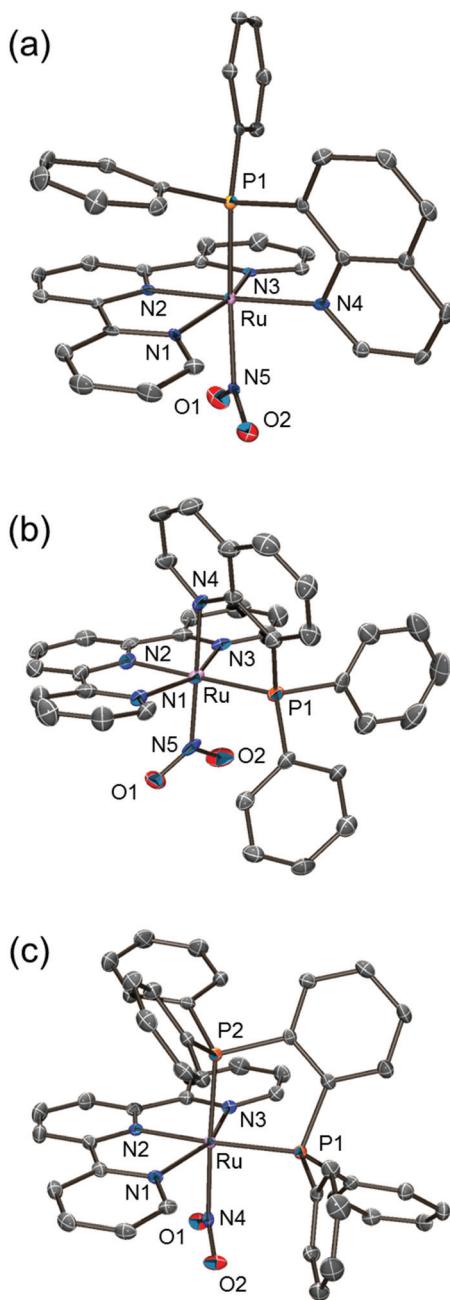


Fig. 1 ORTEP drawings (50% probability level) of cationic complexes in (a) *trans*-NO₂, (b) *cis*-NO₂', and (c) PP-NO₂. Hydrogen atoms are omitted for clarity.

two crystallographically independent ruthenium complexes, two BPh₄⁻ anions, and one acetonitrile molecule as the crystal solvent in the asymmetric unit of the triclinic *P*1 space group. The asymmetric unit of the monoclinic *P*2₁/c crystal of PP-NO₂ contained one cationic ruthenium complex, one PF₆⁻ anion, and two methanol molecules. For each complex, the ratio of ruthenium to counter anion indicated that the oxidation state of the ruthenium centre was +2. The coordination geometry of each Ru atom was that of a distorted octahedron composed of

a meridionally coordinated terpyridine ligand, a bidentate ligand, and a nitrito ligand.

The bond distances between the ruthenium and nitrogen atoms of the nitrito ligand of *trans*-NO₂ and PP-NO₂ were 2.146(4) (Ru1-N5) and 2.124(2) Å (Ru1-N4), respectively (Fig. 2), and were longer than those found in [Ru(trpy)(bpm)(NO₂)]PF₆ (2.034(5) Å, bpm = 2,2'-bipyrimidine).²⁵ By contrast, the Ru-N(NO₂) distances in *cis*-NO₂' (2.0362(18) and 2.0290 (18) Å for Ru1-N5 and Ru2-N10, respectively, Fig. 2) were similar to those of [Ru(trpy)(bpm)(NO₂)]PF₆ (2.034(5) Å). These results indicated a stronger *trans* influence of the phosphorus atom of Pqn or dppbz compared with that of the nitrogen atom of bpm or bpy. This tendency was also observed in *trans*-MeCN, *cis*-MeCN, and PP-MeCN in our previous study.²¹

UV-vis absorption spectra

Fig. 3 shows the UV-Vis absorption spectra of the nitrito- κ N complexes, *trans*-NO₂, *cis*-NO₂, and PP-NO₂, in acetonitrile solution. The spectral data for these complexes and related compounds are listed in Table 2. All complexes displayed intense absorption bands in the UV region that were assigned to ligand-based π - π^* transitions. Additionally, a moderately intense band was observed in the visible region for each complex. TD-DFT calculations that were performed at the B3LYP/LANL2DZ and B3LYP/SDD level of theory indicated that the visible region band could be assigned to metal-to-ligand charge transfer (MLCT) transitions from the d π orbitals of ruthenium to the π^* orbitals of trpy and Pqn or dppbz (for details, see Table S1 and Fig. S5-9 in the ESI[†]). The molar absorption coefficient of PP-NO₂ was nearly half of those of *trans*-NO₂ and *cis*-NO₂. The absorption maximum (λ_{max}) of the MLCT transition of *trans*-NO₂, *cis*-NO₂, and PP-NO₂ was 443, 431, and 402 nm, respectively, and was blue-shifted compared with that of [Ru(trpy)(bpm)(NO₂)]PF₆,²⁵ suggesting the stabilisation of the d π orbitals of the ruthenium centre upon introduction of the phosphine donors. Note that the MLCT band of *cis*-NO₂ was more blue-shifted than that of *trans*-NO₂ despite their isomeric relationship. A similar pattern was noted for the acetonitrile complexes, *trans*-MeCN, *cis*-MeCN, and PP-MeCN.²¹

The UV-vis absorption spectra of the *cis*-isomers with different ligands L, *cis*(P,L)-[Ru(trpy)(Pqn)(L)]ⁿ⁺ (L = Cl⁻, NO₂⁻, MeCN, and NO⁺), in ethylene glycol solution are shown in Fig. 4. These complexes each exhibited ligand-based π - π^* transitions in the UV region and MLCT transitions in the visible region. The MLCT transition of *cis*-NO was observed at $\lambda_{\text{max}} = 383$ nm and is comparable to similar Ru-NO complexes (Table 3). For the different Ls, the lowest energy MLCT bands of the *cis*-isomers are in the following order: L = Cl⁻ (468 nm) < NO₂⁻ (423 nm) < MeCN (413 nm) < NO⁺ (383 nm). This result can be attributed to the competing σ -donor/ π -acceptor properties of the respective ligands.

Electrochemical properties

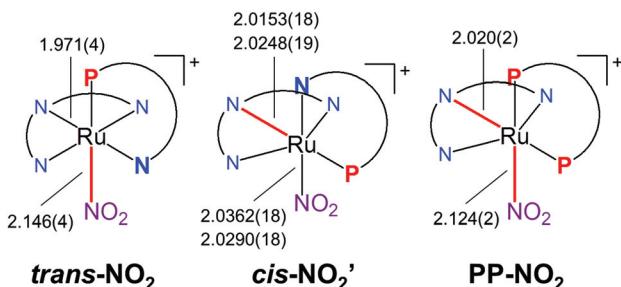
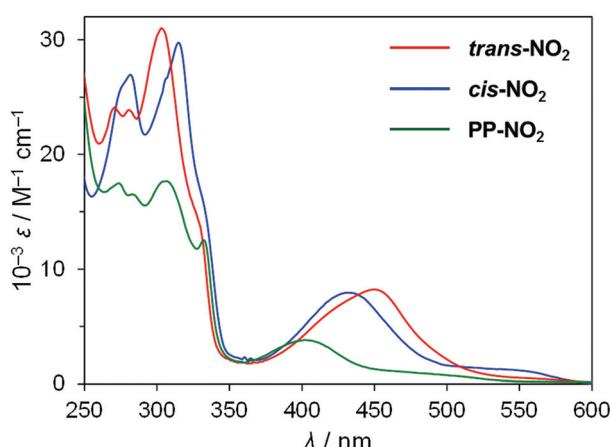
The cyclic voltammograms (CVs) of *trans*-NO₂, *cis*-NO₂, and PP-NO₂ are shown in Fig. 5, and electrochemical data for these



Table 1 Crystallographic data for *trans*-NO₂, *cis*-NO₂', and PP-NO₂

Complex	<i>trans</i> -NO ₂ ·CH ₃ CN	<i>cis</i> -NO ₂ '·0.5CH ₃ CN	PP-NO ₂ ·2CH ₃ OH
Formula	C ₃₈ H ₃₀ F ₆ N ₆ O ₂ P ₂ Ru	C ₆₁ H _{48.5} BN _{5.5} O ₂ PRu	C ₄₇ H ₄₃ F ₆ N ₄ O ₄ P ₃ Ru
Formula weight	879.69	1033.40	1035.83
Crystal colour, habit	Red, needle	Orange-red, platelet	Orange, block
Crystal system	Monoclinic	Triclinic	Monoclinic
Crystal size, mm ³	0.30 × 0.05 × 0.05	0.15 × 0.15 × 0.10	0.15 × 0.10 × 0.05
Space group	P2 ₁ /n	P1̄	P2 ₁ /c
<i>a</i> , Å	12.1909(17)	10.2764(2)	17.1049(6)
<i>b</i> , Å	11.9003(17)	21.2343(4)	13.0763(6)
<i>c</i> , Å	25.260(4)	24.3802(4)	20.1547(8)
α , °	90	77.0060(10)	90
β , °	99.579(3)	78.9530(10)	106.853(3)
γ , °	90	74.9360(10)	90
<i>V</i> , Å ³	3613.5(9)	4955.30(16)	4314.4(3)
<i>Z</i>	4	4	4
<i>D</i> _{calc} , g cm ⁻³	1.617	1.385	1.595
μ , mm ⁻¹	0.599	0.400	0.552
<i>F</i> (000)	1776	2132	2112
<i>R</i> ₁ ^a	0.0596	0.0337	0.0397
w <i>R</i> ₂ ^b	0.1678	0.1071	0.0941
Goodness-of-fit <i>S</i>	1.032	1.178	1.004

^a $R_1 = -\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$.

**Fig. 2** Comparison of bond distances (Å) around the ruthenium centres of *trans*-NO₂, *cis*-NO₂', and PP-NO₂.**Fig. 3** UV-Vis absorption spectra of *trans*-NO₂, *cis*-NO₂, and PP-NO₂ in acetonitrile at room temperature.

complexes and related compounds are listed in Table 4. The CVs were measured in 0.1 M tetraethylammonium perchlorate (TEAP)/acetonitrile. *cis*-NO₂ displayed one reversible oxidation wave in the positive region at $E_{1/2} = 0.79$ V vs. ferrocene/ferrocenium (Fc/Fc⁺), which was assigned to a Ru(III)/Ru(II) redox couple. By contrast, *trans*-NO₂ and PP-NO₂ exhibited one irreversible ($E_{pa} = 0.79$ for *trans*-NO₂ and 0.95 V for PP-NO₂) and one reversible ($E_{1/2} = 0.97$ for *trans*-NO₂ and 1.27 V for PP-NO₂) redox waves in the positive region. The former irreversible oxidation peak can be attributed to oxidation of the (Ru-NO₂)⁺ centre, and the latter reversible wave was observed exactly at the same potential as the Ru(III)/Ru(II) redox couple of the corresponding acetonitrile complex ($E_{1/2} = 0.97$ for *trans*-MeCN and 1.27 V for PP-MeCN, Table 4 and Fig. S10b and S10d in the ESI†).²¹ These observations suggest that the one-electron oxidation of *trans*-NO₂ and PP-NO₂ results in the release of NO₂, owing to the labilising effect of the *trans*-phosphine in each case. This leads to the formation of the respective ruthenium(II) acetonitrile complexes, which are oxidised reversibly on further sweep to more positive potential (Scheme 3). In the absence of a *trans*-labilising phosphine, the oxidation of the (Ru-NO₂)⁺ centre of *cis*-NO₂ occurs at a similar potential to the *trans*-isomer, but reversibly (Fig. 5 and Table 4).

In the negative potential region, *cis*-NO₂ displayed two reversible reduction waves at -1.70 and -1.99 V, which were assigned to the trpy/trpy⁻ and Pqn/Pqn⁻ redox couple, respectively. *trans*-NO₂ exhibited two redox waves at $E_{1/2} = -1.77$ and -2.13 V, and these redox potentials were the same as that of *trans*-MeCN (Table 4 and Fig. S10a in the ESI†). PP-NO₂ displayed two irreversible waves ($E_{pc} = -1.70$ V and $E_{pa} = -1.47$ V) and one reversible ($E_{1/2} = -2.49$ V) redox wave in the negative region. The reversible wave at $E_{1/2} = -2.49$ V and the



Table 2 UV-Vis absorption data ($\lambda_{\text{max}}/\text{nm}$ ($10^{-3} \epsilon/\text{M}^{-1} \text{cm}^{-1}$)) in acetonitrile and infrared data (ν/cm^{-1}) for *trans*-NO₂, *cis*-NO₂, PP-NO₂, and related compounds at room temperature

Complex	λ_{max}	IR	
		$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$
<i>trans</i> -NO ₂	443 (8.02), 327 ^c , 303 (31.0), 281 (23.9), 271 (24.1)	1349	1304
<i>cis</i> -NO ₂	431 (7.95), 331 ^c , 315 (29.7), 282 (26.9), 276 ^c	1339	1286
PP-NO ₂	402 (3.82), 332 (12.6), 307 (17.7), 283 (16.5), 273 (17.5)	1354	1311
[Ru(trpy)(bpy)(NO ₂)]PF ₆ ^a	472	^d	^d
[Ru(trpy)(bpm)(NO ₂)]PF ₆ ^b	470 (6.50), 362 (6.10), 330 ^c , 308 (25.6), 264 (23.3)	1342	1286

^a Ref. 26. ^b Ref. 25. ^c Absorption shoulder. ^d Data not collected.

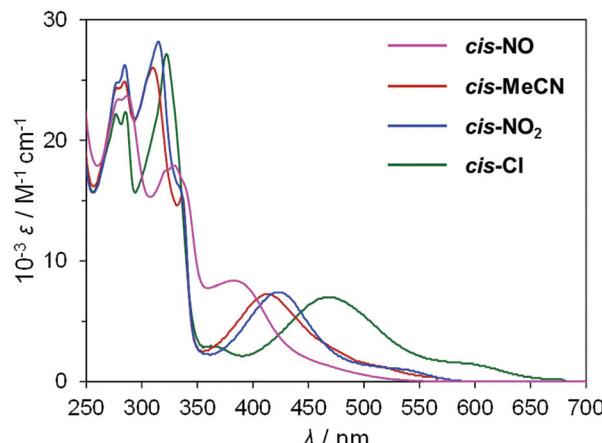


Fig. 4 UV-Vis absorption spectra of *cis*(P,X)-[Ru(trpy)(Pqn)(L)]ⁿ (L = Cl⁻, NO₂⁻, MeCN, NO⁺) in ethylene glycol at room temperature.

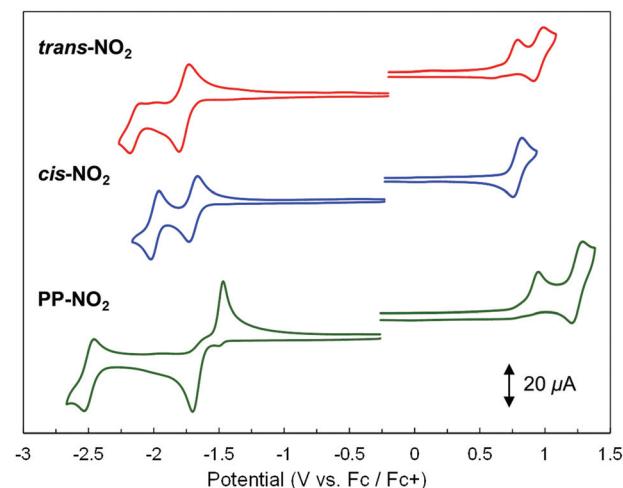


Fig. 5 Cyclic voltammograms of *trans*-NO₂, *cis*-NO₂, and PP-NO₂ (0.5 mM) in 0.1 M TEAP/acetonitrile under an Ar atmosphere (WE: GC, CE: Pt wire, RE: Ag/Ag⁺; scan rate: 100 mV s⁻¹).

irreversible anodic wave at $E_{\text{pa}} = -1.47$ V were similar to those observed for PP-MeCN (Table 4 and Fig. S10c in the ESI[†]). These redox behaviours of *trans*-NO₂ and PP-NO₂ revealed that the reduction of these complexes induced the dissociation of NO₂⁻ and the formation of MeCN-coordinated species; this behaviour was similar to that observed in the positive potential region. The electrochemical behaviours of the nitrito- κ N complexes are summarised in Scheme 3.

cis-NO displayed one reversible redox wave at $E_{1/2} = 0.05$ V and one irreversible reduction peak at $E_{\text{pc}} = -0.61$ V (Fig. 6). Comparison with similar nitrosyl compounds^{24,25} revealed that the former redox wave was attributed to the NO⁺/NO[•] redox

couple and the latter peak could be assigned to the reduction of NO[•] to NO⁻. Note that a Ru(III)/Ru(II) redox couple was not observed in the potential region between -1.6 and 1.5 V due to the low HOMO energy level originating from the poor donating ability of the NO⁺ ligand.

Cyclic voltammograms of *cis*-isomers with various ligands L are shown in Fig. 7. The redox potentials of a Ru(III)/Ru(II) redox couple for each complex were observed at 0.49, 0.79, and 1.05 V for *cis*(P,Cl)-[Ru(trpy)(Pqn)(Cl)]⁺ (*cis*-Cl), *cis*-NO₂, and *cis*-MeCN, respectively. This result indicated the increase in the HOMO

Table 3 UV-Vis absorption data ($\lambda_{\text{max}}/\text{nm}$ ($10^{-3} \epsilon/\text{M}^{-1} \text{cm}^{-1}$)) in acetonitrile, infrared data (ν/cm^{-1}), and redox potentials ($E_{1/2}/\text{V}$ vs. Fc/Fc⁺) in acetonitrile for *cis*-NO and related compounds at room temperature

Complex	λ_{max}	$\nu_{\text{N-O}}$	$E_{1/2}(\text{NO}^+/\text{NO}^\bullet)$	$E_{1/2}(\text{NO}^\bullet/\text{NO}^-)$
<i>cis</i> -NO ^a	383 (8.38), 329 (17.9), 323 ^d , 287 (23.7), 279 ^d	1929	0.05	-0.61 ^e
[Ru(trpy)(bpm)(NO)](PF ₆) ₃ ^b	362 (5.12), 331 ^d , 312 ^d , 291 (8.93), 265 (10.8)	1957	0.17	-0.47 ^f
<i>trans</i> (P,P)-[Ru(trpy)(PPh ₃) ₂ (NO)](ClO ₄) ₃ ^c	393 ^d , 330 (32)	1900	0.12	

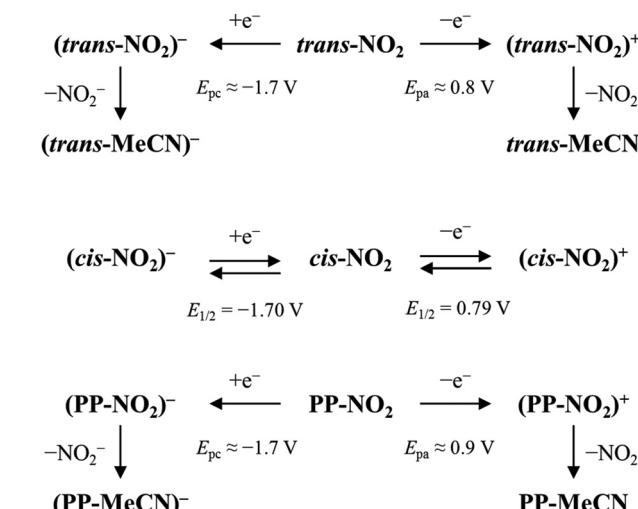
^a UV-Vis absorption data and redox potentials in ethylene glycol and γ -butyrolactone, respectively. ^b Ref. 25. ^c Ref. 24. ^d Absorption shoulder. ^e E_{pc} value for the irreversible process. ^f Data not collected.



Table 4 Redox potentials (V vs. Fc/Fc⁺) in acetonitrile for *trans*-NO₂, *cis*-NO₂, PP-NO₂, and related compounds at room temperature

Complex	Red.			Ox.	
	E(1)	E(2)	E(3)	E(1)	E(2)
<i>trans</i> -NO ₂	-1.77 ^b		-2.13 ^{e,g}	0.79 ^{c,f}	0.97 ^g
<i>cis</i> -NO ₂	-1.70	-1.99	—	0.79	—
PP-NO ₂	-1.70 ^{b,e}		-2.49 ^g	0.95 ^{c,f}	1.27 ^g
<i>trans</i> -MeCN ^a	-1.70 ^d	-1.77 ^d	-2.13 ^d	0.97	—
<i>cis</i> -MeCN ^a	—	—	—	1.05	—
PP-MeCN ^a	-1.50	-1.46	-2.49	1.27	—

^a Ref. 21. ^b These reductions induced the dissociation of NO₂⁻ and the formation of MeCN-coordinated species. ^c NO₂ was released upon these oxidation processes, and subsequent coordination of MeCN resulted in the formation of corresponding acetonitrile complexes. ^d *cis*-MeCN underwent isomerization to *trans*-MeCN upon reduction. ^e E_{pc} values for the irreversible processes. ^f E_{pa} values for the irreversible processes. ^g Redox processes correspond to MeCN-coordinated complexes.



Scheme 3 Electrochemical behaviour of nitrito- κ N complexes.

energy level by electron donation from monodentate ligands and was consistent with the UV-vis absorption spectroscopy.

Photostability of a nitrosyl complex

The photostability of *cis*-NO was investigated by UV-vis absorption spectroscopy and by using a Sievers nitric oxide analyser (NOA) to evaluate NO release. When a solution of *cis*-NO in ethylene glycol (0.05 mM) was irradiated at $\lambda_{\text{irr}} = 355$ nm, the slow spectral changes seen in Fig. 8 were observed. The quantum yields of NO release, Φ_{NO} , were quite low, 0.0048 in air saturated solution and 0.003 under helium (ESI Fig. S11 and S12[†]). These Φ_{NO} values are about two orders of magnitude smaller than that measured by Silva *et al.* for the photolysis of the analogous ruthenium nitrosyl complex, [Ru(tpy)(bpy)-(NO)]³⁺ (bpy = 2,2'-bipyridine).²⁷ Notably, exhaustive photolysis led to a nearly quantitative conversion to a spectrum ana-

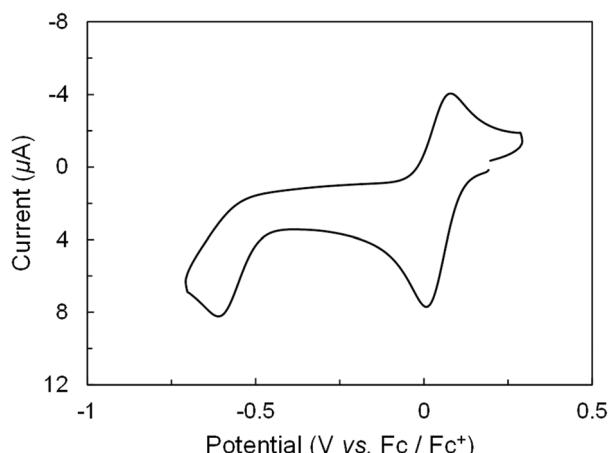


Fig. 6 Cyclic voltammogram of *cis*-NO (0.5 mM) in 0.1 M TEAP/γ-butyrolactone under an Ar atmosphere (WE: GC, CE: Pt wire, RE: Ag/Ag⁺; scan rate: 100 mV s⁻¹).

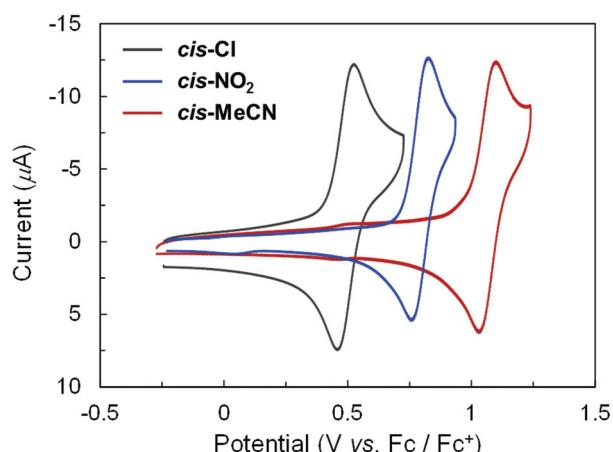


Fig. 7 Cyclic voltammograms of *cis*-Cl, *cis*-NO₂, and *cis*-MeCN (0.5 mM) in 0.1 M TEAP/acetonitrile under an Ar atmosphere (WE: GC, CE: Pt wire, RE: Ag/Ag⁺; scan rate: 100 mV s⁻¹).

logous to that of *trans*-L (L = solvent, see Fig. S13 in the ESI[†]), which suggests that the photodissociation of NO and the isomerization of the complex from *cis* to *trans* form proceeds in a step-wise manner. The result is consistent with the multi-step spectral change shown in Fig. 8. It should further be noted that a Ru(II) complex, rather than the Ru(III) species is obtained upon NO photodissociation from *cis*-NO (ESI Fig. S13[†]). There are several possible explanations, one being that the Ru(III) intermediate is readily reduced by the solvent. Another is that the principal photo-reaction is release of NO⁺ rather than NO²⁷ owing to phosphine stabilization of the low-valent Ru(II) state. However, this question was not explored in greater detail.

Substitution lability of nitrogen oxide

The substitution lability of the monodentate ligand L in the [Ru(TL)(BL)(L)]ⁿ⁺-type complexes is an important factor in



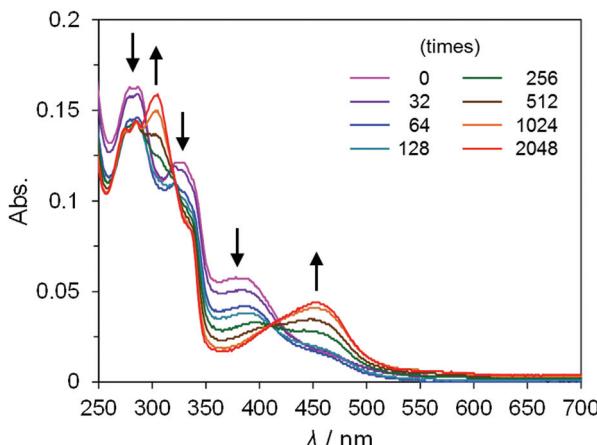


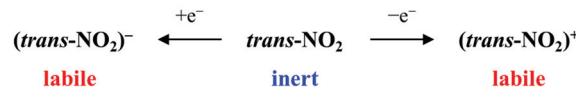
Fig. 8 UV-Vis absorption spectra of *cis*-NO in ethylene glycol at room temperature during photolysis using a Nd/YAG laser operating at 355 nm. "Times" indicates the number of the laser pulses used to irradiate the sample.

determining the reactivity of the complexes in various catalytic and photo-induced reactions. Several experimental results described above enabled us to discuss in detail the lability of the monodentate ligand in the complexes. First, the reaction of *cis*-NO₂ with HPF₆ afforded the desired *cis*-NO. However, similar reactions of *trans*-NO₂ and PP-NO₂ resulted in the formation of *trans*-MeCN and PP-MeCN *via* the dissociation of a monodentate labile ligand, N(O)OH or NO⁺ (probably the former). Second, UV-vis absorption spectroscopy revealed that the nitrito ligands of *trans*-NO₂, *cis*-NO₂, and PP-NO₂ did not dissociate, even in strongly coordinating solvents such as acetonitrile, whereas ligand exchange reactions of *trans*-MeCN and PP-MeCN easily occurred under analogous conditions (Fig. S14 in the ESI†). *cis*-NO was not stable in coordinating solvent and was easily converted to a solvent-coordinated form (Fig. S4 in the ESI†).

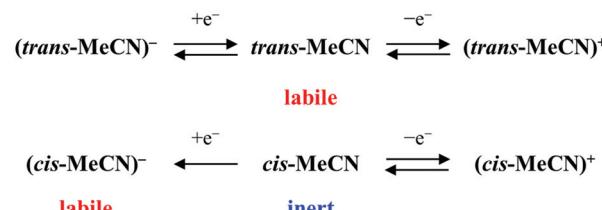
The difference in lability of the oxidised and reduced state can also be clarified by the results of the electrochemical measurements. In the one-electron oxidised states, *trans*-NO₂ and PP-NO₂ were labile and were converted to the solvent-coordinated forms, *trans*-MeCN and PP-MeCN, respectively. By contrast, *cis*-NO₂ was inert during the oxidation process, and a reversible redox wave was observed in the electrochemical measurement. Similarly, in the reduced states, the nitrito ligands of *trans*-NO₂, and PP-NO₂ easily dissociated, although *cis*-NO₂ was stable during the whole electrochemical process. However, this stability of *cis*-NO₂ was quite different from that of *cis*-MeCN: the acetonitrile ligand of *cis*-MeCN became labile upon reduction, and the dissociation of the ligand resulted in the isomerisation of *cis*-MeCN to *trans*-MeCN.²¹ The stability of the monodentate labile site for each complex is shown in Scheme 4.

The difference in the lability of these complexes can be explained by considering the following factors. First, the σ-donor character of the phosphine group significantly elongates the bond length between the ruthenium centre and

(a) NO₂ complex



(b) MeCN complex



Scheme 4 Changes in lability upon oxidation or reduction.

the ligand *trans* to the phosphine group. This *trans* influence of the phosphine group was clearly observed in the X-ray structure for the series of nitrito- κ N complexes; the bond distances between the ruthenium and nitrogen atom of the nitrite ligand are 2.141(3), 2.124(2), and *ca.* 2.03 Å for *trans*-NO₂, PP-NO₂, and *cis*-NO₂, respectively. Therefore, the *trans*-isomers and PP complexes exhibited greater lability compared with the corresponding *cis*-isomers. Second, the electron donation from labile ligands can stabilise Ru-L bonds. The donating ability of labile ligands was confirmed by the comparison of the HOMO energy levels obtained from the electrochemical measurements of the *cis*-isomers and follows the order NO₂⁻ > MeCN > NO⁺ and was in accordance with the stability of the complexes. Third, oxidation decreases the electron density of the Ru centre, and the π back-donating ability of Ru centres should be weakened. DFT calculations revealed that π back-donation from Ru to the nitrito ligand occurs and stabilises the Ru-L bond (Fig. S6 in the ESI†). Finally, the reduction of the complexes stabilises the five-coordinated species, as rationalised for the Ru(II)-MeCN complexes in our previous report.²¹ The formation of five-coordinated species in MeCN results in ligand exchange in *trans*-NO₂ and PP-NO₂ or isomerisation of *cis*-MeCN to *trans*-MeCN, whereas no observable chemical process exists in the case of *trans*-MeCN and PP-MeCN. These results suggest that the (1) number and position of P atom(s), (2) coordinating ability of the monodentate ligand, and (3) oxidation state of the complexes are all factors in defining the lability of complexes.

Conclusions

This study describes the syntheses, crystal structures and spectroscopic and electrochemical properties of a series of phos-



phine-substituted ruthenium(II) polypyridine complexes with nitrogen oxides. Three nitrito- κN complexes, *trans*-NO₂, *cis*-NO₂, and PP-NO₂, were synthesised by the reaction of the corresponding acetonitrile complex with NaNO₂ in an ethanol/water mixed solution, and a nitrosyl complex, *cis*-NO, was obtained by the reaction of *cis*-NO₂ with HPF₆ in acetone. Crystallographic, spectroscopic, and electrochemical analyses for these complexes revealed that the σ -donating and π -accepting characters of the phosphine ligands clearly affected the d σ and d π orbitals of the ruthenium centre, respectively. The investigation of the substitution lability of the monodentate ligand of each complex suggested that the (1) number and position of the phosphine groups, (2) coordinating ability of the monodentate ligand, and (3) oxidation state of the metal centre are all factors in determining the lability of the complex. As a further extension of our studies, investigations on various catalytic and photo-induced reactions of the phosphine-substituted ruthenium(II) polypyridine complexes are in progress in our laboratories.

Experimental

Materials

NaNO₂ was purchased from Kanto Chemical Co., Inc. NH₄PF₆ and HPF₆ were purchased from Wako Pure Chemical Industries, Ltd. All solvents and reagents were of the highest quality available and were used as received. *cis*(P,Cl)-[Ru(trpy)-(Pqn)Cl]PF₆ (*cis*-Cl), *trans*(P,MeCN)- and *cis*(P,MeCN)-[Ru(trpy)-(Pqn)(MeCN)](PF₆)₂ (*trans*-MeCN and *cis*-MeCN), and [Ru(trpy)-(dppbz)(MeCN)](PF₆)₂ (*PP*-MeCN) were prepared following methods found in the literature.²¹

Measurements

¹H and ³¹P{¹H} NMR spectra were recorded at room temperature on a JEOL JNM-LA500 spectrometer using tetramethylsilane as an internal reference for the ¹H NMR spectra and phosphoric acid as an external reference for the ³¹P{¹H} NMR spectra. UV-vis absorption spectra were obtained on a Shimadzu UV-2450SIM spectrophotometer at room temperature. Elemental analyses were carried out on a Yanagimoto MT-5 elemental analyser. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. ESI-TOF mass spectra were recorded on a JEOL JMS-T100LC mass spectrometer. All the ESI-TOF mass spectrometric measurements were recorded in the positive ion mode at a cone voltage of 20 V. Typically, each sample solution was introduced in the spectrometer at a flow rate of 10 mL min⁻¹ using a syringe pump. Cyclic voltammograms were measured at room temperature on a BAS ALS Model 650DKMP electrochemical analyser in acetonitrile ([complex] = 0.5 mM; 0.1 M tetraethylammonium perchlorate (TEAP)). A glassy carbon disk, platinum wire, and Ag/Ag⁺ electrode (Ag/0.01 M AgNO₃) were used as the working, auxiliary, and reference electrodes, respectively. The redox potentials of the samples were

calibrated against the redox signal for the ferrocene/ferrocenium (Fc/Fc⁺) couple. The photochemical experiments shown in Fig. 8 were made using a photolysis apparatus consisting of a LS-2134UTF Nd/YAG laser (Tokyo Instruments, INC.) with excitation provided by the third harmonic at λ = 355 nm. The pulse width was 5 ns, the beam diameter incident on the sample was 6 mm, and the repetition rate was 5 Hz.

Synthetic procedures

Synthesis of *trans*(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]PF₆ (*trans*-NO₂). A mixture of *trans*-MeCN (26.8 mg, 0.0252 mmol) and NaNO₂ (38.8 mg, 0.562 mmol) in ethanol (4 cm³)/water (4 cm³) was heated at 100 °C for 3 hours and then cooled to room temperature. Acetonitrile (2 cm³) and a NH₄PF₆ (188.4 mg, 1.16 mmol)/water (2 cm³) solution was added to the above-mentioned solution. The resulting red solution was concentrated to *ca.* 5 cm³ under reduced pressure. The red product was collected by filtration and washed with water and diethyl ether. Yield 19.1 mg (0.0216 mmol, 86%). Single red crystals suitable for X-ray crystallography were grown by the slow diffusion of diethyl ether into a mixture of methanol and a few drops of acetonitrile solution of *trans*-NO₂. ESI-TOF MS (positive ion, acetonitrile): *m/z* 694 ([Ru(trpy)(Pqn)(NO₂)]⁺). ¹H NMR (CD₃CN): δ 6.56 (t, 2H, *J* = 9.0 Hz), 6.98 (t, 4H, *J* = 7.0 Hz), 7.14 (t, 2H, *J* = 7.0 Hz), 7.21 (t, 2H, *J* = 8.0 Hz), 7.65 (d, 2H, *J* = 5.0 Hz), 7.80 (t, 2H, *J* = 8.0 Hz), 7.91 (m, 3H), 8.03 (d, 2H, *J* = 8.0 Hz), 8.09 (t, 1H, *J* = 7.5 Hz), 8.23 (d, 2H, *J* = 8.0 Hz), 8.46 (d, 1H, *J* = 7.0 Hz), 8.75 (d, 1H, *J* = 8.0 Hz), 9.93 (d, 1H, *J* = 5.0 Hz). ³¹P{¹H} NMR (CD₃CN): δ 53.10 (s). FT-IR: ν_s (NO₂) 1304, ν_{as} (NO₂) 1349 cm⁻¹. Anal. Found: C, 48.50; H, 3.59; N, 8.22. Calcd for C₃₆H₃₂F₆N₅O_{4.5}P₂Ru (*trans*-NO₂·2.5H₂O): C, 48.93; H, 3.65; N, 7.93.

Synthesis of *cis*(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]PF₆ (*cis*-NO₂). This complex was prepared from *cis*-MeCN (26.0 mg, 0.0250 mmol) instead of *trans*-MeCN by a method similar to that for *trans*-NO₂. Yield 19.5 mg (0.0221 mmol, 88%). ESI-TOF MS (positive ion, acetonitrile): *m/z* 694 ([Ru(trpy)(Pqn)(NO₂)]⁺). ¹H NMR (CD₃CN): δ 6.81 (t, 2H, *J* = 6.5 Hz), 7.06 (m, 1H), 7.41 (d, 2H, *J* = 5.5 Hz), 7.52 (m, 4H), 7.63 (t, 2H, *J* = 7.5 Hz), 7.73 (m, 4H), 7.84 (t, 2H, *J* = 8.0 Hz), 7.92 (d, 1H, *J* = 5.5 Hz), 7.97 (t, 1H, *J* = 7.5 Hz), 8.18 (d, 1H, *J* = 8.0 Hz), 8.23 (d, 1H, *J* = 8.0 Hz), 8.36 (m, 3H), 8.55 (d, 2H, *J* = 8.0 Hz) 8.78 (t, 1H, *J* = 8.0 Hz). ³¹P{¹H} NMR (CD₃CN): δ 54.06 (s). FT-IR: ν_s (NO₂) 1286, ν_{as} (NO₂) 1339 cm⁻¹. Anal. Found: C, 50.38; H, 3.44; N, 8.19. Calcd for C₃₆H₂₉F₆N₅O₃P₂Ru (*cis*-NO₂·H₂O): C, 50.47; H, 3.41; N, 8.18.

Synthesis of *cis*(P,NO₂)-[Ru(trpy)(Pqn)(NO₂)]BPh₄ (*cis*-NO₂′). This complex was prepared by a method similar to that for *cis*-NO₂ with an excess of NaBPh₄ instead of NH₄PF₆. The product was recrystallised from dichloromethane and a small amount of acetonitrile/diethyl ether to afford orange-red crystals of *cis*-NO₂′. Anal. Found: C, 70.54; H, 4.72; N, 6.92. Calcd for C₆₀H₄₈BN₅O_{2.5}PRu (*cis*-NO₂′·0.5H₂O): C, 70.52; H, 4.73; N, 6.85.



Synthesis of *cis*(P,NO)-[Ru(trpy)(Pqn)(NO)][PF₆]₃ (*cis*-NO₂). (22.4 mg, 0.0261 mmol) was dissolved in acetone (1 cm³). An excess of 60% HPF₆ acid solution was added dropwise until the solution changed colour from red to yellow with the shielding of light in an ice-water bath. The resulting yellow solution was concentrated under reduced pressure, and 10 cm³ of diethyl ether was added to precipitate the product. Yield 27.4 mg (0.0223 mmol, 85%). ¹H NMR (acetone-*d*₆): δ 7.47 (t, 2H, *J* = 7.0 Hz), 7.66 (m, 1H), 7.80 (d, 2H, *J* = 6.0 Hz), 7.86 (m, 4H), 8.01 (t, 2H, *J* = 7.5 Hz), 8.12 (dd, 4H, *J* = 7.5, 13.0 Hz), 8.42 (t, 1H, *J* = 7.5 Hz), 8.49 (m, 2H), 8.55 (m, 1H), 8.80 (d, 1H, *J* = 8.0 Hz), 9.01 (m, 3H), 9.10 (m, 1H), 9.22 (m, 3H). ³¹P {¹H} NMR (acetone-*d*₆): δ 54.23 (s). FT-IR: ν _s(NO) 1929 cm⁻¹. Anal. Found: C, 35.03; H, 2.95; N, 5.59. Calcd for C₃₆H₄₀F₁₈N₅O_{7.5}P₄Ru (*cis*-NO₂·6.5H₂O): C, 35.16; H, 3.28; N, 5.70.

Synthesis of [Ru(trpy)(dppbz)(NO₂)][PF₆] (PP-NO₂**).** This complex was prepared from **PP-MeCN** (31.5 mg, 0.0263 mmol) instead of **trans-MeCN** by a method similar to that for **trans-NO₂**. Yield 22.9 mg (0.0227 mmol, 86%). Single orange crystals suitable for X-ray crystallography were grown through the slow diffusion of diethyl ether into a mixture of methanol and a few drops of acetonitrile solution of **PP-NO₂**. ESI-TOF MS (positive ion, acetonitrile): *m/z* 827 ([Ru(trpy)(dppbz)(NO₂)]⁺). ¹H NMR (CD₃CN): δ 6.50 (m, 4H), 6.78 (m, 2H), 6.88 (m, 4H), 7.08 (d, 2H, *J* = 5.5 Hz), 7.17 (m, 2H), 7.45 (t, 4H, *J* = 7.5 Hz), 7.61 (m, 7H), 7.77 (m, 3H), 7.87 (t, 1H, *J* = 7.5 Hz), 8.03 (d, 2H, *J* = 8.0 Hz), 8.23 (m, 3H), 8.39 (t, 1H, *J* = 7.5 Hz). ³¹P {¹H} NMR (CD₃CN): δ 62.65 (d, ²J_{P-P} = 14.2 Hz), 68.59 (d, ²J_{P-P} = 14.2 Hz). FT-IR: ν _s(NO₂) 1311, ν _{as}(NO₂) 1354 cm⁻¹. Anal. Found: C, 53.62; H, 4.05; N, 5.46. Calcd for C₄₅H₃₉F₆N₄O₄P₃Ru (**PP-NO₂**·2H₂O): C, 53.63; H, 3.90; N, 5.56.

X-ray crystallography

The X-ray data collection and processing was performed on a Kappa APEX II CCDC diffractometer by using graphite-monochromated Mo-K α radiation (0.71075 Å) for **trans-NO₂** and **PP-NO₂**. Single-crystal X-ray diffraction measurement of **cis-NO₂'** was performed with a RAXIS-RAPID Imaging Plate diffractometer equipped with confocal monochromated Mo-K α (0.71075 Å) radiation, and the data were processed using RAPID-AUTO (Rigaku). The structure was solved by the direct methods using SIR-92²⁸ and refined on *F*² with the full-matrix least squares technique using SHELXL-2014.²⁹ All non-hydrogen atoms were refined anisotropically. Molecular graphics were generated using ORTEP-3 for Windows³⁰ and POV-RAY.³¹ A summary of the crystallographic data and structure refinement parameters is given in Table 1.

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: deposition numbers CCDC 1040452, 1040453, and 1040454 for **trans-NO₂**, **cis-NO₂'**, and **PP-NO₂**, respectively.

DFT calculations

Calculations were performed using the DFT method implemented in the Gaussian 09 package.³² The structures

were fully optimised using the hybrid B3LYP method, which uses Becke's three-parameter exchange functional³³ with the correlation energy functional of Lee, Yang, and Parr.³⁴ All calculations were performed using the standard double- ζ type LANL2DZ basis set^{35a-c} or SDD basis set^{35d} implemented in Gaussian 09, without adding any extra polarisation or diffuse functions. The LANL2DZ basis set also uses a relativistic effective core potential (RECP) for the Ru atom to account for the scalar relativistic effects of the inner 28 core electrons ([Ar] 3d¹⁰). All calculations were performed using the polarisable continuum model (PCM)³⁶ to compute the structures in acetonitrile media. All stationary points were characterised as minima of the potential energy surface by their harmonic vibrational frequencies. The free energies at 298 K and 1 atm were obtained through thermochemical analysis of the frequency calculation using the thermal correction to Gibbs free energy as implemented in Gaussian 09. The excited states were calculated using the TDDFT³⁷ method within the Tamm-Danoff approximation as implemented in Gaussian 09. These calculations employ the hybrid B3LYP functional along with the basis sets described above. A minimum of 100 excited states was computed in each calculation. To obtain the simulated spectrum of each species, transition energies and oscillator strengths were interpolated by a Gaussian convolution with a common σ value of 0.2 eV.

Quantum yield measurements

Nitric oxide was detected and analysed using a GE Sievers model 280i nitric oxide analyser (NOA).³⁸ Known volumes of the gases from the solution headspace were injected into the NOA purge vessel, and these gases were entrained to the detector using helium or medical grade air. The NO present in the sample was quantified using a calibration curve generated from the reaction of NaNO₂ with acidic KI. Chemical actinometry was performed with ferric oxalate solutions.³⁹ The photolysis source was the output from a 200 W high-pressure mercury lamp passed through an IR filter and collimated with lenses. An appropriate interference filter was used to select the desired λ_{irr} . A shutter shielded the sample from the arc lamp. A sample of a known volume in a 1 cm square cuvette with a magnetic stirring bar was irradiated for determined time periods.⁴⁰ The NO quantum yields (Φ_{NO}) were calculated based on the nitric oxide release measured using the NOA.

Acknowledgements

This work was supported by a Grant-in-Aid for Young Scientists (A) (No. 25708011) (to S.M.), a Grant-in-Aid for Challenging Exploratory Research (No. 26620160) (to S.M.), and a Grant-in-Aid for Young Scientists (A) (No. 15H05480) (to M.K) from the Japan Society for the Promotion of Science. This work was also supported by a Grant-in-Aid for Scientific Research on Innovative Areas "AnApple" (No. 25107526). Studies at UCSB were supported by a US National Foundation Grant (CHE-1058794 and CHE-1405062). We thank Dr Guang Wu of UCSB for the



X-ray diffraction studies and Dr John Garcia of UCSB for confirming photochemical results.

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