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Triphenylphosphine Photorelease and Induction of Catalytic Activity from Ruthenium-Arene Complexes Bearing a Photoswitchable *o*-Tosylamide Azobenzene Ligand

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Supporting Information Placeholder

ABSTRACT: The reactivity of cationic arene ruthenium complexes bearing photoswitchable *o*-tosylamide azobenzene ligand towards various phosphorus nucleophiles was investigated. The resulting phosphine-ruthenium complexes containing azobenzene ligand were isolated as the *Z* isomer. Under appropriate reaction conditions, quantitative triphenylphosphine photorelease from the complex was achieved through *Z*→*E* isomerization of the ligand. This process was applied to the photo-initiation of catalytic aza Morita-Baylis-Hillman reaction.

INTRODUCTION

(η^6 -Arene)Ru^{II} complexes have recently emerged as interesting candidates in various fields such as catalysis,¹⁻⁶ medicine^{1,2,5,7-9} and supramolecular chemistry.^{2,5,10} In this context, their photochemistry has been well-studied, and the displacement of arene ligand upon UV illumination has been exploited for both synthetic purposes and photocontrolled activation in a biological environment (Figure 1a).¹¹⁻¹⁷ Light-induced Ru^{II}-nitrogen bond dissociation with pyridine-containing complexes has also been extensively investigated, especially in the context of spatial and temporal control of metallodrugs activity (Figure 1b).^{2,18-26} In contrast, photoswitchable arene ruthenium complexes have been only scarcely reported. While an early example of reversible coordination of azobenzene to bimetallic species was described by Kurosawa *and coll.* in 2000,^{27,28} our group recently reported in 2015 the first utilization of *o*-sulfonamide azobenzenes as photoswitchable ligands, which exhibit an exocyclic N=N bond directly coordinated to the metal center.²⁹ In the continuation of this study, we now wish to report our investigations on the reactivity of such complexes and highlight the control exerted by the geometry (*E* or *Z*) of azobenzene ligand (Figure 1c).

by halogen abstraction from a chloro-ruthenium complex using a silver salt, the chloro complex containing hexamethyl benzene ligand *E*-1²⁹ was treated with AgPF₆ in acetone at rt,³⁰ followed by evaporation and washing with CHCl₃ (in open vessel) to yield 77% of cationic aqua complex *E*-2 (Scheme 1). The presence of aqua ligand was revealed by a characteristic broad signal at 6.65 ppm observed by ¹H NMR spectroscopy in (CD₃)₂CO and two broad bands at 3660 and 3475 cm⁻¹ in the IR spectrum.³⁰ This compound exhibited moderate stability in solution, but could be stored in the solid state at 0°C for months without any notable degradation. Analogous chloro complexes containing benzene or *p*-cymene ligand²⁹ readily reacted under the same reaction conditions, but the resulting aqua complexes were too unstable to be isolated with satisfactory purity.

RESULTS AND DISCUSSION

Formation of Cationic Aqua Complex *E*-2 and its Reaction with Phosphorus Ligands. Following a classical route to reactive cationic ruthenium complexes

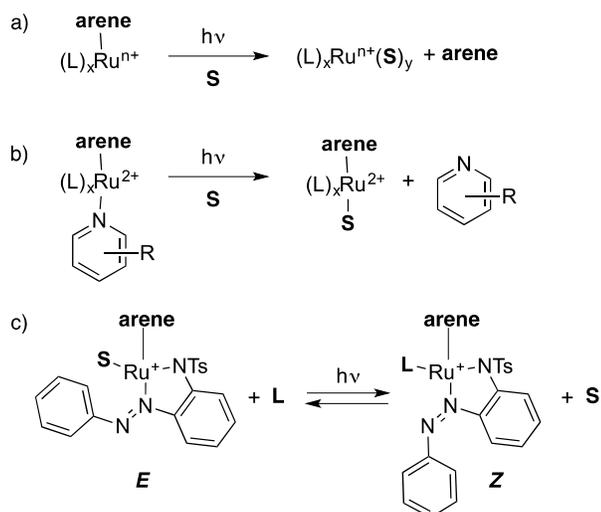


Figure 1. Photo-induced processes involving ruthenium-arene complexes: displacement of arene ligand (a), pyridine release (b), reversible ligand/solvent exchange mediated by $E \rightarrow Z$ photoisomerization of azobenzene ligand (c). L and S refer to ligand and coordinating solvent, respectively.

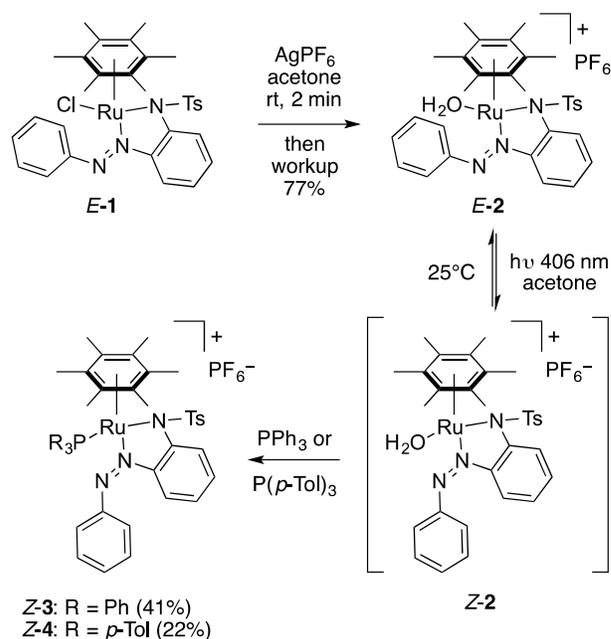
The absorption spectrum of a solution of aqua complex $E-2$ in acetone (μM range concentration) showed a strong band at 375 nm with a shoulder around 445 nm which was assigned to the intra-ligand $\pi \rightarrow \pi^*$ transition (by analogy with the parent chloro compound²⁹), and a weaker broad band centered at 564 nm assigned to the metal-ligand charge transfer transition (Figure S1). The spectrum evolved within a few minutes in the dark at rt, thus revealing rapid transformation of $E-2$ under these conditions. Surprisingly, NMR experiments performed in acetone- d_6 at a significantly higher concentration (mM range) did not reveal any notable degradation of $E-2$ after a few days. Furthermore, irradiation at 406 nm³¹ for 30 min under these conditions (for $E \rightarrow Z$ isomerization) did not result in any evolution of the ^1H NMR spectrum, thereby suggesting a fast $Z \rightarrow E$ relaxation of compound 2. This observation, which precludes determination of photostationary state composition, is in sharp contrast with the reversible photo-isomerization previously reported for chloro complex $E-1$ ($t_{1/2}(Z) = 5.44$ min in acetone).²⁹

Treatment of a solution of $E-2$ (1.8 mM in acetone) with an excess of triphenylphosphine (10 equiv.) at rt in the dark did not lead to any reaction, while illumination at 406 nm (40 mW/cm^2) cleanly induced the formation of a novel cationic complex $Z-3$, isolated in 41% yield (Scheme 1). This moderate yield can be explained by the fact that photo-induced ligand exchange is reversible (see below), thus requiring removal of unreacted starting material. Complex $Z-3$ is indeed obtained after several purification steps, including column chromatography followed by trituration with toluene, dissolution in CHCl_3 and filtration to remove unreacted aqua complex, and a final column chromatography to remove toluene molecules trapped in the solid.

The structure of $Z-3$ was unambiguously assessed by ^1H , ^{13}C and ^{31}P NMR spectroscopy, HRMS, elemental analysis and X-ray crystallographic analysis (Figure 3 and discussion below). ^{31}P NMR spectrum showed a signal at 32.4 ppm corresponding to coordinated PPh_3 and ^1H NMR spectroscopy showed a doublet at 8.53 ppm ($J = 9.2$ Hz), considerably shifted downfield as compared to the other aromatic protons (ranging between 7.78 and 6.38 ppm). This signal was attributed to one of the C-H groups located at the ortho position of the $\text{N}=\text{N}$ bond (Figure 3), which undergoes the deshielding effect of the aromatic ring bearing N -tosyl group.

A similar reactivity pattern was observed with $\text{P}(p\text{-Tol})_3$ under illumination at 406 nm, yielding $Z-4$ in 22% yield after several purification steps. Though crystals suitable for X-ray crystallographic analysis were not obtained for this complex, spectroscopic data matched those reported for $Z-3$, with ^1H and ^{31}P NMR spectrum showing a doublet at 8.51 ppm ($J = 9.2$ Hz) and a signal at 30.9 ppm, respectively, and similar absorption spectrum (Figure 4). Interestingly, reaction of $E-2$ with PCy_3 either in the dark or upon illumination at 406 nm, did not lead to the formation of any novel compound.

Scheme 1. Synthesis of Aqua Complex $E-2$ and its Conversion into $Z-3$ and $Z-4$ upon Illumination

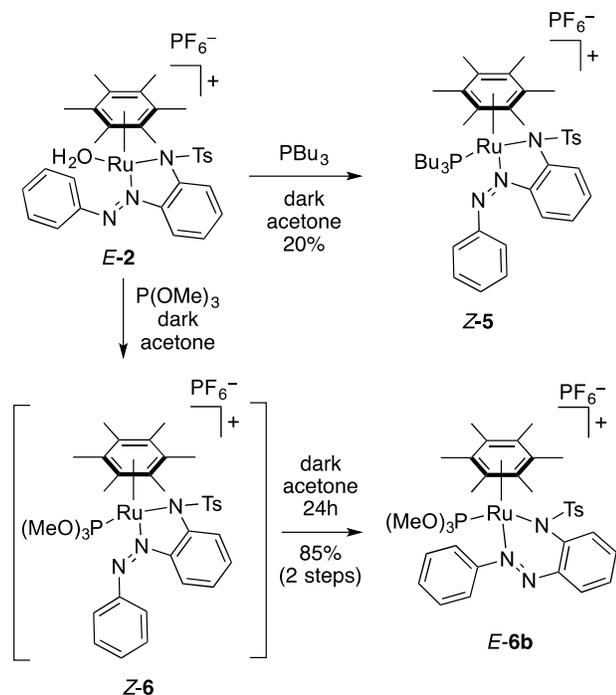


Reaction of PBU_3 with aqua complex $E-2$ was fast at rt without a need for illumination, yielding a novel product within a few minutes (Scheme 2). The structure of this complex was unambiguously ascribed to $Z-5$ by X-ray crystallographic analysis, which also revealed significant disorder around the PBU_3 ligand (Figure 3 and discussion below). The low isolated yield (20%) is in contradiction with the efficiency of the reaction, as revealed by inspection of the NMR spectrum of the crude mixture, and probably originated from a loss of material during purification. ^{31}P NMR spectroscopy shows a signal at -19.8

ppm, corresponding to coordinated PBU_3 , while a characteristic doublet at 8.27 ppm ($J = 8.7$ Hz) was present in the ^1H NMR spectra. The aliphatic hydrogen atoms of PBU_3 moiety appeared as broad signals between 1.94 and 0.74 ppm, and five hydrogen atoms of the azobenzene ligand appeared as a broad signal between 7.68 and 7.43 ppm. This observation presumably originates from the existence of slowly interconverting conformers in solution, consistent with the disorder observed in the solid state.

Using P(OMe)_3 in the dark under otherwise identical conditions resulted in a similar reactivity pattern leading to complex **Z-6**, as confirmed by apparition of a deshielded doublet at 8.19 ppm ($J = 8.7$ Hz) in the ^1H NMR spectrum, analogously to **Z-3**, **Z-4** and **Z-5** (Figure 2). This complex could however not be isolated as it isomerizes to **E-6b** within a few hours under the reaction conditions (Scheme 2). This transformation was revealed in the ^1H NMR spectrum by the disappearance of the signal at 8.19 ppm and the appearance of a novel set of signals between ca. 7.90 and 6.20 ppm (Figure 2). The structure of **E-6b**, showing a coordination pattern in which the Ru center is involved in a six-membered chelate ring with an endocyclic $\text{N}=\text{N}$ bond, was unambiguously assessed by X-Ray crystallographic analysis (Figure 3 and discussion below).

Scheme 2. Reaction of Aqua Complex **E-2** with PBU_3 and P(OMe)_3 in the Dark



The molecular structures determined by X-Ray diffraction of single crystals of **Z-3**, **Z-5** and **E-6b** are represented in Figure 3 and selected bond lengths and angles are given in Table 1. These complexes revealed a classical piano-stool geometry at the Ru center, with

ruthenium-arene centroid distances ranging between 1.783 and 1.815 Å, which are slightly elongated as compared to the corresponding neutral chloro complexes (ca. 1.71 Å).²⁹ The Ru-N₁ distance is around 2.13 Å for all complexes, while the Ru-N₂ bond is longer in **E-6b** (2.103 Å) than in **Z-3** and **Z-5** (2.025-2.037 Å) as a consequence of the different coordination pattern. This does not affect $\text{N}=\text{N}$ bond length (N_2-N_3), which remains in the range 1.258-1.275 Å. The Ru-PPh₃ distance in **Z-3** (2.393 Å), which is slightly longer than the Ru- PBU_3 distance in **Z-5** (2.359 Å), is in agreement with the trends observed with other complexes³²⁻³⁴; as expected, the Ru- P(OMe)_3 bond length in **E-6b** is significantly shorter (2.292 Å).³⁵⁻³⁷ In all structures, the two aromatic rings of azobenzene are significantly twisted, with α angles ranging between 59.41° and 65.43°; notably the values for **Z-3** and **Z-5** are in good agreement with the one calculated by DFT (64.62°) for the corresponding chloro complex **Z-1**.²⁹

Taken together, the results described above concerning the reactivity of **E-2** clearly evidence a strong impact of the size of the P-ligand, as measured by its Tolman cone angle θ (Table 2).³⁸ Indeed, the more sterically demanding PCy_3 ($\theta = 170^\circ$) did not react with aqua complex **E-2** (in the dark) or **Z-2** (upon illumination). Under identical conditions, PPh_3 and $\text{P}(p\text{-Tol})_3$ ($\theta = 145^\circ$ for both) easily reacted with the less hindered **Z-2** isomer, while no reaction was observed with **E-2**. Finally, the less sterically demanding PBU_3 and P(OMe)_3 ($\theta = 132^\circ$ and 107° , respectively) underwent rapid reaction with complex **E-2**, without the need for illumination. Isolation of complex **Z-5** and the spectroscopic evidences for the transient formation of **Z-6** upon reaction of **E-2** in the dark with PBU_3 and P(OMe)_3 , respectively, clearly support a chemically-promoted *E*→*Z* azobenzene isomerization. Based on literature precedents involving nucleophilic addition of tertiary phosphine to the $\text{N}=\text{N}$ double bond of azobenzene derivatives³⁹⁻⁴¹, we propose a mechanism in which **E-2** undergoes nucleophilic attack at the less hindered nitrogen atom, leading to zwitterion **I** (Scheme 3). The latter could undergo rotation about the single $\text{N}-\text{N}$ bond (species **II**) followed by PR_3 elimination, thus leading to **Z-2** then to **Z-5** or **Z-6**. This proposal agrees well with the fact that only the less sterically demanding PBU_3 and P(OMe)_3 could approach the $\text{N}=\text{N}$ bond in **E-2** and form key intermediate **I**, though stereo-electronic effects could also account for the observed reactivity (Scheme 3).

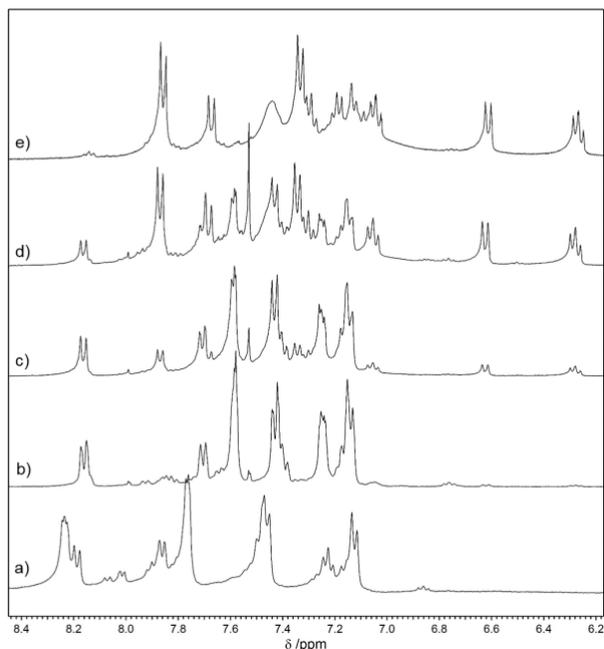


Figure 2. Portion of ^1H NMR spectrum in $(\text{CD}_3)_2\text{CO}$ of a solution of *E*-2 (a); *E*-2 and $\text{P}(\text{OMe})_3$ immediately after

addition of $\text{P}(\text{OMe})_3$ (b), after 4 h at rt (c), after 24 h at rt (d); and ^1H NMR spectrum of *E*-6b (e).

Table 1. Selected bond lengths (\AA) and angles (deg) for complexes *Z*-3, *Z*-5 and *E*-6b.

	<i>Z</i> -3	<i>Z</i> -5	<i>E</i> -6b
Ru-N1	2.138(5)	2.130(4)	2.135(2)
Ru-N2	2.037(5)	2.025(4)	2.103(2)
Ru-P	2.3930(15)	2.3591(14)	2.2921(6)
Ru-cent ^a	1.815	1.788	1.783
N2-N3	1.258(7)	1.275(5)	1.258(3)
N2-Ru-N1	77.11(19)	76.56(14)	80.17(8)
N2-Ru-P	86.08(13)	90.02(11)	88.44(6)
N1-Ru-P	93.99(13)	89.34(12)	93.51(6)
N2-Ru-N1	77.11(19)	76.56(14)	80.17(8)
α^b	62.22	59.41	65.43

^a cent = centroid of arene moiety. ^b α = angle between the planes of the two aromatic rings of azobenzene ligand.

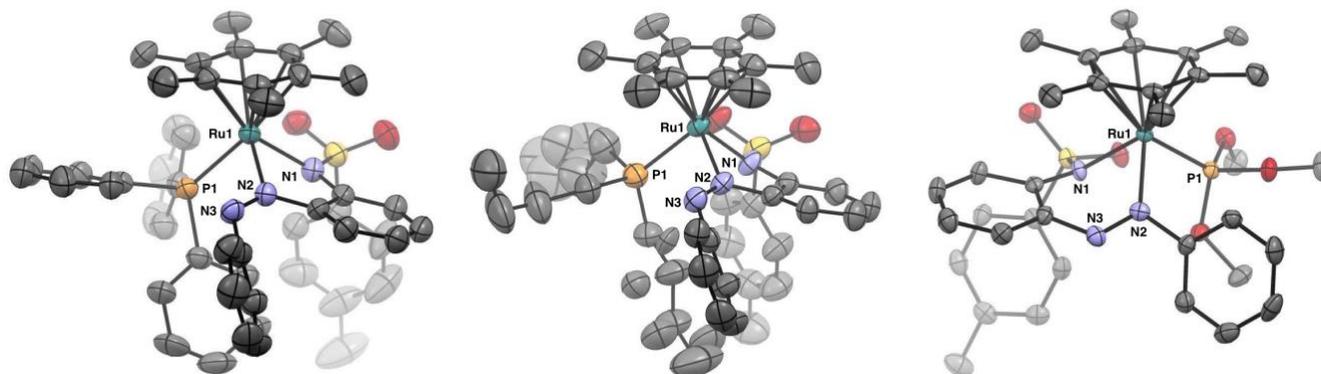
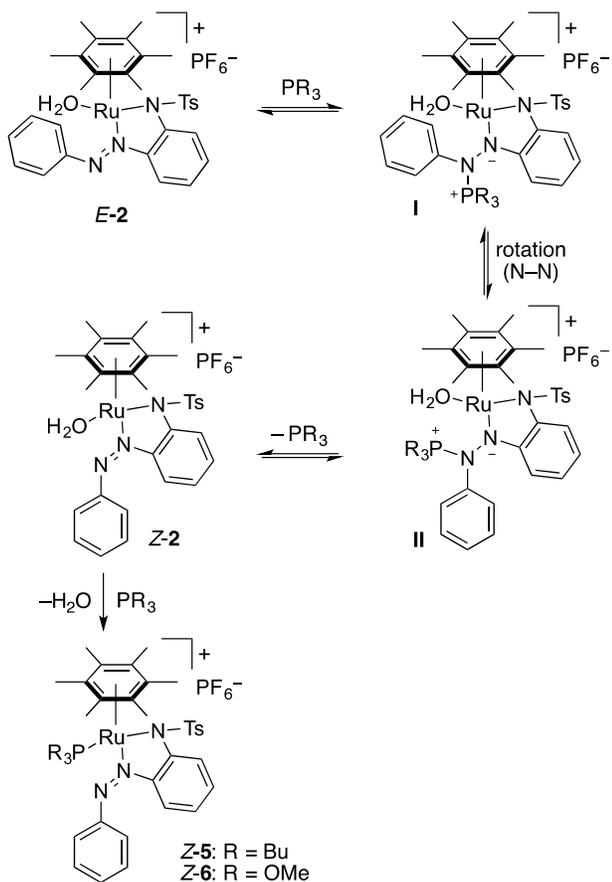


Figure 3. ORTEP representation (thermal ellipsoids drawn at 50% probability level) of complexes *Z*-3 (left), *Z*-5 (middle) and *E*-6b (right) with atom numbering scheme. The hydrogen atoms, PF_6^- anion and one CH_2Cl_2 molecule for *Z*-3 have been removed for clarity.

Scheme 3. Tentative mechanistic proposal for PBU_3 and $\text{P}(\text{OMe})_3$ -promoted azobenzene isomerization and formation of *Z*-5 and *Z*-6 in the dark.



Ligand	θ^a	Conditions ^b	Product ^c	Yield
PCy ₃	170°	dark	n.r.	-
		hv 406 nm	n.r.	-
PPh ₃	145°	dark	n.r.	-
		hv 406 nm	Z-3	41%
P(<i>p</i> -Tol) ₃	145°	dark	n.r.	-
		hv 406 nm	Z-4	22%
PBu ₃	132°	dark	Z-5	20%
P(OMe) ₃	107°	dark	Z-6 → E-6b ^d	85% ^e

^a Tolman cone angle.³⁸ ^b All reactions were performed in acetone at rt at a concentration of 6.4 mM (in the dark) or 1.3 mM (under irradiation); illumination at 406 nm (40 mW/cm²) was applied for 2 h. ^c n.r.: no reaction. ^d Compound Z-6 rapidly isomerizes to E-6b under reaction conditions. ^e Isolated yield for E-6b.

Properties of Complexes Z-3-Z-5 and Photo-Initiation of Catalytic Activity through PPh₃ Release from Z-3. The absorption spectra of complexes Z-3, Z-4 and Z-5 in acetone (μM range concentration) are reported in Figure 4. They show similar features, with two strong bands at 391-398 nm and 505-508 nm. No evolution of the absorption spectra was observed when the samples were left in the dark for 2 h, while irradiation of Z-3 and Z-4 at 406 nm induced an increase of the band at 391-398 nm (associated with a blue shift to 377-381 nm) and a decrease of the band at 505-508 nm. In line with the behavior of aqua complex E-2, no equilibrium could be reached upon prolonged irradiation, suggesting an irreversible reaction. In contrast, evolution of Z-5 showed significantly lower amplitude, and most importantly a stabilization after ca. 30 s of irradiation, though the process was irreversible.

Table 2. Tolman Cone Angle of various Phosphorous Ligands and their Reactivity towards Aqua Complex E-2.

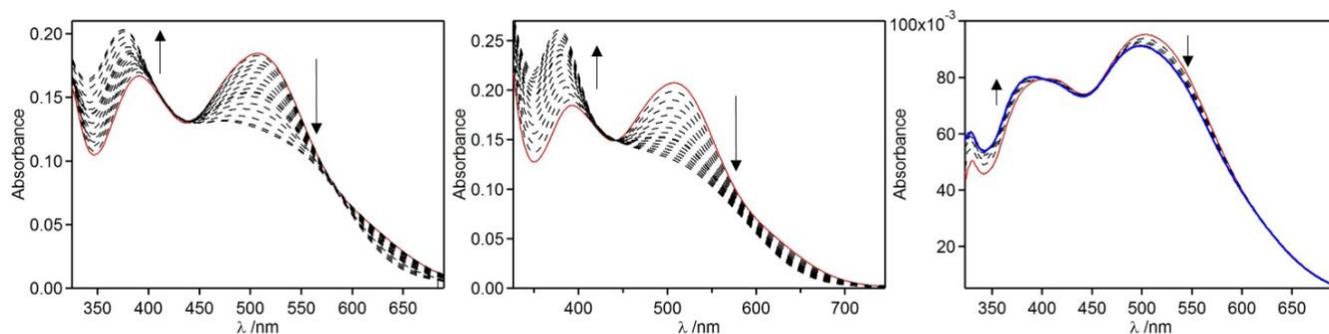


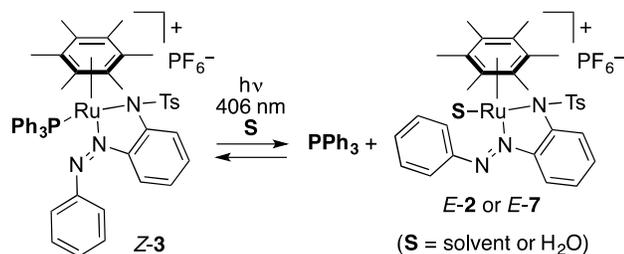
Figure 4. Absorption spectra of complexes Z-3 (left), Z-4 (middle) and Z-5 (right) in acetone (μM range concentration) at 25°C (red solid lines) and their stepwise evolution upon irradiation at 406 nm with $P = 12 \text{ mW/cm}^2$ (black dashed lines). Total irradiation time is 10 min for Z-3 and Z-5, 30 s for Z-4. The blue line in the spectrum of Z-5 corresponds to equilibrium.

The photo-induced transformation of Z-3 was then followed by ¹H NMR in acetone-d₆ (13 mM concentration). The spectra recorded upon stepwise irradiation at 406 nm, clearly revealed the apparition of a new set of signals

between 7.46 and 7.27 ppm corresponding to unbounded PPh₃, with concomitant formation of a solvate complex E-2 or E-7 (Scheme 4 and Figure S2). Surprisingly, the reaction could not be driven to completion and the

amount of released phosphine was maintained to only 50% after 2 h of irradiation (Figure 5). Performing the same reaction in CD_2Cl_2 led to a similar conversion (50%), however the use of solvents with stronger coordinating ability such as DMSO- d_6 , pyridine- d_5 and CD_3CN allowed conversion of 95%, 97% and 100%, respectively (Figure 5 and Figure S3). When *Z*-5 was irradiated under the same conditions, no difference in the ^1H NMR spectrum was observed, suggesting either the absence of PBU_3 , photo-release or its fast recombination to the ruthenium center.

Scheme 4. PPh_3 release from complex *Z*-3 upon illumination.



These results prompted us to evaluate the potential of complex *Z*-3 to act as a “photo-caged” triphenylphosphine, that could initiate a chemical transformation upon illumination.^{42–44} As a proof of principle, we focused on the benchmark aza-Morita-Baylis-Hillman reaction between *N*-tosylimine **8** and butenone **9** to produce *N*-tosylamine **10** (Scheme 5 and Figure 6).⁴⁵ The mechanism of such reaction has been well-studied and is known to be efficiently catalyzed by triphenylphosphine.⁴⁶ As expected, stirring in the dark a solution of **8** and **9** in the presence of a catalytic amount of *Z*-3 (10 mol%) in MeCN only produced trace amounts of **10** (ca. 3% after 24 h). However, irradiation of the solution at 406 nm for 2 h triggered *Z*→*E* photoisomerization of **3** with concomitant release of PPh_3 (see Scheme 4). The latter clearly initiated the catalytic transformation of **8** and **9** to **10**, formed in 92% yield after 120 h. To confirm the role of PPh_3 in such reaction, a control experiment was performed with aqua complex *E*-2 under the same conditions, either in the dark or upon irradiation at 406 nm, yielding as expected no detectable amount of **10**.

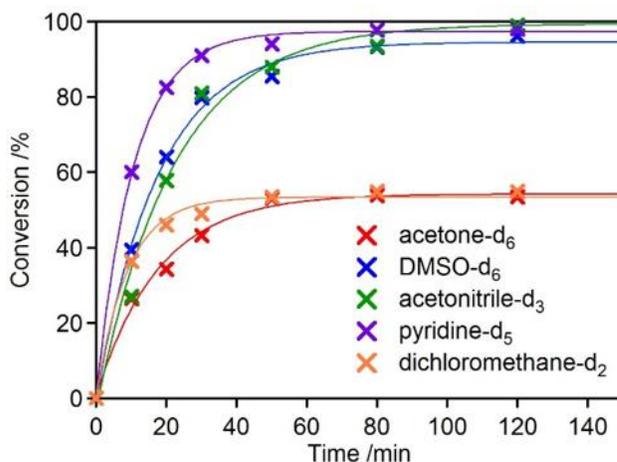


Figure 5. Quantification by ^1H NMR spectroscopy of PPh_3 release from *Z*-3 (4.8 mM) in various solvents upon irradiation at 406 nm ($20 \text{ mW}/\text{cm}^2$).

Scheme 5. Aza-Morita-Baylis-Hillman reaction **8 and **9** to produce **10** catalyzed by *Z*-3.**

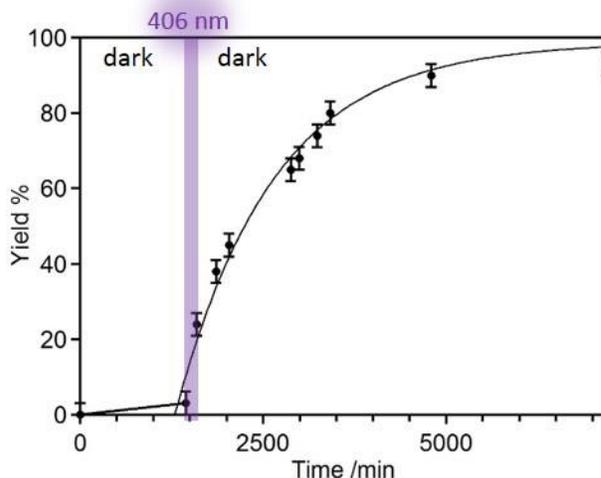
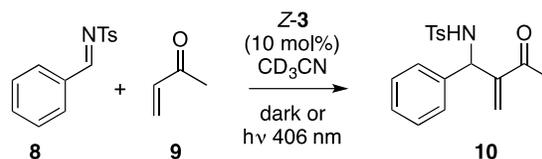


Figure 6. Photo-initiation of aza-Morita-Baylis-Hillman reaction of **8** and **9** catalyzed by complex *Z*-3. The yield of resulting amine **10** was determined by ^1H -NMR spectroscopy using an internal standard. Purple zone refer to irradiation at 406 nm ($40 \text{ mW}/\text{cm}^2$).

CONCLUSION

The reactivity of arene ruthenium aqua complex *E*-2, containing a photoswitchable *N*-tosylaminoazobenzene ligand, towards various phosphines was investigated in

the dark and upon irradiation. The results clearly evidence a strong influence of the steric crowding of the phosphine, as measured by its Tolman cone angle, on the outcome of the reaction. Several stable phosphine ruthenium complexes containing azobenzene ligand trapped in *Z*-configuration were isolated, and their properties under illumination were evaluated. Remarkably, compound *Z*-3 in acetonitrile underwent *Z*→*E* photoisomerization associated with quantitative release of triphenylphosphine. This property was exploited for the photo-controlled initiation of catalytic aza-Morita-Baylis-Hillman reaction. The organometallic complexes described in the present study open new perspectives in the field of “photo-caged” compounds, and their scope of application is currently being investigated.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise stated, all reagents were used as received without further purification. Manipulations in anhydrous conditions were carried out under an atmosphere of argon in dried glassware. Solvents were dried with a mBraun MB-SPS-800 purification system. ¹H, ¹³C{¹H} and ³¹P NMR spectra were recorded on a JEOL 400 spectrometer and referenced to the resonances of solvent residual peak. Infrared (IR) spectra were recorded with a Nicolet Nexus FT-IR spectrometer equipped with an ATR-Germanium unit and are reported as wavenumbers (cm⁻¹). Melting points were determined using a Kofler bench. High-resolution mass spectra (HRMS) were performed on a Bruker maXis Q-TOF mass spectrometer by the “Fédération de Recherche” ICOA/CBM (FR2708) platform. Elemental analyses were carried out by the Laboratory for Microanalysis at ICSN (Gif-sur-Yvette).

Spectroscopic Measurements. Acetone used for absorption measurements was of spectrometric grade. UV/Vis absorption spectra were recorded on a Cary4000 spectrophotometer from Agilent Technologies. Photoisomerization was induced by a continuous irradiation Hg/Xe lamp (Hamamatsu, LC6 Lightningcure, 200 W) equipped with narrow band interference filter of appropriate wavelength (Semrock FFO1-406/15-25 for λ_{irr} = 406 nm). The irradiation power was measured using a photodiode from Ophir (PD300-UV).

Complex E-2. To a solution of chloro complex *E*-1 (82 mg, 0.13 mmol) in acetone (10 mL) under argon was added AgPF₆ (48 mg, 0.19 mmol, 1.5 equiv). After stirring at rt for 2 min, the solid was filtered off and the filtrate was evaporated under reduced pressure. The solid was washed with CHCl₃ (3 x 5 mL) and Et₂O (3 x 10 mL) to afford *E*-2 (76 mg, 0.10 mmol, 77%). Brown solid; R_f: 0.50 (CH₂Cl₂/MeOH: 9/1); Mp: 152°C (dec.); IR (ATR): 3660, 3475, 2987, 2899, 1391, 1251, 1126, 1079, 844, 775 cm⁻¹; ¹H NMR (400 MHz, (CD₃)₂CO): δ ppm 8.25-8.20 (m, 2H), 8.18 (d, 1H, *J* = 8.7 Hz), 7.86 (d, *J* = 7.8 Hz, 1H), 7.77-7.76 (m, 3H), 7.49-7.45 (m, 3H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.65 (br s, 2H, H₂O), 2.23 (s, 3H), 2.02 (s, 18H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ ppm 156.8, 145.7, 144.3, 138.5, 135.8, 135.7, 132.7, 130.4, 130.2, 128.7, 126.2, 124.9, 124.1, 96.1, 21.2, 16.4; HRMS (ESI): calcd. for C₃₁H₃₄N₃O₂RuS⁺, [M-PF₆-H₂O]⁺ *m/z* 614.1417, found *m/z* 614.1416.

Complex Z-3. A solution of *E*-2 (70 mg, 0.090 mmol) and PPh₃ (240 mg, 0.900 mmol, 10 eq) in acetone (70 mL) was irradiated for 2 h at 406 nm (P = 40 mW.cm⁻²). The mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel-CH₂Cl₂/MeOH: 95/5). The solid obtained was triturated with

toluene (3 x 15 mL), dissolved in CHCl₃ and the remaining insoluble by-products were filtered off. After evaporation, the residue was purified by a short column chromatography (silica gel-CH₂Cl₂/MeOH: 95/5) to remove traces of toluene trapped within the product. Final trituration with Et₂O (3 x 15 mL) afforded *Z*-3 (38 mg, 0.037 mmol, 41%). Crystals suitable for X-Ray analysis were obtained by vapor diffusion of petroleum ether into a solution of complex in acetone and CH₂Cl₂. Dark red solid; R_f: 0.58 (CH₂Cl₂/MeOH: 9/1); Mp: 170°C (dec.); IR (ATR): 2985, 2889, 1464, 1436, 1318, 1232, 1138, 1080, 927, 840, 737, 699 cm⁻¹; ¹H NMR (400 MHz, (CD₃)₂CO): δ ppm 8.53 (d, *J* = 9.2 Hz, 1H), 7.80-7.76 (m, 1H), 7.76-7.65 (m, 3H), 7.63 (d, *J* = 6.4 Hz, 1H), 7.62-7.55 (m, 3H), 7.43-7.32 (m, 6H), 7.26-7.15 (m, 2H), 6.98-6.89 (m, 5H), 6.75-6.72 (m, 1H), 6.70-6.57 (m, 4H), 6.38 (t, *J* = 7.8 Hz, 1H), 2.25 (s, 3H), 2.00 (s, 18H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ ppm 155.9, 154.3, 148.6, 143.9, 139.3, 137.0, 136.9, 135.3, 135.2, 134.8, 134.7, 134.2, 132.9, 132.5, 130.3, 129.9, 129.8-129.6 (m), 129.5, 129.4, 128.1, 123.8, 119.8, 117.7, 106.6, 21.2, 16.4; ³¹P NMR (161.8 MHz, (CD₃)₂CO): δ ppm 32.4 (s), -143.7 (hept., *J* = 707 Hz); HRMS (ESI): calcd. for C₄₉H₄₉N₃O₂PRuS⁺, [M-PF₆]⁺ *m/z* 876.2334, found *m/z* 876.2331; Elemental analysis: calc. for C₄₉H₄₉F₆N₃O₂P₂RuS, C: 57.64, H: 4.84, N: 4.12, found C: 56.67, H: 4.51, N: 4.39.

Complex Z-4. A solution of *E*-2 (50 mg, 0.064 mmol) and P(*p*-Tol)₃ (190 mg, 10 eq) in acetone (50 mL) was irradiated for 2 h at 406 nm (P = 40 mW.cm⁻²). The mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel-CH₂Cl₂/MeOH: 95/5). The solid obtained was triturated with toluene (3 x 15 mL), dissolved in CHCl₃ and the remaining insoluble by-products were filtered off. After evaporation, the residue was purified by a short column chromatography (silica gel-CH₂Cl₂/MeOH: 95/5) to remove traces of toluene trapped within the product. Final trituration with Et₂O (3 x 15 mL) afforded *Z*-4 (15 mg, 0.014 mmol, 22%). Dark red solid; R_f: 0.58 (CH₂Cl₂/MeOH: 9/1); Mp: 218°C (dec.); IR (ATR): 2975, 2895, 1462, 1323, 1236, 1140, 1082, 928, 836, 770 cm⁻¹; ¹H NMR (400 MHz, (CD₃)₂CO): δ ppm 8.51 (d, *J* = 9.2 Hz, 1H), 7.90-7.40 (m, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.39-7.34 (m, 3H), 7.31-7.17 (m, 6H), 6.98-6.93 (m, 5H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.47-6.43 (m, 4H), 6.40-6.36 (m, 1H), 2.52 (s, 3H), 2.40 (s, 3H), 2.26 (s, 3H), 2.13 (s, 3H), 1.99 (s, 18H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ ppm 155.8, 154.2, 148.6, 143.8, 143.3, 142.9, 141.8, 139.3, 136.9, 136.8, 135.2, 135.1, 134.7, 134.6, 134.1, 130.3-129.8, 129.3, 128.2, 123.7, 119.7, 117.6, 106.4, 21.5, 21.4, 21.2, 20.9, 16.4; ³¹P NMR (161.8 MHz, (CD₃)₂CO): δ ppm 30.9 (s), -143.7 (sept., *J* = 706 Hz); HRMS (ESI): calcd. for C₃₁H₃₄N₃O₂RuS⁺, [M-PF₆-P(*p*-Tol)₃]⁺ *m/z* 614.1417, found *m/z* 614.1416; Elemental analysis: calc. for C₅₂H₅₆F₆N₃O₂P₂RuS, C: 58.75, H: 5.21, N: 3.95, found C: 58.67, H: 4.98, N: 3.95.

Complex Z-5. To a solution of *E*-2 (50 mg, 0.064 mmol) in acetone (10 mL) was added PBu₃ (160 μL, 0.640 mmol, 10 equiv). After stirring at rt for 1 h, the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel-CH₂Cl₂/MeOH: 95/5) and the solid obtained was triturated with Et₂O (3 x 10 mL) to afford *Z*-5 (12 mg, 0.013 mmol, 20%). Crystals suitable for X-Ray analysis were obtained vapor diffusion of petroleum ether into a solution of complex in acetone and CH₂Cl₂. Dark purple solid; R_f: 0.68 (CH₂Cl₂/MeOH: 9/1); Mp: 97°C (dec.); IR (ATR): 2961, 1464, 1240, 1138, 1081, 936, 836, 770 cm⁻¹; ¹H NMR (400 MHz, (CD₃)₂CO): δ ppm 8.27 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.68 - 7.43 (m, 5H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H) 6.47 (t, *J* = 7.8 Hz, 1H), 2.39 (s, 3H), 2.18 (s, 18H), 1.94-1.20 (m, 18H), 0.96-0.74 (m, 9H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ ppm 156.0, 153.8, 149.2, 144.0, 141.9, 133.8, 130.6, 130.5, 127.0, 123.5, 119.5, 118.0, 104.6, 27.7, 27.6, 25.7, 25.4, 25.2, 25.1, 21.3, 16.2, 13.9, 13.6; ³¹P NMR (161.8 MHz, (CD₃)₂CO): δ ppm -19.8 (s), -146.7 (sept., *J* = 706 Hz); HRMS (ESI): calcd. for C₄₃H₆₁N₃O₂PRuS⁺, [M-PF₆]⁺ *m/z* 816.3271, found *m/z* 816.3272;

Elemental analysis: calc. for $C_{43}H_{61}F_6N_3O_2P_2RuS$, C: 53.74, H: 6.40, N: 4.37, found C: 51.69, H: 6.47, N: 3.66.

Procedure for the monitoring of Z-6 formation and its evolution into E-6b. The reaction was performed in a NMR tube and monitored by 1H NMR spectroscopy. A solution of *E-2* (10 mg, 0.013 mmol) in $(CD_3)_2CO$ (0.5 mL) was treated with $P(OMe)_3$ (4.5 μ L, 0.040 mmol, 3 equiv.) and monitored at regular time intervals for 24 h.

Complex E-6b. To a solution of *E-2* (50 mg, 0.064 mmol) in acetone (10 mL) was added $P(OMe)_3$ (76 μ L, 0.64 mmol, 10 equiv). After stirring at rt for 24 h, the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel- $CH_2Cl_2/MeOH$: 95/5) and the solid obtained was triturated with Et_2O (3 x 10 mL) to afford *E-6b* (48 mg, 0.054 mmol, 85%). Crystals suitable for X-Ray analysis were obtained vapor diffusion of petroleum ether into a solution of complex in acetone and CH_2Cl_2 . Dark purple solid; Rf: 0.64 ($CH_2Cl_2/MeOH$: 9/1); Mp: 108°C (dec.); IR (ATR): 2967, 1467, 1247, 1141, 1033, 937, 838, 791, 728 cm^{-1} ; 1H NMR (400 MHz, $(CD_3)_2CO$): δ ppm 7.89 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.7$ Hz, 1H), 7.51-7.47 (m, 2H), 7.42-7.29 (m, 3H), 7.26-7.24 (m, 1H), 7.24-7.22 (m, 1H), 7.22-7.08 (m, 1H), 6.65 (dd, $J = 8.7, 1.4$ Hz, 1H), 6.36-6.28 (m, 1H), 3.93-3.90 (m, 9H), 2.37 (s, 3H), 2.22 (m, 18H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ ppm 155.7, 155.3, 148.3, 143.6, 140.2, 133.4, 131.0, 130.2, 129.8, 129.7, 129.0, 128.6, 126.1, 122.8, 120.4, 117.6, 106.84, 106.80, 55.7, 55.6, 21.3, 16.1; ^{31}P NMR (161.8 MHz, $(CD_3)_2CO$): δ ppm 116.3 (s), -143.7 (sept., $J = 706$ Hz); HRMS (ESI): calcd. for $C_{34}H_{43}N_3O_5PRuS^+$, $[M-PF_6]^+$ m/z 738.1708, found m/z 738.1708; Elemental analysis: calc. for $C_{34}H_{43}F_6N_3O_5P_2RuS$, C: 46.26, H: 4.91, N: 4.76, found C: 46.03, H: 4.83, N: 4.55.

Procedure for the quantification of PPh_3 release from Z-3 upon irradiation in various solvents. The reaction was performed in a NMR tube and monitored by 1H NMR spectroscopy. The conversion was determined by relative integration of an appropriate signal of Z-3 and of the solvated complex formed upon release of PPh_3 . A solution of Z-3 (2.5 mg, 2.4 μ mol) in deuterated solvent (0.5 mL) was irradiated at 406 nm ($P = 20$ mW. cm^{-2}) and monitored at regular time intervals for 2 h.

Preparation of 10 by photo-initiated aza-Baylis-Hillman reaction. The reaction was performed in a NMR tube and monitored by 1H NMR spectroscopy by comparing integration of an aromatic signal of the product with an internal standard (1,3,5-trimethoxybenzene). To a solution of *N*-tosylimine **8**⁴⁷ (26 mg, 0.10 mmol, 1 equiv), methyl vinyl ketone **9** (10 μ L, 0.12 mmol, 1.2 equiv), and 1,3,5-trimethoxybenzene (7.3 mg, 0.043 mmol, 0.43 equiv) in CD_3CN (0.5 mL) was added Z-3 (10 mg, 9.8 mmol, 0.1 equiv). After resting in the dark at 20°C for 24 h, the sample was irradiated at 406 nm ($P = 40$ mW. cm^{-2}) for 2 h and left in the dark at 20°C until completion of the reaction. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel-PE/EA: 9/1) to afford **10**⁴⁸ (22 mg, 0.84 mmol, 84%). White solid; Rf: 0.42 (PE/EA: 6/4); Mp: 110°C; IR (ATR): 3261, 2986, 2901, 1664, 1454, 1324, 1251, 1163, 1085, 1061, 931, 811, 742, 703 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ ppm 7.65 (d, $J = 8.2$ Hz, 2H), 7.30-7.16 (m, 5H), 7.13-7.06 (m, 2H), 6.11 (s, 1H), 6.10 (s, 1H), 5.67 (d, $J = 8.7$ Hz, 1H), 5.27 (d, $J = 8.7$ Hz, 1H), 2.41 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 199.0, 146.6, 143.5, 139.0, 137.6, 129.6, 128.7, 128.4, 127.8, 127.4, 126.5, 59.1, 26.5, 21.7.

ASSOCIATED CONTENT

Supporting Information

Additional UV-vis absorption spectra, 1H NMR monitoring of PPh_3 release in $(CD_3)_2CO$ and CD_3CN , copy of NMR spectra

and details concerning X-ray structure determination. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Note

The authors declare no competing financial interest.

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