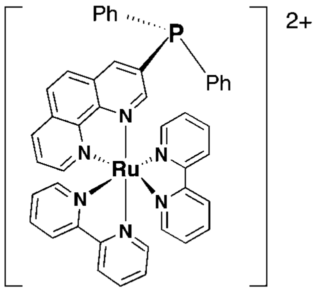
A Light-Harvesting *tert*-Phosphane Ligand Bearing a Ruthenium(II) Polypyridyl Complex as Substituent

Masahisa Osawa,* Mikio Hoshino, and
Yasuo Wakatsuki

Polypyridine ruthenium(II) complexes have been used extensively as visible-light active photosensitizers because they display metal-to-ligand charge transfer (MLCT) excited states with outstanding photochemical and photophysical properties.[1] Numerous works are devoted to activating suitable substrates by pathways that involve intermolecular energy transfer and/or electron transfer. While an alternative approach that involves intramolecular sensitization is also described in the literature,[2] to date this method is mainly directed to photophysical observation and photochemical net reactions are less explored. Since chromophore and substrate are fixed in close proximity, the photochemical reaction by intramolecular sensitization has the expected advantage of minimized diffusion effect. As a new organometallic approach to such sensitization, we prepared the first *tert*-phosphane ligand (**Pru**) that has a covalently bound Ru^{II} polypyridyl complex ("sensitizer fragment") as a substituent. With such a "colored phosphane" ligand coordinated to a transition metal center, we should be able to construct a system that can perform reactions promoted by visible photo-energy absorbed at the sensitizer fragment in the phosphane ligand and transmitted to the metal center through the metal–P bond. To our knowledge, however, there is no precedent for triplet electronic energy efficiently migrating to a transition metal through a coordinating *tert*-P atom and, therefore, this is the most challenging point of the present study. If this approach works, then photo-active phosphanes such as those presented here can open the way to a wide variety of complexes and applications because *tert*-phosphane is one of the most frequently used ligands classes in organometallic chemistry and homogeneous catalysis. Herein we report one such complex, a CpRu–**Pru** (Cp = cyclopentadiene) system that actually demonstrates efficient visible-light activity at the CpRu center.



Pru(Λ-isomer)

Lithiation of [(bipy)$_2$Ru(3-bromo-1,10-phenanthroline)](PF$_6$)$_2$[3] (bipy = 2,2′-bipyridine) with *n*BuLi at −78 °C in CH$_2$Cl$_2$ took place smoothly and was followed by addition of an equimolar amount of PClPh$_2$. After purification by column chromatography under Ar, eluting with acetonitrile, the desired [(bipy)$_2$Ru(1,10-phenanthroline-3-yl)PPh$_2$](PF$_6$)$_2$ (**Pru**(PF$_6$)$_2$) was obtained as orange red powder in 83 % yield. In the ^{31}P NMR spectrum (in CD$_2$Cl$_2$) of **Pru**(PF$_6$)$_2$ the signal at $\delta = -7.07$ is close to that of free PPh$_3$ ($\delta = -5.65$). Free **Pru** is easily converted into its oxide in CH$_2$Cl$_2$ solution under air when illuminated with visible light, in sharp contrast to related triarylphosphanes such as PPh$_3$. But in the dark, a solution of **Pru** is fairly stable and does not react with oxygen.

The reaction of **Pru**(PF$_6$)$_2$ with one equivalent of [CpRu(CH$_3$CN)$_2$(CO)]PF$_6$[4] in CH$_2$Cl$_2$ at room temperature gave **1** almost quantitatively. FT-infrared (IR) spectrum of **1** in CH$_3$CN shows ν(CO) at 1996 cm^{-1}, which is comparable to the PPh$_3$ analogue **2** (1989 cm^{-1}), which indicate that the electron-donating ability of the ground-state **Pru** in **1** is a little less than that of PPh$_3$.

[CpRu(CH$_3$CN)(CO)(**Pru**)](PF$_6$)$_3$ **1**

[CpRu(CH$_3$CN)(CO)(PPh$_3$)]PF$_6$ **2**

The ^{1}H NMR spectrum of **1** shows two singlets at $\delta = 5.18$ and 5.14 (ca. 1:1) attributable to Cp protons, and two doublets (J(P,H) = 1.20 Hz) at $\delta = 2.00$ and 1.97 (ca. 1:1) assigned to the coordinated acetonitrile, thus suggesting that two isomers are present. Apparently, the combination of two asymmetric centers, Δ and Λ on **Pru** and the CpRu-centered (*R*)- and (*S*)-epimers, results in two diastereomers.[5]Photophysical properties of **Pru**(PF$_6$)$_2$ and **1** are compared in Figure 1, the reduced emission intensity of coordinated **Pru** in **1** compared to that of free **Pru** is clear. In **1** an intramolecular triplet energy transfer

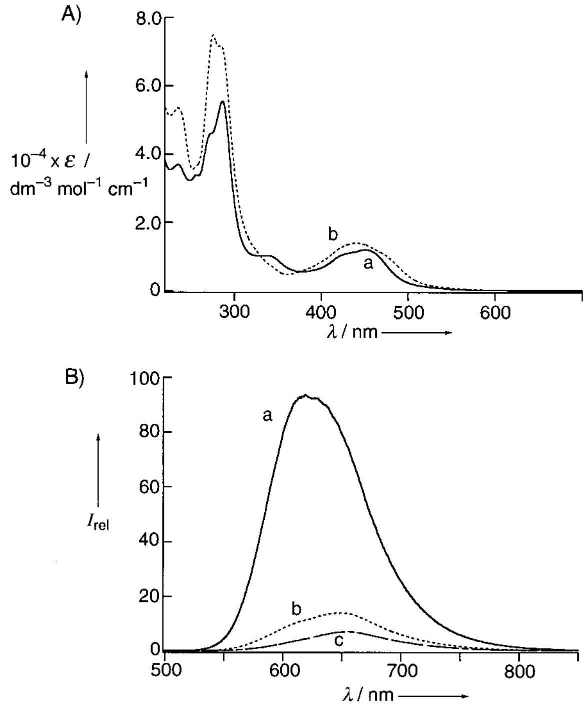


Figure 1. A) Absorption spectra of a) **Pru**(PF$_6$)$_2$ and b) **1** in CH$_3$CN. B) Emission spectra excited at 440 nm in de-aerated CH$_3$CN at 293 K: a) **Pru**; $\lambda_{max} = 619$ nm, b) **1**; $\lambda_{max} = 653$ nm, and c) **1** in aerated CH$_3$CN; $\lambda_{max} = 655$ nm.

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[*] Dr. M. Osawa, Dr. M. Hoshino, Dr. Y. Wakatsuki
RIKEN (The Institute of Physical and Chemical Research)
Wako-shi, Saitama 351-0198 (Japan)
Fax: (+81) 48-462-4665
E-mail: osawa@postman.riken.go.jp

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process takes place between the "sensitizer unit" in **Pru** and the $[CpRu]^+$ fragment, which leads to quenching of the luminescence from the excited state of the Ru^{II}–polypyridyl unit by about 85 %. The remaining 15 % emission from Ru^{II}–polypyridyl fragment in **1** was further quenched when the spectrum was recorded in aerated solution (curve c in Figure 1 B). Quenching of the emission from $[Ru(bipy)_3]^{2+}$ by oxygen is known.[6]

The CH_3CN ligand in **1** and **2** is strongly coordinated to the metal center and replacement by CD_3CN or $[D_5]$pyridine was not observed at room temperature in the dark after 48 h. In contrast, the facile substitution of CH_3CN in **1** by the solvent took place on irradiation with visible light (400 W high-pressure mercury lamp, $\lambda > 450$ nm). Thus, after 40 min irradiation, $[CpRu(CD_3CN)(CO)(\mathbf{Pru})](PF_6)_3$ (**3**), or $[CpRu(C_5D_5N)(CO)(\mathbf{Pru})](PF_6)_3$ (**4**) were obtained in quantitative yields. The reaction was monitored by ^1H NMR spectroscopy. The time-conversion curve (Figure 2) was independent of solvent (CD_3CN or C_5D_5N) and of CD_3CN concentration (neat or 9/1 mixture of CD_2Cl_2/CD_3CN). Also, the presence of air exerts no effect though oxygen is known to quench the emission from polypyridine Ru^{II} species. All these observations are consistent with unimolecular dissociation of the coordinated CH_3CN in **1**, brought about by efficient intramolecular photosensitization from the Ru^{II}–polypyridyl group in **Pru**. As expected, similar irradiation of **2** did not cause exchange of the coordinated CH_3CN. Evidence that the dissociation of CH_3CN is not caused by mutual intermolecular sensitization between two molecules of **1** was obtained when a CD_3CN solution of **2** was irradiated in the presence of an equimolar amount of $[Ru(bipy)_3]^{2+}$: there was no reaction.

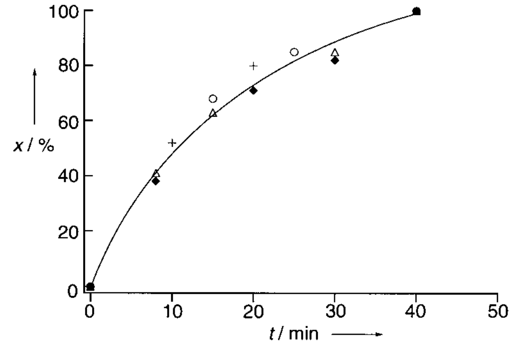
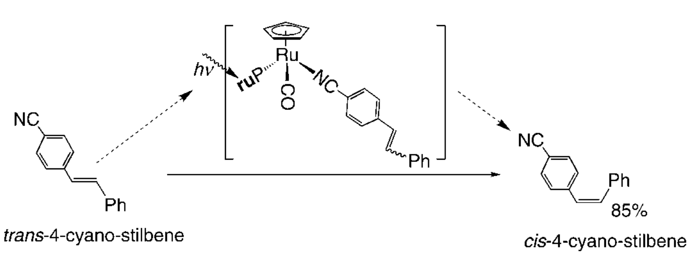


Figure 2. Rate for the CH_3CN–solvent exchange reaction of **1** on irradiation ($\lambda > 450$ nm) in: (+) CD_3CN; (○) CD_2Cl_2/CD_3CN (9/1); (△) $[D_5]$pyridine; (◆) aerated CD_3CN. t = irradiation time, x = extent of CH_3CN substitution in **1**.

When *trans*-4-cyano-stilbene,[7] was employed instead of acetonitrile this visible-light induced substitution of the nitrile ligand resulted in concomitant isomerization of the C–C double bond to the *cis* form (Scheme 1). In the presence of a catalytic amount of **1** (8.0 mg, 0.006 mmol), pure *trans*-4-cyano-stilbene (55 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) was irradiated by visible light (400 W lamp, $\lambda > 450$ nm) at 25 °C. After 2 h, a *cis* rich product mixture (*cis*/*trans* = 5.7/1) was formed as determined by gas chromatography (GC) and ^1H NMR spectroscopy. The reaction was carried out under aerated conditions to minimize direct (intermolecular) sensitization of 4-cyano-stilbene by the Ru^{II}–polypyridyl unit. Addition of CH_3CN (1.2 mL), thereby blocking the coordination of 4-cyano-stilbene to the CpRu center, leads to a dramatic retardation of the *trans* → *cis* isomerization to less than 10 % of the original rate (Figure 3). The curve b in Figure 3 is independent of further addition of CH_3CN (2.0 mL), which suggests that the slow isomerization observed under these conditions may be attributed to direct intermolecular sensitization. The *trans* → *cis* isomerization of stilbene and styrylpyridines by intermolecular triplet–triplet energy transfer from $[Ru(bipy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ has been observed in acetonitrile solution.[8] Under the concentration used here, intramolecular sensitization is much more effective than intermolecular (Figure 3).



Scheme 1. The *trans* → *cis* isomerization on photo-induced nitrile ligand substitution.

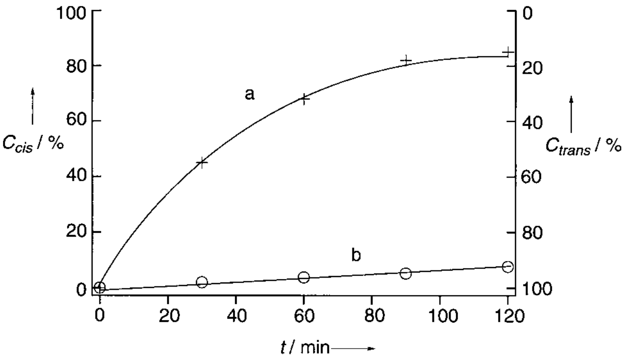


Figure 3. Rate curves for the *trans* → *cis* photo-isomerization of 4-cyano-stilbene on irradiation in the presence of **1** (2 mol %); a) in CH_2Cl_2 (5 mL); b) in the mixture solvent of CH_2Cl_2 (3.8 mL) and CH_3CN (1.2 mL). t = irradiation time.

In conclusion, herein we have shown that coordination of the new phosphane ligand **Pru** is a useful and convenient way of changing a transition metal complex into visible-light harvesting reaction center. Synthesis of other metal complexes containing **Pru** and the development of their photochemical reactions are now in progress.

Experimental Section

All reactions were carried out under an atmosphere of Ar, unless otherwise indicated.

$\mathbf{Pru}(PF_6)_2$: *n*BuLi (170 mL, 1.54 M in hexane) was added by microsyringe to a solution of $[(bipy)_2Ru(3\text{-bromo-}1,10\text{-phenanthroline})](PF_6)_2$[3] (250 mg, 0.26 mmol) in CH_2Cl_2 (20 mL) at −78 °C. A brown precipitate formed immediately. After 10 min, neat PPh_2Cl (80 mL, 0.52 mmol) was added by microsyringe. After stirring for 30 min at −78 °C the reaction mixture was allowed to warm to room temperature. The crude compound was purified by flash chromatography on alumina eluting with CH_3CN to give analytically pure **Pru**$(PF_6)_2$ (200 mg, 83 %). ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = -7.07$ (s); MS (ES): *m*/*z* 922.9 $[M - PF_6]^+$, 389.0 $[M - 2PF_6]^{2+}$; UV/Vis (CH_3CN): λ_{max} [nm] (ε [$dm^3mol^{-1}cm^{-1}$]): 450 (12000), 339 (10000), 285 (56000), 273sh (48000), 255 (35000), 235 (38000); elemental analysis (%) calcd for $C_{44}H_{33}F_{12}N_6P_3Ru_1$: C 49.49, H 3.11, N, 7.87; found C 49.77, H 3.21, N, 7.69.

1: A solution of **Pru**$(PF_6)_2$ (100 mg, 0.094 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of $[CpRu(CH_3CN)_2(CO)]PF_6$[4] (39.4 mg, 0.094 mmol) in CH_2Cl_2 (10 mL). After 24 h the solvent was evaporated under vacuum. The crude product was purified by column chromatography on alumina, eluting first with CH_3CN/Toluene (1/1) and then with CH_3CN to afford the pure product **1** (94.3 mg, 88 %). FT-IR (CH_3CN): $\tilde{\nu} = 1996\ cm^{-1}$ (C≡O); ^1H NMR (400 MHz, CD_3CN, TMS): $\delta = 5.18$ (s, 5H, C_5H_5), 5.14 (s, 5H, C_5H_5), 2.00 (d, J(P,H) = 1.20 Hz, 3H, CH_3CN), 1.97 (d, J(P,H) = 1.20 Hz, 3H, CH_3CN); ^{31}P NMR (162 MHz, CD_3CN): $\delta = 48.77$ (s), 48.67 (s); UV/Vis (CH_3CN): λ_{max} [nm] (ε [$dm^3mol^{-1}cm^{-1}$]): 441 (14000), 284 (72000), 275 (75000), 235 (53500); elemental analysis (%) calcd for $C_{52}H_{41}F_{18}N_7O_1P_4Ru_2$: C 43.13, H 2.85, N 6.77; found C 43.52, H 2.96, N 6.54.

Photosubstitution of CH_3CN in **1**: The photochemical reaction was carried out with a 400 W high-pressure mercury lamp through a Toshiba Y-47 glass filter ($\lambda > 450$ nm). The exchange reaction was monitored by the intensity of the ^1H NMR resonance signals of the CH_3CN and Cp units.

3: 40 min irradiation of **1** in CD_3CN; yield 100 %; spectroscopic data are identical to **1**.

4: 40 min irradiation of **1** in [D_5]pyridine; yield 92 %; FT-IR (CH_3CN): $\tilde{\nu} = 1979\ cm^{-1}$ (C≡O); ^1H NMR (400 MHz, CD_3CN, TMS): $\delta = 5.30$ (s, 5H, C_5H_5), 5.24 (s, 5H, C_5H_5); ^{31}P NMR (162 MHz, CD_3CN): $\delta = 51.26$ (s), 51.16 (s).

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The Hexaphosphapentaprismane $P_6C_4tBu_4$: A “Jaws-Like” Cage Molecule That Bites!**

Mahmoud M. Al-Ktaifani, Daniel P. Chapman, Matthew D. Francis, Peter B. Hitchcock, John F. Nixon,* and László Nyulászi*

Organophosphorus cage compounds are of considerable current interest.[1] Two major synthetic routes to these compounds are the cyclooligomerization of phosphaalkynes (often metal-mediated)[2] and the coupling of polyphospholyl anions.[3] Examples include 1) the tetraphosphacubane $P_4C_4tBu_4$ from the thermal oligomerization of PC*t*Bu or treatment of $[ZrCp_2(P_2C_2tBu_2)]$ with C_2Cl_6;[4] and 2) the $FeCl_3$-mediated oxidative coupling of a mixture of the anions $[1,2,4\text{-}P_3C_2tBu_2]^-$ (**1**) and $[1,3\text{-}P_2C_3tBu_3]^-$ (**2**) to afford the pentaphospha cage compound $P_5C_5tBu_5$.[5] More recently, we reported the structurally characterized hexaphospha cage compound $P_6C_6tBu_6$, which to date is the largest phosphaalkyne oligomer known.[6]

We were interested in expanding this area to include cages containing an additional heteroatom, and recently we showed that treatment of **1** with EI_4 (E = Si, Ge) leads to the two structurally different cage compounds $P_6C_4tBu_4GeI_2$ (**3**) and $P_6C_4tBu_4SiI_2$ (**4**).[7] These cages are probably formed by two successive [2+2] cycloadditions of adjacent triphospholyl rings of the bis-η^1 intermediate $(P_3C_2tBu_2)_2EI_2$. We now report the synthesis of the related phosphorus–chalcogen cages $P_6C_4tBu_4E$ (E = S, Se, Te), with full structural characterization (E = Se, Te) or NMR spectroscopic characterization (E = S). These compounds were obtained by an unprecedented reaction involving the facile specific insertion of the chalcogen atom into a P–P bond of the hexaphosphaprismane $P_6C_4tBu_4$ (**5**). Compound **5** was first synthesized by Breit, Mack, and Regitz by an indirect method, but more recently improved syntheses involving coupling of two $(P_3C_2tBu_2)^-$ anions were independently developed by Nixon et al. and Zenneck et al.[1b,8]

In view of the ease and specificity of the insertion reactions of several carbene-like species into **5**, we have likened this behavior to that of the well-known shark “Jaws”. This novel feature of its reactivity is further exemplified by the ready reaction of **5** with the stable germylene GeR_2, stannylene SnR_2 ($R = N(SiMe_3)_2$), and the plumbylene PbR'_2 ($R' = C_6H_3(NMe_2)_2$) to afford the structurally characterized

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[*] Prof. Dr. J. F. Nixon, M. M. Al-Ktaifani, D. P. Chapman,
Dr. M. D. Francis, Dr. P. B. Hitchcock
School of Chemistry, Physics and Environmental Sciences
University of Sussex, Brighton, BN1 9QJ (UK)
Fax: (+44) 1273-677196
E-mail: j.nixon@sussex.ac.uk

Prof. Dr. L. Nyulászi
Department of Inorganic Chemistry
Technical University of Budapest
Gellért tér 4, 1521 Budapest (Hungary)
E-mail: nyulaszi.inc@chem.bme.hu

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