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Light Switches the Ligand! Photochromic Azobenzene–Phosphanes

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Three phosphanes containing azobenzene groups were synthesized, and the photochemical behaviour of their platinum complexes was studied by using the light-induced (*E*)/(*Z*) isomerization as a switch to change ligand properties.

Introduction

Molecular switches toggle reversibly between different (meta)stable states. This change (or switch) can be triggered by external stimuli such as light, heat, pressure, electric or magnetic fields, etc. Nature relies on this phenomenon to regulate many biological functions using switchable molecules. Numerous examples of synthetic counterparts based on spiropyrans, azobenzenes, diarylethenes, etc. have been used to switch properties of materials, and more recently to develop nanoscale functional devices.[1–5]

We are interested in the application of such molecular switches for the construction of light-tunable ligands for homogeneous catalysis. There are several examples in the literature of ligands containing photoreversible, bistable systems.[6–16] In these cases, the photosensitive group in the ligand undergoes a conformational change when irradiated at the appropriate wavelength. Surprisingly, ligand properties, crucial parameters for a potential catalytic application, have been scarcely studied while undergoing changes due to irradiation.[7]

Herein, we present the synthesis, coordination and switchability of phototunable, azobenzene–phosphanes. Early examples of azo-containing phosphanes appeared in 1996,[11–15,17–19] but only two examples of catalytic applications are known, and their photochromic properties have never been investigated in depth.[9,10]

Results and Discussion

Triarylphosphanes containing only one azo group in *para* and *meta* positions (**1** and **2**) have been chosen as simple model compounds to study the isomerization process. The previously reported *ortho* derivative has not been studied here, because either the possible coordination of the N atom to the metal atom or its equilibrium with the inner phosphonium salt could interfere with the catalytic process.[20]

Aiming at light-induced steric effects in catalysis, phosphane **3** was synthesized (Scheme 1). As shown by molecular modelling,[21] one might expect that (*E*)/(*Z*) isomerization of the three azo bonds of phosphane **3** generates a structure resembling the reported bowl-shaped phosphanes, which found several applications in catalysis (Figure 1).[22–27] Even if only two of its azo groups adopt a (*Z*) conformation, a ligand with steric properties different from those of the tri-(*E*) isomer could be generated.

The synthesis of the ligands involves Pd-mediated P–C coupling of diphenylphosphane and 4- or 3-iodoazobenzene for **1** and **2**, respectively, and lithiation of 3-iodoazobenzene and reaction with PCl_3 for tris(azobenzene)–phosphane **3** (Scheme 1).[28,29]

The switchability of the free ligands was initially studied by $^{31}P\{^{1}H\}$ NMR spectroscopy.[30] A $CDCl_3$ solution of phosphane **1** shows a singlet at δ = –1.97 ppm (Figure 2a) of the pure (*E*) isomer. After irradiation at λ = 350 nm during 1 h, a new singlet appeared at δ = –2.7 ppm [attributed to the (*Z*) isomer], whilst the initial signal at δ = –1.97 ppm [(*E*) isomer] decreased in intensity. When the sample was left in the dark, the reversibility of the process was confirmed; the original singlet due to the (*E*) form of the azo bond was progressively recovered.

The isomerization process and its reversibility were also studied by UV/Vis spectroscopy. A solution of **1** in toluene was irradiated at λ = 350 nm during 1 h; then the sample was placed in the UV/Vis quartz cell, and spectra were recorded at fixed time intervals to study the (*Z*)/(*E*) isomerization process. In the spectra two bands were observed; a very intense one at 325 nm due to the transition $\pi_1 \rightarrow \pi_1^*$, characteristic of the (*E*)-azo isomer, and a less intense one at 440 nm, attributed to the partly forbidden transition $n_s \rightarrow \pi_1^*$, typical of a (*Z*)-azo moiety. The former one progressively increases when the irradiated sample is left in the dark. Accordingly, the weak band decreases when the (*Z*)

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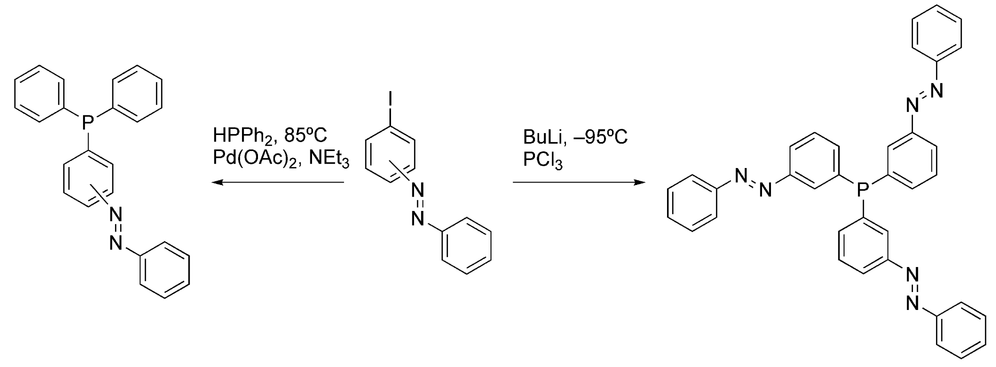

1 = *para*
2 = *meta*

3

Scheme 1. Synthesis of the ligands.

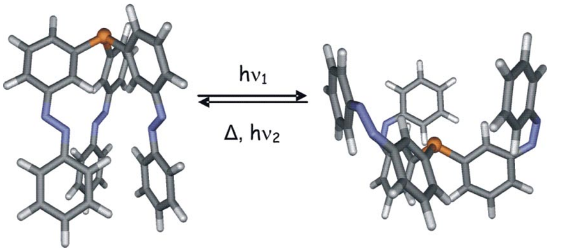

Figure 1. Molecular modelling of tris(azobenzene)–phosphane **3** in tri-(*E*)- and tri-(*Z*)-azo conformations showing maximized steric difference.

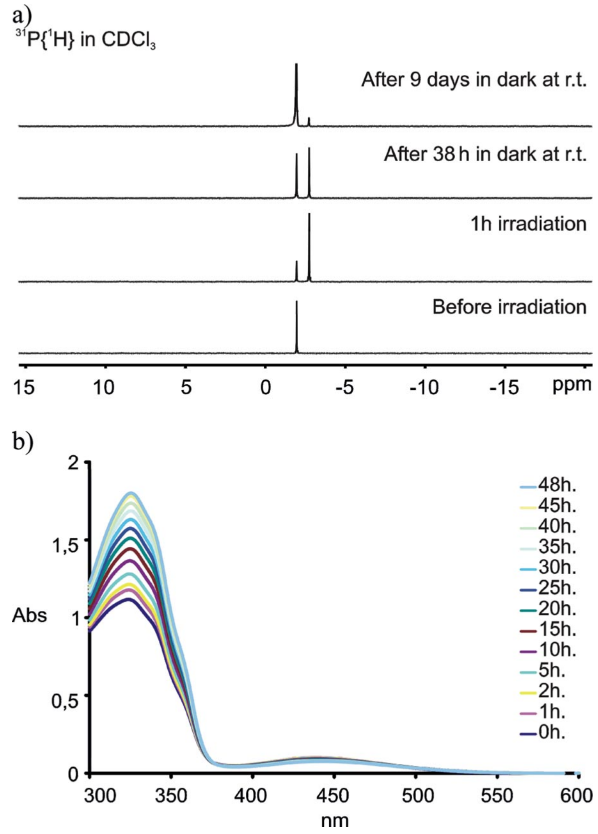

Figure 2. Isomerization of phosphane **1**: (a) $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$; (b) UV/Vis absorption spectroscopic change after irradiation of the sample at $\lambda = 350$ nm in toluene during 1 h.

form returns to the (*E*) form (Figure 2b). The same behaviour was observed for phosphane **2** (see Supporting Information).

As regards tris(azobenzene)–phosphane **3**, the three azo groups in the molecule may isomerize independently rendering up to four different compounds [(*EEE*), (*EEZ*), (*EZZ*), (*ZZZ*)]. Ligand **3** before irradiation shows one $^{31}P\{^1H\}$ NMR signal, indicating that all azo groups have an (*E*) conformation. After irradiation at $\lambda = 350$ nm during 1 h, only two additional signals at δ = –2.48 and –2.84 ppm appeared next to the initial singlet at δ = –1.94 ppm (Figure 3). As was observed for the monoazo ligands **1** and **2**, the initial singlet was recovered after several days in the dark.

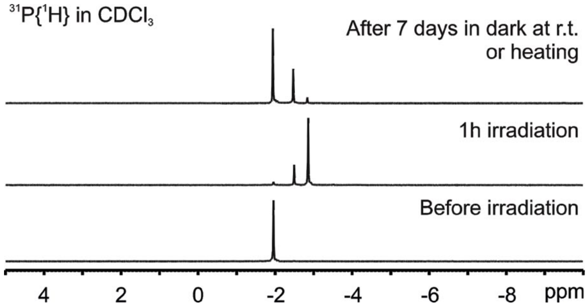

Figure 3. Isomerization of phosphane **3** monitored by $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$.

Because of our interest in catalysis, we subsequently studied if the presence of a metal complex or coordination of the phosphane ligand to a metal atom affect the (*E*)/(*Z*)/(*E*) isomerization processes of the azo group. First the photochemical (*E*)/(*Z*) isomerization was studied. The coordination properties of the ligands were studied by in situ $^{31}P\{^1H\}$ NMR analysis of the platinum dichloride complexes $[Cl_2PtL_2]$ of ligand **1**. The $^{31}P\{^1H\}$ NMR spectra show the formation of *cis*-$[Cl_2PtP_EP_E]$ as major compound (Figure 4a, Table 1). At δ = 23 ppm, traces of the *trans* complex are observed.[31] When the sample is irradiated at λ = 350 nm for 1 h, the original signal at δ = 17.33 ppm evolves to a pair of doublets at δ = 17.91 and 16.70 ppm, and a new singlet at δ = 17.25 ppm (with their corresponding satellites). The former signals are attributed to a *cis*-[$Cl_2PtP_EP_Z$] species and the latter to a *cis* complex in which both ligands were converted into the (*Z*) form *cis*-[$Cl_2PtP_ZP_Z$]. As for the free phosphanes, the original signal is recovered after five days, demonstrating that metal coordination neither inhibits nor catalyses the (*Z*)/(*E*) isomerization. Secondly, the metal complexes do not catalyze (*Z*)/(*E*) conversion either. The latter is somewhat surprising as Nakamura et al. reported rapid catalytic (*Z*)/(*E*) isomerization of azobenzene for several metal complexes. $Pt(PPh_3)_4$ catalyzed (*Z*)/(*E*) conversion of azobenzene very efficiently ($t_{1/2}$ = 1 min at –20 °C and 0.03 mM Pt). Divalent group 10 metal complexes were found to be inactive in their studies. They proposed that back-donation from a zero-valent metal atom to the azo functionality in a transient complex causes the catalytic (*Z*)/(*E*) transformation; the present complexes are not sufficiently electron-rich to do so.[31] The switchability of *cis*-[Cl_2PtP_2] complexes was also studied by UV/Vis spectroscopy (Figure 4b) corroborating that (*E*) → (*Z*) → (*E*) isomerization is not influenced by coordination to Pt or intermolecular interactions. Similar behaviour was observed when the platinum dichloride complexes of ligand **3** were studied, but the complexity of the signals is much higher due to the many isomers possible (see Supporting Information).

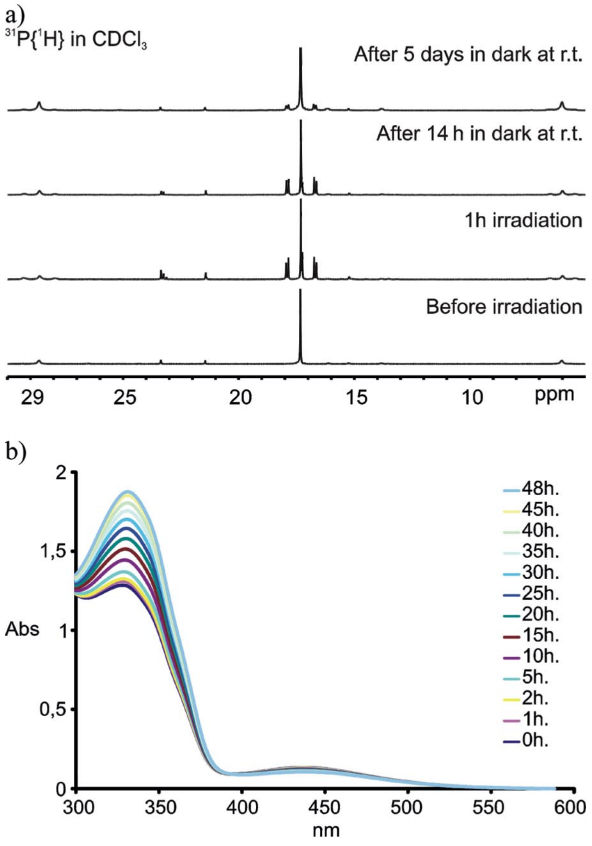

Figure 4. Isomerization of the complex *cis*-[$Cl_2Pt(\mathbf{1})_2$]: (a) $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$; (b) UV/Vis absorption spectroscopic change after irradiation of the sample with λ = 350 nm in toluene during 1 h.

Table 1. $^{31}P\{^1H\}$ NMR spectroscopic data of *cis*-[$Cl_2Pt(\mathbf{1})_2$] complexes in $CDCl_3$.

	δ [ppm]	$^1J(P_E,Pt)$ [Hz]	$^1J(P_Z,Pt)$ [Hz]	$^2J(P_E,P_Z)$ [Hz]
[$Cl_2PtP_EP_E$]	17.33	3662	–	–
[$Cl_2PtP_EP_Z$]	17.91	3683	–	15.85
	16.70	–	3640	
[$Cl_2PtP_ZP_Z$]	17.25	–	3660	–

Conclusions

New light-triggered switchable azobenzene–phosphanes have been synthesized. Herein, we have demonstrated that the molecular switch is compatible with the phosphane functionality, and Pt coordination does not influence the photochemical and thermal isomerization processes. This result is essential for potential applications in catalysis. Preliminary experiments with these model ligands showed, as expected, only a slight influence of the isomerization processes in catalysis (Rh hydroformylation, Pd allylic alkylation, Rh hydrosylilation). This result can be taken as a proof of concept that encourages us to design more elaborated systems.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of compounds, NMR details, complete UV/Vis experiments and experimental conditions for irradiation.

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