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Phosphine steric effects on the catalytic activities of a few chloro(tertiary phosphine)copper(I) oligomers in photoisomerizations of norbornadiene and *trans*-stilbene

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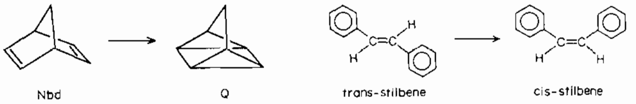
Abstract

Chloro(tertiary phosphine)copper(I) oligomers $[CuCl(PR_2R')]_n$ (**2**–**4**) were prepared for $P(2\text{-}CH_3C_6H_4)_3$, $P(4\text{-}CH_3C_6H_4)_3$ and $PPh_2(C_6F_5)$ as the phosphine PR_2R', respectively. Catalytic activities of **2**–**4**, as well as $[CuCl(PEt_3)]_4$ (**1**), were studied in 2,5-norbornadiene (Nbd)–quadricyclene valence and *trans*–*cis*-stilbene photoisomerizations in THF at 366 nm. The order of activities observed was as follows: **1**, **3**, **4** and **2**, in accord with the reverse order of size of the phosphine cone angles. In the ^{31}P NMR spectra of **1**, **3** and **4** observed in CD_2Cl_2 at −60 °C, addition of Nbd gave the new signals, attributed to their Nbd-adduct copper(I) species. On the other hand, NMR spectra of **2** did not show similar adduct formation. Accordingly, the copper(I) oligomers with sterically bulkier phosphines, having larger cone angles, formed the olefin adducts to a lesser extent, and photoirradiation of their adducts was assumed to release the isomerized products in smaller quantities.

Introduction

Exploitation of solar energy storage systems has been performed with many kinds of model reaction processes, which include 2,5-norbornadiene (Nbd)–quadricyclene (Q)** valence and *trans*–*cis*-stilbene photoisomerizations, using some copper(I) compounds [1]. For these olefin isomerization processes, two distinct mechanisms are conceivable [1]. The first is characterized by the formation of ground-state copper(I) adducts with olefins, and by subsequent photoexcitation of the adducts to release the isomerized products [1f, 1h–i]. An alternative pathway involves bimolecular interaction of the photoexcited copper(I) compounds with ground-state olefins. It appears that the copper(I) compounds have been designated as 'photocatalysts' for the first mechanism and 'photosensitizers' for the second, respectively [1]. We have been interested in the first mechanism, involving formation of the ground-state adducts with olefins. In the previous paper [2] from these laboratories, halo(ferrocenyldiphenylphosphine)copper(I) tetramers have demonstrated Nbd coordination to form adduct species in the ground state, and some moderate quantum yields were evaluated for the Nbd–Q valence isomerization under 366 nm photoirradiation. However, it seems to us that stereochemical bulkiness of the ferrocenyldiphenylphosphine ligand probably depressed the adduct formation to some extent. The present paper deals with the Nbd and *trans*-stilbene photoisomerizations catalyzed by a few chloro(tertiary phosphine)copper(I) oligomers and with stereochemical hindrance effects of the phosphines around the phosphorus coordination site on the quantum yields for the isomerizations.



Experimental

Materials and general procedures

2,5-Norbornadiene (Tokyo Kasei) was purified by distillation under a nitrogen atmosphere, and the distillate was kept in a refrigerator to minimize its peroxide formation. *trans*-Stilbene (Nacalai Tesque) was used after recrystallization from ethanol. The PEt_3 tetramer $[CuCl(PEt_3)]_4$ (**1**) [3] and the phosphine $PPh_2(C_6F_5)$ [4] were prepared according to literature methods. Tetrahydrofuran (THF) was refluxed with lithium aluminum hydride and was distilled immediately prior to use. Wakogel C-200 was used for silica-gel column

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**2,5-Norbornadiene, bicyclo[2.2.1]hepta-2,5-diene; quadricyclene, quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane.

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chromatography. All preparative operations except column chromatography were performed under dry nitrogen.

The melting points were determined with a Yanagimoto MP-S3 microstage apparatus in evacuated capillary tubes and are uncorrected. ^{1}H (399.8 MHz) and ^{31}P (161.9 MHz) NMR spectra were recorded on a JEOL model GX-400 spectrometer, by use of tetramethylsilane as an internal standard and 85% H_3PO_4 as an external standard, respectively. The chemical shifts (δ) are expressed in parts per million from these standards, and downfield shifts are noted as positive in all cases. IR spectra (KBr disc) were obtained by a Shimadzu IR-408 spectrometer.

Preparations of the [CuCl(PR$_3$)] (R=2- and 4-methylphenyl) oligomers

A benzene suspension of CuCl (65 mg, 0.66 mmol) and tris(2-methylphenyl)phosphine $P(2\text{-}CH_3C_6H_4)_3$ (150 mg, 0.49 mmol) was heated under reflux for 24 h, and was filtered hot. Hexane addition to the filtrate gave white microcrystals (60 mg) of the $[CuCl\{P(2\text{-}CH_3C_6H_4)_3\}]$ oligomer (**2**) in 30% yield based on the phosphine. For further purification, silica-gel column chromatographic separation was effective by elution with dichloromethane. *Anal.* Found: C, 62.52; H, 5.34. Calc.: C, 62.53; H, 5.25%. m.p. 256–258 °C. ^{1}H NMR ($CDCl_3$, TMS): 2.63 (s, CH_3) ppm.

The $[CuCl\{P(4\text{-}CH_3C_6H_4)_3\}]$ oligomer (**3**) was obtained as a white powder in 65% yield by similar procedures. Column chromatographic separation was applicable to the case of **3** also. *Anal.* Found: C, 62.19; H, 5.34. Calc.: C, 62.53; H, 5.25%. m.p. 240–243 °C. ^{1}H NMR ($CDCl_3$, TMS): 2.34 (s, CH_3) ppm.

Preparation of the [CuCl{PPh$_2$(C$_6$F$_5$)}] oligomer

The phosphine $PPh_2(C_6F_5)$ (100 mg, 0.28 mmol) was added to a diethyl ether suspension of CuCl (42 mg, 0.42 mmol), and the mixture was stirred at room temperature for 6 h. After filtration, the concentration of the filtrate into a small volume gave white precipitates, which were chromatographed on a silica-gel column. The diethyl ether eluate afforded white microcrystals (45 mg) of the $[CuCl\{PPh_2(C_6F_5)\}]$ oligomer (**4**) in 36% yield based on phosphine. *Anal.* Found: C, 47.77; H, 2.34. Calc.: C, 47.91; H, 2.23. m.p. 87–90 °C. ν(C–F) 1090 cm^{-1}.

Quantum yield measurements

Three-milliliter aliquots of the THF solutions of the copper(I) oligomers ([Cu(I) atom]; 2×10^{-2} M) with 0.5 M olefins were transferred as test solutions to a rectangular Pyrex cuvette (10×10×45 mm) under nitrogen. Photoirradiation was performed under anaerobic conditions for 4 h at 366 nm by use of a 300 W medium-pressure Hg lamp. The extraneous lines other than 366 nm were filtered out using the combination of $CuSO_4$ (aq.) and 5,7-dimethyl-4-azonia-1-azacyclohepta-4,6-diene perchlorate solution filters and a Corning 7-37 glass filter. The light intensity was determined by ferrioxalate actinometry [5], at about 1.8×10^{16} quanta/s.

For analyses of Nbd and Q with a Shimadzu GC-8APF gas chromatograph (FID), a 3 m×3 mm stainless-steel column was used at 84 °C, which was packed with 15% PEG-4000 on Chromosorb W NAW. A similar column with 10% Shimadzu Thermon-3000 on Chromosorb W AW-DMCS was employed at 235 °C for *trans*- and *cis*-stilbene analyses.

Quantum yields were evaluated from the product quantities, irradiation light intensity and incident light absorbances of test solutions. Conversions of the photoisomerizations performed were less than 7%. The light absorbances of the test solutions for **4** with the olefins in the cuvette were larger than 1.2 at 366 nm, whereas those for other oligomers ranged from *c.* 0.015 to 0.5.

Results and discussion

In the present study, we have prepared the copper(I) oligomers $[CuCl(PR_2R')]_n$ (**2**–**4**) with $P(2\text{-}CH_3C_6H_4)_3$, $P(4\text{-}CH_3C_6H_4)_3$ and $PPh_2(C_6F_5)$ as a monodentate tertiary phosphine PR_2R', respectively*, and the oligomers were used for the catalytic photoisomerizations of Nbd and *trans*-stilbene. The cubane-like tetramer $[CuCl(PEt_3)]_4$ (**1**) [3] was tested also, whereas a similar PPh_3 tetramer was not used in this research, because of its comparatively low solubility in THF as a solvent for the olefin photoisomerizations. The four complexes **1**–**4** are expected to have potential coordinative unsaturation, allowing Nbd and *trans*-stilbene coordination to copper(I) in the ground state [2]. In addition, complex-stabilizing properties of tertiary phosphines have been realized in many olefin transition-metal complexes in low oxidation states [6].

THF solutions of the copper(I) oligomers with Nbd or *trans*-stilbene (0.5 M) were irradiated at 366 nm, and olefin-photoisomerization products were analyzed with FID gas chromatography. The isomerizations occurred upon 366 nm irradiation in the presence of the oligomers, and Table 1 summarizes the quantum yields evaluated for Nbd–Q and *trans*–*cis*-stilbene isomeri-

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*To our knowledge, there have been no descriptions so far on the complexes **2**–**4**. Molecular weight determinations of **2**–**4** by use of mass spectroscopy were not performed because of their poor sublimation properties. Vapor pressure osmometry did not provide meaningful data of solution molecular weights for **2**–**4**, owing to their limited solubilities in appropriate organic solvents, in spite of the need of fairly high solute concentrations for this method.

TABLE 1. *trans–cis*-Stilbene and Nbd–Q photoisomerizations at 366 nm

Oligomer	Phosphine	Cone angle[a] (°)	Quantum yield[b]	
			Stilbenes	Nbd-Q
1	PEt_3	132	0.58 ± 0.05	0.49 ± 0.05
3	$P(4\text{-}CH_3C_6H_4)_3$	145	0.13 ± 0.02	0.11 ± 0.02
4	$PPh_2(C_6F_5)$	158	~0.04	0.03
2	$P(2\text{-}CH_3C_6H_4)_3$	194	⩽0.02	0

[a]Ref. 8. [b]Obtained as an average from three experiments for the respective photoisomerizations.

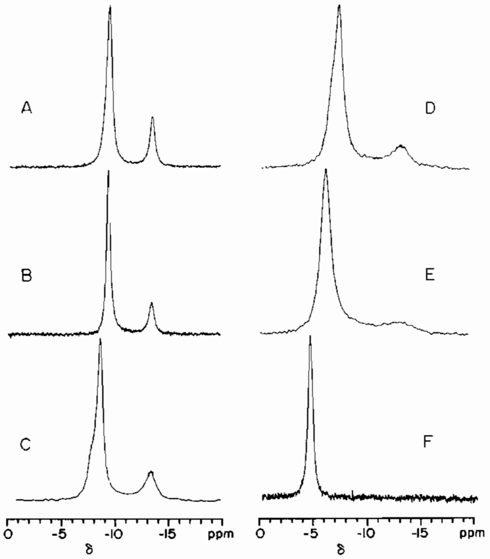

Fig. 1. Nbd-concentration dependent ^{31}P NMR spectra of $[CuCl(PEt_3)]_4$ in CD_2Cl_2 at −60 °C. Cu atom, 0.06 M. Nbd: A, 2.6; B, 1.0; C, 0.49; D, 0.26; E, 0.12; F, 0.0 M.

zations. On the basis of gas-chromatographic analyses, other by-product formations, such as olefin photodimerization [2, 7], under these reaction conditions were not significantly observed. The quantum yields for the Nbd–Q isomerization in the present study were found to be considerably larger than those of the halo(ferrocenyldiphenylphosphine)copper(I) tetramers in the previous paper [2].

At 366 nm, copper(I) halides did not significantly promote the Nbd–Q isomerization. In the case of *trans–cis*-stilbene isomerization, only a small amount of *cis*-stilbene was formed even in the absence of **1–4**, and therefore the quantum yields of stilbene photoisomerization by **1–4** were corrected by subtracting the portions due to contribution by the photoisomerization of stilbene itself without intervention of the oligomers.

As Table 1 shows, the quantum yields for the Nbd and *trans*-stilbene isomerizations decreased with increasing cone angles [8] of the phosphines coordinated to copper. The angles are associated with the stereochemical hindrance around the phosphorus coordination site on copper.

In order to study olefin complexation with these tertiary-phosphine oligomers, we observed their ^{31}P NMR spectra in CD_2Cl_2 at low temperatures. The tetramer **1** at −60 °C showed a slightly broad signal at δ −4.7, whereas addition of Nbd brought about a new small signal at δ *c.* −13 besides the former one, as shown in Fig. 1. The δ value of the former signal was slightly dependent on the molar ratio of Nbd to the copper atom, and with decrease in the ratio from 43 to 2, the δ value increased from −10 to −5.* On the other hand, the δ value of the latter signal remained almost unchanged upon the decrease in the ratio. At room temperature, however, analogous appearance of a new signal was not observed, which corresponds to that one (δ *c.* −13) at −60 °C. When 2-norbornene** was used at −60 °C in place of Nbd, a similar small signal was observed at δ −13.3. Accordingly, we proposed the following equilibrium, where reaction

$$[CuCl(PR_2R')]_n + nL \rightleftharpoons n[CuCl(L)(PR_2R')]$$

L: olefin substrates

rates of olefin coordination and dissociation were fast enough at room temperature to give a single coalesced

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*As the referee suggests, we cannot rule out the possibility of multistage equilibria involving some kinds of dimeric and/or trimeric species (with the olefins), besides the original oligomers $[CuCl(PR_2R')]_n$ and the monomeric olefin adducts $[CuCl(olefin)(PR_2R')]$. As for ^{31}P NMR spectra in Fig. 1, other than **1**, some kinds of dimeric and/or trimeric species also may contribute in some part to the signal at lower fields. On the other hand, chemical shift of the other signal at δ *c.* −13 was hardly affected by the change of the Nbd/Cu molar ratio, and the signal was associated with the Nbd-adduct species $[CuCl(Nbd)(PEt)_3]$. In a two-compartment cuvette for UV–Vis absorption spectroscopy, we placed separately a THF solution of Cu(I) oligomers and another one of olefins, and on mixing the two solutions, we looked for any spectral change, as an attempt to identify the species formed in the solutions, besides the monomeric olefin adducts. However, new well-resolved distinct absorption bands were not observed, and significant success was not obtained by this spectroscopic technique.

**2-Norbornene, bicyclo[2.2.1]-2-heptene.

signal in the ^{31}P NMR spectra, and cooling to −60 °C slowed down the rates to givc two separate signals. Thus, these findings indicated that the olefins cleaved probable halogen bridges in oligomeric complexes and formed some adduct copper(I) species in the ground state. 2,5-Norbornadiene has been reported to undergo monodentate (exo) coordination to copper(I) via only one C=C bond [9]. The above-described signal of **1** around δ −13 was determined to be for its olefin-adduct species. Analogous Nbd-adduct formation of **3** at −30 °C was observed at δ *c.* −3.5.

In the case of the $PPh_2(C_6F_5)$ oligomer **4** at −60 °C, Nbd addition gave only a small shoulder at lower field side (near δ −20.1) of the main NMR signal (at δ −22.4) for **4**, whereas the $P(2\text{-}CH_3C_6H_4)_3$ oligomer **2** did not show any ^{31}P NMR spectral change upon similar Nbd addition, indicating lack of olefin-adduct formation due to high stereochemical hindrance of the phosphine around the phosphorus coordination site [8]. Observation of ^{31}P NMR spectral change by addition of *trans*-stilbene was not carried out owing to its low solubility in CD_2Cl_2 at low temperatures.

Together with the above-described results of the olefin photoisomerizations in Table 1, these findings concerning the ground-state adduct formation with the olefins clearly indicated that the oligomers with sterically bulkier phosphines, having larger cone angles, formed the olefin adducts to a lesser extent, and led to smaller quantities of the isomerized products upon photoirradiation.

Phosphines used in the present study are confined to alkyl and aryl ones, and due considerations seem to be requested for extended application to the superficial comparison with a completely different type of tertiary phosphorus ligand [8], such as phosphite $P(OR)_3$. Further studies in this area are under way.

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