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Syntheses of New Ferrocenylphosphinecopper(I) Complexes and their Application to the Valence Isomerization of Norbornadiene to Quadricyclene

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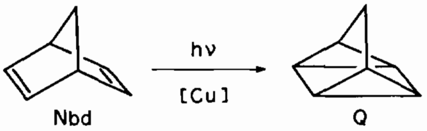
Abstract

Copper(I) chloride and bromide reacted with an equimolar amount of ferrocenyldiphenylphosphine ($PFcPh_2$) in refluxing benzene, affording the new tetrameric complexes $[CuX(PFcPh_2)]_4$ (**1**, X = Cl; **2**, X = Br) as yellow microcrystals. Their bipyridyl (bpy) derivatives $[CuX(bpy)(PFcPh_2)]$ (**3**, X = Cl; **4**, X = Br) were prepared also. When copper(I) chloride was allowed to react with abundant $PFcPh_2$, only the mononuclear complex $[CuCl(PFcPh_2)_2]$ (**5**) was isolated. THF solutions of the copper(I) complexes and 2,5-norbornadiene (Nbd) were irradiated at 366 nm, and the valence isomerization of Nbd to quadricyclene (Q) was observed. Quantum yields with **1** and **2** were about 0.011 and 0.008, respectively, and those with other complexes were very small. ^{31}P NMR studies were performed for the complexes in the presence of Nbd or norbornene, and the key photoactive species in the isomerization with **1** and **2** were determined to be their ground state copper–Nbd adducts, *i.e.* '$CuX(PFcPh_2)(Nbd)$'. Photoexcitation of the adducts was assumed to give rise to the valence isomerization and to release Q.

Introduction

Some copper(I) complexes have been reported to promote the valence isomerization of norbornadiene** (Nbd) to quadricyclene† (Q) under photoirradiation at 313 nm, and the isomerization was proposed as one of the most promising systems for solar energy storaging by Kutal *et al.* [1]. However, there have been only a few papers descriptive of quantum yields for the isomerization with the complexes under irradiation at longer wavelengths than 313 nm [2, 3]. It seems that there are still some subjects for further examination in order to develop highly active and relatively inexpensive copper(I) complexes with light-harvesting abilities in the wavelength region of solar radiation reaching the earth††.

In this paper, we wish to describe syntheses and properties of new halo(ferrocenyldiphenylphosphine)copper(I) tetramers and the related complexes, and their catalytic activities in the Nbd → Q isomerization under irradiation at 366 nm. Incentive for studies on these complexes was derived from the following: (i) introduction of the ferrocenyl subunit as a light-harvesting center effective in near UV and visible regions, in the vicinity of copper reaction sites; (ii) molecular design of copper(I) complexes with potential coordinative unsaturation, allowing Nbd coordination to the complexes in the ground state [5], followed by photoexcitation of the Nbd adducts formed to release Q; and (iii) high stability to air oxidation and high solubility in common organic solvents.



Experimental

Materials and General Procedures

Norbornadiene (Tokyo Kasei) was distilled under a nitrogen atmosphere, and ferrocenyldiphenylphosphine ($PFcPh_2$) was prepared by literature methods [6]. Tetrahydrofuran was dried over $LiAlH_4$. All preparative manipulations except column chromatography were performed under dry nitrogen.

Melting points were measured with a Yanagimoto MP-S3 microstage apparatus in capillary tubes and are uncorrected. IR spectra were obtained using a JASCO A-100 spectrometer. ^{1}H and ^{13}C NMR

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**Norbornadiene, bicyclo[2.2.1]hepta-2,5-diene.

†Quadricyclene, quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane.

††As an another approach to effective utilization of solar radiation in the longer wavelengths, there were some attempts reported to introduce some chromophore substituents on norbornadiene, see ref. 4.

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spectra were run on JEOL model MH-100 and FX-90-Q spectrometers, and chemical shifts (δ) are expressed in parts per million relative to TMS. ^{31}P NMR spectra were recorded on a JEOL GX-400 spectrometer, and were referenced to external $P(OCH_3)_3$ set at δ 140.0 ppm relative to 85% H_3PO_4. Molecular weights of copper(I) complexes were determined in benzene using a Corona model 114 vapour pressure osmometer. Irradiated test solutions were analyzed for Nbd and Q with a Shimadzu GC-8APF gas chromatograph (FID) containing a 3 m × 3 mm stainless-steel column, which was packed with 15% PEG 4000 on Chromosorb W NAW (60–80 mesh). The injection and detector temperatures were set at 110 °C, and the column temperature was at 84 °C.

Preparation of [CuX(PFcPh₂)]₄

Ferrocenyldiphenylphosphine (745 mg, 2.0 mmol) was added to the benzene suspension (20 ml) of copper(I) chloride (200 mg, 2.0 mmol), and the mixture was heated under reflux for 12 h. After evaporation *in vacuo* to dryness, the residue was recrystallized from THF and n-hexane, affording yellow microcrystals (385 mg) of $[CuCl(PFcPh_2)]_4$ (**1**). Vis(THF) 440 nm (ϵ 640). The bromo analogue (**2**) was prepared by similar procedures except that recrystallization was performed from dichloromethane and n-hexane. Vis(THF) 444 nm (ϵ 980).

Preparation of [CuX(bpy)(PFcPh₂)]

Complex **1** (140 mg, 0.075 mmol) was treated with 2,2′-bipyridyl (bpy) (47 mg, 0.30 mmol) in benzene (20 ml), and the mixture was stirred overnight at room temperature. Color of the solution turned orange. The solvent was removed under vacuum, and recrystallization of the residue from THF and diethyl ether gave orange microcrystals (63 mg) of $[CuCl(bpy)(PFcPh_2)]$ (**3**). Vis(THF) 402 nm (sh, ϵ 590). Analogous reaction of **2** yielded the complex $[CuBr(bpy)(PFcPh_2)]$ (**4**). Vis(THF) 416 nm (sh, ϵ 620).

Reaction of CuCl with Abundant PFcPh₂

Fourfold moles of $PFcPh_2$ (520 mg, 1.4 mmol) was added to the benzene suspension (20 ml) of CuCl (35 mg, 0.35 mmol), and the mixture was refluxed for 4 h. After filtration of the hot solution and concentration of the filtrate into a small volume, addition of diethyl ether precipitated the reddish yellow powder (230 mg) of $[CuCl(PFcPh_2)_2]$ (**5**). For further purification of the powder, column chromatography was effective by use of silica gel (Wako C-200). Vis(THF) 444 nm (ϵ 300).

Quantum Yield Measurements of the Valence Isomerization of Nbd to Q

In a typical photochemical run, three-milliliter aliquots of the THF solutions of the copper(I) complexes ([Cu(I) atom]; 2×10^{-3} M) with 0.5 M Nbd were prepared and transferred by syringes under nitrogen to a Thunberg-tube with a rectangular Pyrex cuvette (10 × 10 × 45 mm). After the aliquots were deaerated, photoirradiation was performed 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 [7], at about 2.0×10^{16} quanta/s.

Results and Discussion

(Ferrocenyldiphenylphosphine)copper(I) Complexes

Copper(I) chloride and bromide reacted with an equimolar amount of ferrocenyldiphenylphosphine $PFcPh_2$ in refluxing benzene to afford new stable (halo) (ferrocenyldiphenylphosphine)copper(I) tetramers $[CuX(PFcPh_2)]_4$ (**1**, X = Cl; **2**, X = Br) as yellow microcrystals. They were very soluble in many organic solvents, such as benzene, THF, and dichloromethane. The ^{13}C NMR spectrum of **1** in CD_2Cl_2 showed a large signal at δ 70.3 for the unsubstituted cyclopentadienyl group, and signals at δ 74.0, 72.0, and 70.0 for the monosubstituted one.

Treatment of **1** and **2** with 2,2′-bipyridyl bpy afforded the stable mononuclear complexes $[CuX(bpy)(PFcPh_2)]$ (**3**, X = Cl; **4**, X = Br), as orange and yellow microcrystals, respectively.

When copper(I) chloride was treated with fourfold moles of $PFcPh_2$ under benzene reflux, the reaction mixture gave only the mononuclear complex $[CuCl(PFcPh_2)_2]$ (**5**), in contrast to the case of PPh_3 which forms $[CuCl(PPh_3)_3]$ [8]. This contrast was reasonably attributed to higher steric bulkiness of $PFcPh_2$ than that of PPh_3. Analytical data and properties of the highly colored complexes **1**–**5** are summarized in Tables I and II. Their non-ionic character was confirmed by low conductivities in common organic solvents.

In the ^{31}P NMR spectra, complex **1** in CD_2Cl_2 showed a slightly broad singlet at δ −9.6 at 25 °C, which shifted to δ −14.2 on cooling to −30 °C. Figure 1 demonstrates the temperature-dependent NMR spectra (A and B) of **1** in the presence of Nbd (the molar ratio of [Nbd]/[Cu atom] = 108), and a new signal was observed at δ −10.3 at −30 °C, besides the signal at δ −14.6 attributable to **1**. The δ values of the two signals were slightly dependent on the molar ratio of Nbd to the copper atom in **1**. When the ratio was changed in the region of 260 to 30, the former signal ranged from δ −10.5 to −9.5, and the latter one from δ −15.3 to −14.0.

TABLE I. Syntheses of New (ferrocenyldiphenylphosphine)copper(I) Complexes

Formula		Yield[a] (%)	Melting point[e] (°C)	Analyses, Found(calc.) (%)		
				C	H	N
$[CuCl(PFcPh_2)]_4$	1	41	125–130	56.12(56.32)	4.33(4.08)	
$[CuBr(PFcPh_2)]_4$	2	60	200–202	51.37(51.44)	3.87(3.73)	
$[CuCl(bpy)(PFcPh_2)]$	3	34[b]	205–208	61.20(61.46)	4.40(4.35)	4.24(4.48)
$[CuBr(bpy)(PFcPh_2)]$	4	84[c]	216–219	57.31(57.38)	4.31(4.06)	4.12(4.18)
$[CuCl(PFcPh_2)_2]$	5	78[d]	219–221	63.00(62.96)	4.77(4.56)	

[a]Based on $PFcPh_2$, unless noted elsewhere. [b]Based on 1. [c]Based on 2. [d]Based on CuCl. [e]With decomposition.

TABLE II. Properties of New (Ferrocenyldiphenylphosphine)copper(I) Complexes

Formula	Selected ^1H NMR Data[a]			Molecular weight[b] Found(calc.)
	$P\text{-}C_5H_4$		C_5H_5	
	2- and 5-H	3- and 4-H		
$[CuCl(PFcPh_2)]_4$	4.36(bs)		4.08(s)	1869(1877)
$[CuBr(PFcPh_2)]_4$	4.44(m)	4.50(m)	4.12(s)	2018(2055)
$[CuCl(bpy)(PFcPh_2)]$	4.20(bs)	4.33(bs)	3.97(s)	
$[CuBr(bpy)(PFcPh_2)]$	4.21(m)	4.33(m)	3.86(s)	
$[CuCl(PFcPh_2)_2]$	4.18(m)	4.34(m)	4.07(s)	817(839)

[a]δ Value from TMS; in $CDCl_3$; bs = broad singlet, s = singlet, m = multiplet. [b]In benzene at 42 °C.

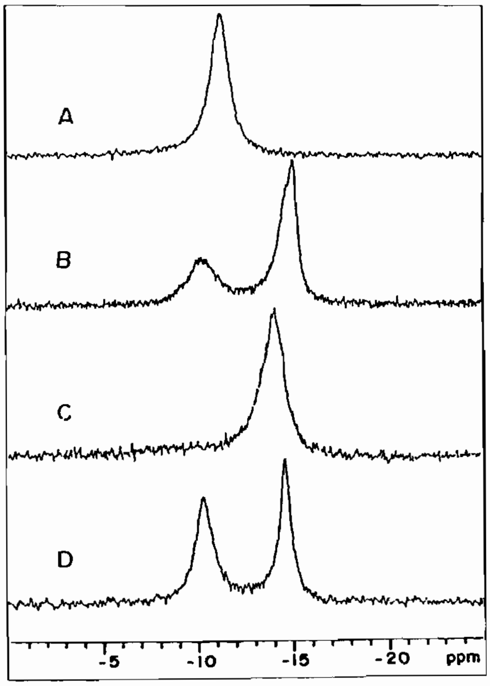

Fig. 1. ^{31}P NMR spectra of 1 in CD_2Cl_2. A: [Nbd]/[Cu atom] = 108, at 25 °C; B: [Nbd]/[Cu atom] = 108, at −30 °C; C: free of olefins, at −30 °C; D: [Norbornene]/[Cu atom] = 108, at −30 °C.

When norbornene* was used in place of Nbd, a similar signal appeared also at δ −10.4 (D in Fig. 1). The signals around δ −10 at −30 °C were attributed to the adduct species (*vide infra*) with Nbd or norbornene. We proposed the following equilibrium (1)

$$[CuCl(PFcPh_2)]_4 + 4L \rightleftharpoons 4[CuCl(PFcPh_2)L] \qquad (1)$$

L; Nbd, Norbornene

where reaction rates for olefin-coordination and -dissociation were fast enough at room temperature to give a single coalesced signal in the ^{31}P NMR spectra. On the other hand, the rates were slowed down on cooling to −30 °C and we observed two separate signals.

For the CD_2Cl_2 solution of 1 at −30 °C with a small amount of $PFcPh_2$ added, there was a small broad signal around δ −9 in addition to the signal of 1 at δ −14.2. When four moles of $PFcPh_2$ were mixed with one mole of the tetramer 1 (*i.e.* $[PFcPh_2]/[Cu\ atom] = 2$), the spectra showed only one signal at δ −13.0, and was the same as that of 5. Further increase in quantities of $PFcPh_2$ relative to 1 shifted the signal at δ −13.0 upfield close to δ −18.3, where free $PFcPh_2$ at −30 °C was expected

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

TABLE III. Quantum Yields for the 366 nm Photoisomerization of Nbd to Q[a]

$[CuCl(PFcPh_2)]_4$	1.1×10^{-2}	$[CuCl(bpy)(PFcPh_2)]$	5.6×10^{-4}
$[CuBr(PFcPh_2)]_4$	8.0×10^{-3}	$[CuBr(bpy)(PFcPh_2)]$	4.0×10^{-4}
$[CuCl(PFcPh_2)_2]$	3.9×10^{-4}	$PFcPh_2$	$<10^{-4}$

[a] [Cu(I)] = 2×10^{-3} M (based on Cu(I) atom); [Nbd] = 0.5 M; in THF; performed for 4 h at 30 °C.

to resonate. Lack of the signal due to free $PFcPh_2$ indicated fast exchange of free $PFcPh_2$ with the phosphines in 5.

When we treated the bromo complex 2 in CD_2Cl_2 with the additive such as Nbd, norbornene, and $PFcPh_2$, spectral changes of ^{31}P NMR were observed similarly to the above-described case of 1.

Thus, these neutral ligands cleaved halogen-bridges [8c] in tetrameric 1 and 2 to form some adduct species, and the complexes were determined to have potentially coordinatively unsaturated nature. On the contrary, for mononuclear bipyridyl complexes 3 and 4, the presence of Nbd and norbornene did not give any additional NMR signals attributable to the formation of some species of the olefin adducts, and the bipyridyl copper complexes were coordinatively saturated so far as these olefins are concerned as the incoming ligands. It is noted that a similar ^{31}P NMR observation of 5 with the olefins did not give any indication of formation of the adduct species, either.

Valence Isomerization of Nbd to Q with the Copper(I) Complexes

THF solutions of the copper(I) complexes and Nbd (0.5 M) were irradiated at 366 nm, and formation of Q was determined by FID gas chromatography. Table III shows compilation of quantum yields for the isomerization of Nbd to Q. Several points are worthy of note. (i) The isomerization to Q occurred upon 366 nm irradiation in the presence of the complexes 1–5. At this irradiation wavelength, copper halides did not promote the isomerization practically. (ii) The observed quantum yields with 1 and 2 were larger than those with other complexes, and their high abilities were attributed to the above-described formation of the Nbd adducts without photoirradiation (*i.e.* in the ground state). Photoexcitation of the adducts was expected to release converted Q [1a, 1c]. In the cases of 3, 4, and 5, the isomerization resulted probably from bimolecular interaction [1b, 5b] of the photoexcited copper(I) complexes with ground state Nbd to give Q, but with small quantum yields. The absence of Nbd adduct formation in the ground state would be responsible for the low activities of 3, 4, and 5 in the Nbd → Q isomerization. It is noted that the inverse isomerization of Q to Nbd was tried for 1 under irradiation, but Nbd was not formed.

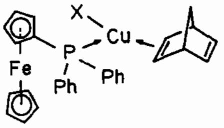

Fig. 2. Nbd-adduct species with π-olefin–copper bonds.

Thus, the complexes 1 and 2 promoted Nbd → Q isomerization under irradiation at 366 nm, and the present paper suggests the importance of the potentially coordinatively unsaturated nature of the copper center, in the molecular design of highly active complexes for the isomerization.

As described above, addition of Nbd to the solutions of 1 and 2 showed the ^{31}P NMR spectral change in a similar manner to that of norbornene. Norbornadiene has been reported to prefer monodentate (exo) coordination to copper(I) through only one C=C bond [9], instead of the bidentate (endo) one which is well-known in the case of palladium(II) [10]. Moreover, we did not observe significant photodimerization [11]* of Nbd and norbornene in the presence of the $PFcPh_2$ copper(I) complexes, and this fact was untenable for possible 1:2 copper–Nbd adduct species [1a, 1e, 12]. On the basis of the results of the Nbd valence isomerization and of the ^{31}P NMR observation, the key photoactive species formed from 1 and 2 were determined to have the structure as shown in Fig. 2. The steric bulkiness of $PFcPh_2$ in the species would prefer the monomeric structure, to possible halogeno-bridged dimeric ones, as was the case for the complex 5.

Acknowledgement

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