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Preparation and Reactivities of Phenylethynyl[1,1,1-tris(diphenylphosphinomethyl)ethane]copper(I) Complex

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Phenylethynyl[1,1,1-tris(diphenylphosphinomethyl)ethane]copper(I), [Cu(C≡CPh)(tdpme)]{tdpme=1,1,1-tris(diphenylphosphinomethyl)ethane}, has been prepared in good yield by a reaction between phenylethynylcopper(I), [{Cu(C≡CPh)}$_n$], and tdpme. From physicochemical and spectroscopic studies the complex is considered to have a monomeric tetrahedral structure. It reacts with *p*-cresol to give [Cu(O–C_6H_4–CH_3-*p*)(tdpme)] and also with highly active hydrogen compounds, methyl cyanoacetate and methyl nitroacetate, to give [Cu{CH(CN)CO_2CH_3}(tdpme)] and [Cu{CH(NO_2)CO_2CH_3}(tdpme)], respectively. However, moderately active hydrogen compounds, such as acetonitrile, dimethyl malonate, and nitromethane, do not react with [Cu(C≡CPh)(tdpme)]. The reactivities of the complex with active hydrogen compounds are discussed in correlation with the pK_a values of the latter compounds.

Recently, the syntheses of organocopper compounds have been widely investigated in view of the fact that copper compounds play important roles in various copper-assisted organic reactions.

Alkyl-$^{1)}$ and arylcopper(I)$^{2,3)}$ complexes containing uni- or bidentate phosphorus ligand have been prepared and converted into substituted alkylcopper(I) complexes by reactions with active hydrogen compounds.$^{4,5)}$ Coates and Parkin,$^{6)}$ and Camus and Marsich$^{3)}$ prepared tertiary phosphine-bonded phenylethynylcopper(I) complexes, which have complicated compositions depending on the phosphine or molar ratio of phosphine/copper, such as [Cu(C≡CPh)(PR_3)$_n$] (R=Me, n=1,2,3; R=Et and Ph, n=1) and [(CuC≡CPh)$_m${$Ph_2P(CH_2)_kPPh_2$}$_n$] (k=1, m/n=4/3; k=2, m/n=1/1,2/3,4/3).

A triphosphine ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane, (tdpme), has a three-fold axis of symmetry (Fig. 1) and serves as a bidentate or a tridentate ligand in tetrahedral,$^{7-9)}$ square pyramidal,$^{7)}$ and octahedral$^{10)}$ complexes. As for copper(I) complexes, the ligand afforded the tetrahedral complexes, [CuX(tdpme)] (X=halogen,$^{8)}$ ONO_2, and $OClO_3$$^{9)}$) and a complex, [Cu($BH_4$)(tdpme)], which seems to have a very distorted square pyramidal structure.$^{11)}$

In this paper, we report the preparation and characterization of [Cu(C≡CPh)(tdpme)] **1**, and its reactivities towards active hydrogen compounds.

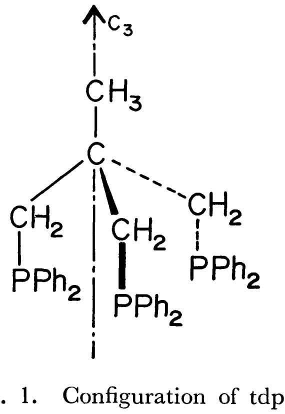

Fig. 1. Configuration of tdpme.

Experimental

Materials and Procedures. All the experiments were carried out in an atmosphere of dry nitrogen. Solvents were dried by the usual procedure and distilled.

1,1,1-Tris(diphenylphosphinomethyl)ethane (tdpme)$^{12)}$ and phenylethynylcopper(I) [{Cu(C≡CPh)}$_n$]$^{13)}$ were prepared according to published procedures. Methyl nitroacetate was also prepared and purified by distillation under reduced pressure.$^{14)}$

General Procedures. IR spectra were measured on a Hitachi 285 spectrophotometer and ^{1}H-NMR spectra on a JEOL JNM-MH-100 spectrometer. Conductivity measurements were carried out for 1.0×10^{-3} M acetone solution at 25 °C on a Toa Electronics CM-6A conduct meter. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. Molecular weight was determined in benzene by means of a cryoscopic method.

Preparation of [Cu(C≡CPh)(tdpme)] ***1***. To a suspension of phenylethynylcopper(I) (158 mg, 0.96 mmol) in 20 ml of benzene was added tdpme (600 mg, 0.96 mmol) in 20 ml of benzene at room temperature. After the resulting pale yellow solution had been stirred for 24 h, the solvent was removed under reduced pressure. Recrystallization from toluene–hexane gave 637 mg of pale yellow crystals of **1** (yield 84%).

Reaction of ***1*** *with* p-*Cresol.* *p*-Cresol (30.2 mg, 0.28 mmol) in 5 ml of THF was added to a solution of **1** (200 mg, 0.25 mmol) in 30 ml of THF at room temperature. After being stirred for 5 h, the solvent was removed under reduced pressure. Recrystallization from benzene–hexane gave 80 mg of pale yellow crystals, [Cu(O–C_6H_4–CH_3-*p*)(tdpme)] **2** (yield 40%).

Reaction of ***1*** *with Methyl Cyanoacetate.* Methyl cyanoacetate (57.1 mg, 0.58 mmol) in 5 ml of THF was added to a solution of **1** (455 mg, 0.58 mmol) in 20 ml of THF at 0 °C. After being stirred for 5 h at 0 °C, the solvent was removed under reduced pressure and the resulting solid was washed with benzene. Recrystallization from dichloromethane–hexane gave 210 mg of white crystals, [Cu{CH(CN)CO_2CH_3}(tdpme)] **3** (yield 46%).

Reaction of ***1*** *with Methyl Nitroacetate.* This reaction was carried out at 0 °C in the same way as described for **3**, and pale yellow crystals, [Cu{CH(NO_2)CO_2CH_3}(tdpme)] **4** were produced (yield 33%).

Reaction of ***1*** *with Other Active Hydrogen Compounds.* Complex **1** did not react with other moderately active hydrogen

Table 1. Some properties of the complexes **1**—**4**

No.	Mp (°C)	Elemental analyses[a] (%)			¹H-NMR (δ ppm)[b]			
		C	H	N	tdpme -CH_3	-CH_2	≡CH	other CH_3
1	207—208	73.92 (74.56)	5.70 (5.62)	—	1.56	2.40	—	—
2	130—132 (dec)	73.42 (72.49)	6.11 (5.83)	—	1.50	2.40	—	2.24
3	159—164 (dec)	68.57 (68.74)	5.52 (5.51)	1.46 (1.78)	1.58	2.42	0.64	3.74
4	144—147.5 (dec)	65.55 (65.54)	5.59 (5.38)	1.69 (1.74)	1.34	2.38	0.90	3.67

a) Calculated values in parentheses. b) In $CDCl_3$ (TMS as the internal standard).

compounds, *i.e.*, acetonitrile, dimethyl malonate, and nitromethane in THF either at 0 °C, room temperature, or 65 °C (refluxing conditions), only the starting complex **1** being recovered.

Results and Discussion

Preparation and Properties of [*Cu(C≡CPh)(tdpme)*] ***1***. Complex **1** was prepared by the reaction of phenylethynylcopper(I) with tdpme in benzene at room temperature. The complex is considerably stable in air and soluble in common organic solvents.

$$[\{Cu(C\equiv CPh)\}_n] + n\,tdpme \xrightarrow[r.\ t.]{benzene} n[Cu(C\equiv CPh)(tdpme)]\ \mathbf{1}$$

The IR spectrum of **1** shows a $\nu(C\equiv C)$ band at 2030 cm^{-1}, higher (*ca.* 100 cm^{-1}) than that of phenylethynylcopper(I), and is assigned to the ethynyl group bonded to copper. Such shift of the $\nu(C\equiv C)$ band was observed in other phenylethynylcopper(I) complexes containing phosphine ligands.[3] Molecular weight determination revealed that **1** is monomeric in benzene: Found: 828 (2.25 wt%). Calcd for $C_{49}H_{44}CuP_3$: 789.4. Conductivity of **1** ($\Lambda = 5.75\ \Omega^{-1}\ cm^2\ mol^{-1}$) in acetone solution did not change significantly on addition of excess methyl iodide. This indicates that tdpme serves as a tridentate ligand, leaving no uncoordinated phosphine group expected to yield a phosphonium salt on addition of methyl iodide,[7] and that **1** has a tetrahedral structure as shown in Fig. 2.

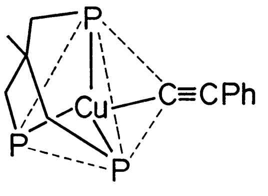

Fig. 2. Configuration of [Cu(C≡CPh)(tdpme)] **1**.

Reactivities of [*Cu(C≡CPh)(tdpme)*] ***1***. Complex **1** reacted with *p*-cresol, methyl cyanoacetate, and methyl nitroacetate in THF to give new tdpme-copper complexes, $[Cu(O\text{-}C_6H_4\text{-}CH_3\text{-}p)(tdpme)]$ **2**, $[Cu\{CH(CN)CO_2CH_3\}(tdpme)]$ **3**, and $[Cu\{CH(NO_2)CO_2CH_3\}(tdpme)]$ **4**, respectively, which were characterized by elemental analyses, IR and ¹H-NMR spectroscopy. Some properties of the complexes are summarized together with those of **1** in Table 1.

$$[Cu(C\equiv CPh)(tdpme)] + BH \xrightarrow[THF]{} [CuB(tdpme)] + HC\equiv CPh$$

B: Conjugated base

Complexes **2**, **3**, and **4** show considerable thermal stability, and are moderately stable in air; they can be stored for a long time in dry nitrogen atmosphere. Their IR spectra show no $\nu(C\equiv C)$ band, which is found in the starting complex **1**.

A tetrahedral structure can be ascribed also to complex **2** in view of its ¹H-NMR showing only one methylene resonance for tdpme moiety.

The IR spectrum of **3** shows a $\nu(C\equiv N)$ band at 2155 cm^{-1} and a $\nu(C=O)$ band at 1610 cm^{-1}. The ¹H-NMR spectrum of **3** shows methine signal at a considerably high field ($\delta = 0.64$) and one methylene resonance at δ 2.42, indicating that the three methylene groups of tdpme moiety are equivalent. This indicates that **3** assumes a tetrahedral complex containing a copper-carbon σ-bond.

The conjugated base of methyl nitroacetate in **4** should be coordinated to copper either with methine carbon (structure A) or with an *aci*-nitro group (structure B), as shown in Fig. 3. In fact, $[Cu(O_2NCH_2)(PPh_3)_2]$[15] and $[Cu\{O_2NCPh(NO_2)\}(PPh_3)_2]$[16] were confirmed by X-ray analysis to be tetrahedral complexes, in which the nitro group is coordinated to copper with the *aci*-nitro form. Methylene protons in the *aci*-nitro group of $[Cu(O_2NCH_2)(PPh_3)_2]$ show resonance at a very low field ($\delta = 4.35$).[15] On the other hand, the ¹H-NMR spectrum of **4** exhibits methine resonance at a considerably high field ($\delta = 0.90$), and only one methylene resonance at δ 2.38, similar to the respective one of **3**. This indicates that **4** has structure A, in which copper is coordinated with tdpme at three sites of phosphine groups. In order to confirm whether

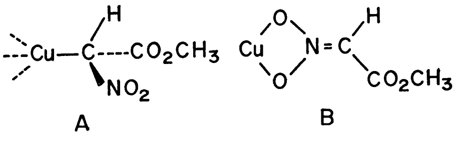

Fig. 3. Possible configurations of **4**.

TABLE 2. COMPARISON BETWEEN pK_a VALUE AND REACTIVITY

Compound	Reactivity of **1**	pK_a value	Ref.[a)]
$C_6H_5C{\equiv}CH$	—	21	17
CH_3CN	No	25	17
$CH_2(CO_2CH_3)_2$	No	13.5	18
$CH_2(CN)_2$	Yes	11.2	17, 18
CH_3NO_2	No	10.2	17, 18
$NCCH_2CO_2CH_3$	Yes		
$O_2NCH_2CO_2CH_3$	Yes	5.8	18
$HO\text{-}C_6H_4\text{-}CH_3\text{-}p$	Yes	10.2	19

a) See references presented in the last part of this paper.

4 contains an uncoordinated phosphine group, conductivity of an acetone solution of **4** containing excess methyl iodide was measured. The experiment was unsuccessful owing to the immediate precipitation of a white solid , which was ascribed to [CuI(tdpme)][8)] on the basis of elemental analysis and IR spectrum. Complex **4** seems to prefer structure A to B, owing to the chelating effect of the tridentate phosphine group which prevents the bidentate *aci*-nitro group from coordinating to copper. As for the IR spectrum of **4**, bands at 1440, 1620, and 1680 cm^{-1} were ascribed to $\nu_a(NO_2)$, $\nu_{as}(NO_2)$, and $\nu(C{=}O)$, respectively.

No reaction took place between **1** and other moderately active hydrogen compounds, *i.e.*, acetonitrile, dimethyl malonate, and nitromethane, even under refluxing conditions of THF. Malononitrile reacted with **1** to give yellow powder, which could not be isolated in a pure state.

As a whole, it appears that the reaction between **1** and active hydrogen compounds depends on the pK_a values of the latter[17—19)] (Table 2). Complex **1** reacts with highly active hydrogen compounds having a pK_a value below 10, but not with less active hydrogen compounds with pK_a above 13. **1** shows fairly complicated reactivity towards the active hydrogen compounds with pK_a values in the range 10—13, while **1** reacts smoothly with *p*-cresol, a week Brönsted acid having a pK_a of 10.2. Such hydrogen activity is important for a similar exchange reaction with the phenylcopper(I)–triphenylphosphine system.[4)]

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