

Organopalladium(II) Complexes Derived from Chloro[4-[2-(diphenylphosphino)ethylamino]-3-penten-2-onato-*O,N,P*]palladium(II)

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A new tertiary phosphine containing α,β -unsaturated β -amino ketone, 4-[2-(diphenylphosphino)ethylamino]-3-penten-2-one (Hdpeap), reacts with sodium tetrachloropalladate(II) in the absence or presence of sodium ethoxide to give $[\text{PdCl}_2(\text{Hdpeap})_2]$ or $[\text{PdCl}(\text{dpeap})]$ [$\text{dpeap} \equiv 4\text{-[2-(diphenylphosphino)ethylamino]-3-penten-2-onato-}O,N,P]$, respectively. The latter complex reacts with terminal acetylenes in the presence of catalytic amounts of copper(I) iodide to produce alkynyl complexes, $[\text{Pd}(\text{C}\equiv\text{CR})(\text{dpeap})]$. Carbanions derived from active methylene compounds, and sodium dimethyldithiocarbamate also react with $[\text{PdCl}(\text{dpeap})]$ to afford $[\text{Pd}(\text{CHYY})(\text{dpeap})]$ and $[\text{Pd}(\text{S}_2\text{CNMe}_2)_2]$, respectively.

Many investigations have been reported about the quadridentate Schiff bases derived from β -diketones and primary diamines¹⁾ and about their transition metal complexes.²⁾ However, there have been only few papers on tridentate Schiff bases, derived from acetylacetone and primary monoamines containing a hetero atom on their β -position, except the diamines.^{3–5)} Uhlig and Gottschling⁴⁾ reported that 4-(2-picolylamino)-3-penten-2-one (Hpip), produced from acetylacetone and 2-picolylamine, forms univalent ONN-type tridentate chelates to nickel(II) and copper(II) ions. The previous paper from our laboratory dealt with the preparation of chloro[4-(2-picolylamino)-3-penten-2-onato-*O,N,N*]-palladium(II) and with the reactions of this complex with carbanions derived from active methylene compounds.⁵⁾

In this paper, we present the preparation of a new, tertiary phosphine-containing tridentate α,β -unsaturated β -amino ketone, 4-[2-(diphenylphosphino)ethylamino]-3-penten-2-one (Hdpeap), and its reactions towards tetrachloropalladate(II) in the absence and presence of sodium ethoxide, resulting in the formation of $[\text{PdCl}_2(\text{Hdpeap})_2]$ and $[\text{PdCl}(\text{dpeap})]$ [$\text{dpeap} \equiv 4\text{-[2-(diphenylphosphino)ethylamino]-3-penten-2-onato-}O,N,P]$, respectively. In addition, the reactions of the latter complex with terminal acetylenes, carbanions, and sodium dimethyldithiocarbamate $[\text{Na}(\text{dmdc})]$ are reported.

Experimental

Materials and General Procedures. 2-(Diphenylphosphino)ethylamine,⁶⁾ methyl propiolate,⁷⁾ and thallium(I) acetylacetonate $[\text{Tl}(\text{acac})]$ ⁸⁾ were prepared according to the published procedures. Solvents were dried by standard methods and distilled. The other reagents were commercial samples and were used without further purification.

Melting points were measured in capillary tubes on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. IR and ¹H-NMR spectra were recorded according to the previous paper.⁵⁾ All preparative operations were performed in an atmosphere of dry nitrogen.

Preparation of Hdpeap. A benzene solution of 2-(diphenylphosphino)ethylamine (26 mmol) and acetylacetone (52 mmol) was heated under reflux for 3.5 h. After the reaction mixture had been evaporated to dryness, the residue was recrystallized from hexane to give crystalline solids, 4-[2-(diphenylphosphino)ethylamino]-3-penten-2-one (Hdpeap) 1.

Reaction of Hdpeap with Sodium Tetrachloropalladate(II).

An ethanol solution (100 ml) containing Hdpeap (3.93 mmol) and $\text{Na}_2[\text{PdCl}_4]$ (1.96 mmol) was stirred at room temperature for 15 h. After the solvent had been evaporated, the residue was extracted with 30 ml of benzene. The benzene-extract was evaporated *in vacuo*, and the resulting solids were recrystallized from THF and hexane to afford crystalline solids $[\text{PdCl}_2(\text{Hdpeap})_2]$ 2. Hdpeap (2.15 mmol) was added to an ethanol solution (40 ml) of sodium ethoxide (2.15 mmol). The resulting solution was added dropwise to an ethanol solution of $\text{Na}_2[\text{PdCl}_4]$ (2.36 mmol) for 2 h, and the reaction mixture was stirred at room temperature for 6 h. After filtration, the filtrate was concentrated to give a precipitate, which was collected by filtration and washed with diethyl ether to yield $[\text{PdCl}(\text{dpeap})]$ 3.

Halogen Metathesis of 3. An acetone suspension (30 ml) containing 3 (0.66 mmol) and $\text{LiBr}\cdot\text{H}_2\text{O}$ (2.86 mmol) was heated under reflux for 10 h. The reaction mixture was evaporated to dryness, and the residue was extracted with benzene. The extract was diluted with diethyl ether to give a precipitate of $[\text{PdBr}(\text{dpeap})]$ 4.

Reactions of 3 with Terminal Acetylenes. A diethyl ether solution (8 ml) of methyl propiolate (6.4 mmol) was added to a diethylamine solution (50 ml) containing 3 (1.28 mmol) and copper(I) iodide (3.8×10^{-2} mmol). The reaction mixture was heated under reflux for 31 h. After the volatile matters had been evaporated, the residue was washed with water and recrystallized from benzene and diethyl ether to give $[\text{Pd}(\text{C}\equiv\text{CCO}_2\text{Me})(\text{dpeap})]$ 5. Complex 3 reacted with phenylacetylene (at room temperature for 6.5 h) or 1-hexyne (under reflux for 13 h) in a diethylamine–diethyl ether mixture in the presence of a catalytic amount of copper(I) iodide followed by the similar recrystallization to yield $[\text{Pd}(\text{C}\equiv\text{C-Ph})(\text{dpeap})]$ 6 or $[\text{Pd}(\text{C}\equiv\text{C-}n\text{-C}_4\text{H}_9)(\text{dpeap})]$ 7, respectively.

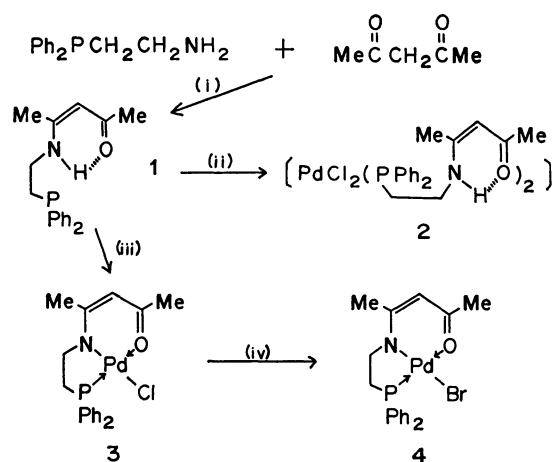
Reaction of 3 with $\text{Tl}(\text{acac})$. Thallium (I) acetylacetonate (0.51 mmol) was added to a dichloromethane solution (10 ml) of 3 (0.44 mmol). The resulting suspension was stirred at room temperature for 16.5 h. After filtration, the filtrate was concentrated and diluted with hexane to give a precipitate of $[\text{Pd}\{\text{CH}(\text{COMe})_2\}(\text{dpeap})]$ 8.

Reactions of 3 with Carbanions Formed from Active Methylene Compounds. A THF suspension containing 3 (0.44 mmol), malononitrile (0.55 mmol) and sodium methoxide (0.55 mmol) was stirred at room temperature for 24 h. After filtration, the resulting filtrate was evaporated *in vacuo*. The residue was recrystallized from dichloromethane–diethyl ether to afford $[\text{Pd}\{\text{CH}(\text{CN})_2\}(\text{dpeap})]$ 9. Complex 3 was analogously treated with carbanion formed from methyl cyanoacetate, followed by recrystallization from dichloromethane and hexane to yield $[\text{Pd}\{\text{CH}(\text{CN})\text{CO}_2\text{Me}\}(\text{dpeap})]$ 10.

Reaction of 3 with Sodium Dimethyldithiocarbamate-water (1/2). A dichloromethane suspension (30 ml) containing **3** (0.79 mmol) and sodium dimethyldithiocarbamate-water (1/2) (0.84 mmol) was stirred at room temperature for 27 h. The resulting solids were collected and washed with water and then diethyl ether to give yellow powders, $[\text{Pd}(\text{S}_2\text{CNMe}_2)_2]$ [in 54% yield, based on **3**, and in 100%, based on $\text{Na}(\text{S}_2\text{CNMe}_2) \cdot 2\text{H}_2\text{O}$]. $\text{Mp} > 300^\circ\text{C}$ (lit.⁹) $> 300^\circ\text{C}$.

Results and Discussion

Preparation of Hdpeap and its Palladium(II) Complexes. 2-(Diphenylphosphino)ethylamine and acetylacetone reacted easily in refluxing benzene to give a new tridentate Schiff base ligand, Hdpeap **1**. This ligand was treated with $\text{Na}_2[\text{PdCl}_4]$ in ethanol in the absence of alkali metal alkoxide, resulting in the formation of the adduct, $[\text{PdCl}_2(\text{Hdpeap})_2]$, **2**. The Schiff base **1** reacted with equimolar amounts of sodium ethoxide and $\text{Na}_2[\text{PdCl}_4]$ in ethanol to afford $[\text{PdCl}(\text{dpeap})]$, **3**. Complex **3** reacted with $\text{LiBr} \cdot \text{H}_2\text{O}$, terminal acetylenes, $\text{Ti}(\text{acac})_3$, and carbanion formed from active methylene compounds, such as malononitrile and methyl cyanoacetate, giving new complexes **4**, **5–7**, **8**, and **9–10**, respectively. The yields, elemental analyses, and some physical properties of compounds **1–10** are summarized



Scheme 1. Formation and reactions of Hdpeap, **1**.

i) Reflux in benzene; ii) $\text{Na}_2[\text{PdCl}_4]$; iii) $\text{Na}_2[\text{PdCl}_4] + \text{NaOEt}$; iv) $\text{LiBr} \cdot \text{H}_2\text{O}$.

in Table 1. Complexes **2–7** are stable in the air and soluble in chloroform and dichloromethane.

The Schiff base **1** and its adduct **2** showed a $\nu(\text{NH})$ frequency at 3160 and 3400 cm^{-1} , respectively. Furthermore, they exhibited three bands near 1510, 1560, and 1590 cm^{-1} , characteristic of the 4-amino-3-penten-2-one moiety. The $^1\text{H-NMR}$ spectra of **1** and **2** showed a broad signal near δ 10.8, assignable to NH proton, in addition to three singlets near δ 1.77 (3H, Me), 1.93 (3H, Me), and 4.91 (1H, CH) and two multiplets near δ 2.3–2.7 (2H, CH_2P) and 3.43 (2H, CH_2N) (Table 3). These data confirm unambiguously that **2** retains the uncoordinated 4-amino-3-penten-2-one moiety. This was in contrast with the case of 4-(2-picolyamino)-3-penten-2-one, which had acted also as a proton acceptor.⁵⁾

The IR spectra of **3–10** showed two bands near 1575 and 1505 cm^{-1} , attributable to the coordinated 4-amino-3-penten-2-onato-*N,O* group. The $^1\text{H-NMR}$ spectra of **3–10** exhibited three singlets near δ 2.0 (3H, Me), 2.1 (3H, Me), and 5.0 (1H, CH), and two double triplets in the ranges δ 2.2–2.7 [2H, CH_2P , $^2J(\text{PH}) = ca. 10 \text{ Hz}$, $^3J(\text{HH}) = ca. 6 \text{ Hz}$] and 3.0–3.7 [2H, CH_2N , $^3J(\text{PH}) = 23\text{--}30 \text{ Hz}$]. These facts indicate that **3–10** have the tridentate dpeap group.

The Ethynyl Type Complexes 5–7. Complex **3** reacted smoothly with phenylacetylene at room temperature in the diethylamine-diethyl ether mixture in the presence of 1 mol percent of copper(I) iodide.¹⁰⁾ Complex **3** reacted fairly slowly with methyl propiolate in the same conditions, because about 30% of **3** remained unchanged after stirring at room temperature for 3.5 d. However, **3** did not react with 1-hexyne at room temperature even in the presence of CuI . It was found from the above results that the order of the reactivity of terminal acetylenes towards **3** was; phenylacetylene $>$ methyl propiolate \gg 1-hexyne. Taking the $\text{p}K_a$ values of the terminal acetylenes [$\text{Bu}^n\text{C}\equiv\text{CH}$ (26.2¹¹⁾) $>$ $\text{PhC}\equiv\text{CH}$ (23.7,¹¹⁾ 21¹²⁾) $>$ $\text{MeO}_2\text{CC}\equiv\text{CH}$] into consideration, it seems likely that the ethynylation of **3** is influenced by two factors: one is the susceptibility of the acetylenes to deprotonation, resulting in the formation of the intermediates, ethynyl-copper complexes¹⁰⁾ and the other is the reactivity of the intermediates toward **3**.

TABLE 1. YIELDS AND ELEMENTAL ANALYSES

Compound	Yield %	Color	Mp ^{a)} °C	Found (Calcd) (%)		
				C	H	N
Hdpeap	1 91	White	80–80.5	72.87(73.29)	7.20(7.12)	4.51(4.50)
$[\text{PdCl}_2(\text{Hdpeap})_2]$	2 41	Pale yellow	90–95	56.70(57.05)	5.84(5.54)	3.58(3.50)
$[\text{PdCl}(\text{dpeap})]$	3 65	Yellow	238–240	50.30(50.47)	4.75(4.68)	3.09(3.10)
$[\text{PdBr}(\text{dpeap})]$	4 79	Yellow	241–242	44.92(45.94)	4.22(4.26)	2.70(2.82)
$[\text{Pd}(\text{C}\equiv\text{CCO}_2\text{Me})(\text{dpeap})]$	5 34	Pale yellow	190	54.82(55.27)	4.75(4.84)	2.73(2.80)
$[\text{Pd}(\text{C}\equiv\text{CPh})(\text{dpeap})]$	6 46	Pale yellow	185–188	62.10(62.52)	5.11(5.06)	2.14(2.70)
$[\text{Pd}(\text{C}\equiv\text{C-C}_4\text{H}_9)(\text{dpeap})]$	7 39	Pale yellow	165	60.31(60.31)	6.26(6.07)	2.74(2.81)
$[\text{Pd}\{\text{CH}(\text{COMe})_2\}(\text{dpeap})]$	8 80	Pale yellow	178–179	55.26(55.88)	5.46(5.47)	2.66(2.72)
$[\text{Pd}\{\text{CH}(\text{CN})_2\}(\text{dpeap})]$	9 80	Pale yellow	195–196	55.06(54.84)	4.57(4.60)	8.78(8.72)
$[\text{Pd}\{\text{CHCN}(\text{CO}_2\text{Me})\}(\text{dpeap})]$	10 75	Pale yellow	189–190	53.42(53.66)	4.87(4.89)	5.35(5.44)

a) With decomposition except for **1**.

TABLE 2. CHARACTERISTIC IR BANDS^{a)}

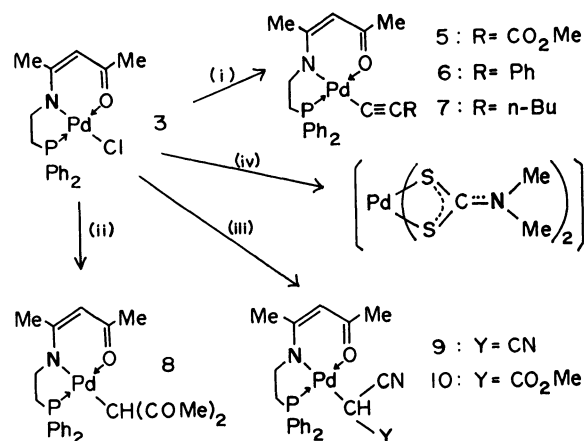
Compound	$\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}=\text{O})$	Others ^{b)}
1	—	—	3160[$\nu(\text{NH})$]
2	—	—	3400[$\nu(\text{NH})$]
5	2090	1655	1220[$\nu(\text{C}-\text{O})$]
6	2100	—	—
7	2120	—	—
8	—	1660, 1635sh	—
9	—	—	2225[$\nu(\text{C}\equiv\text{N})$]
10	—	1715	2220[$\nu(\text{C}\equiv\text{N})$]

a) In cm^{-1} , in KBr disk. b) Assignment is given parentheses.

Complexes **5**—**7** showed a strong $\nu(\text{C}\equiv\text{C})$ band near 2100 cm^{-1} , lower (*ca.* 35, 55, and 5 cm^{-1} , respectively) than those of the corresponding free acetylenes. Attempts to isolate **8**, **10**, and $[\text{Pd}\{\text{CHNO}_2(\text{CO}_2\text{Me})\}(\text{dpeap})]$ by reactions of **7** with acetylacetone, methyl cyanoacetate, and methyl nitroacetate, respectively, were fruitless, **7** being recovered quantitatively after refluxing in THF for 5 h. The inertness of **7** toward the active methylene compounds is in contrast with phenylethynyl¹³⁾ and 1-hexynyl[1,1,1-tris(diphenylphosphinomethyl)ethane]-copper(I).¹⁴⁾ However, the phenylethynyl complex **6** easily reacted with dimethyl acetylenedicarboxylate in dioxane at room temperature to afford an insertion product. It seems likely that this insertion reaction is comparable with that between halogeno(phenylethynyl)-bis(trialkylphosphine)palladium(II) and dimethyl acetylenedicarboxylate in dioxane at 85°C .¹⁵⁾ Details of the former insertion reaction will be reported later.

The Disubstituted Alkyl Type Complexes **8**—**10**.

The ^1H -NMR spectra of complexes **8**—**10** exhibited a doublet in the range $\delta\ 2.8$ — 3.9 [1H, $^3J(\text{PH})=2$ — 5 Hz], characteristic of a palladium-bonded methine proton. The IR spectrum of **8** showed a strong $\nu(\text{C}=\text{O})$ band at 1660 cm^{-1} , implying two free and equivalent acetyl groups. Complexes **9** and **10** showed a medium $\nu(\text{C}\equiv\text{N})$ band near 2220 cm^{-1} , attributable to an uncoordinated cyano group. These data indicate unambiguously that the disubstituted alkyl groups were σ -bonded to

Scheme 2. Reactions of $[\text{PdCl}(\text{dpeap})]$, **3**.

i) $\text{HC}\equiv\text{CR} + \text{CuI}$ (3 mol %) in NH_4Et_2 ; ii) $\text{Tl}(\text{acac})$; iii) $\text{CH}_2(\text{CN})\text{Y} + \text{NaOMe}$; iv) $\text{Na}(\text{S}_2\text{CNMe}_2) \cdot 2\text{H}_2\text{O}$.

palladium in an analogous fashion to those in $[\text{Pd}(\text{pip})-(\text{CHYY})]$ type complexes.⁵⁾ Complexes **8**—**10** are stable in the solid state and in dichloromethane and chloroform and unreactive towards water or ethanol. The stability of **8**—**10** is possibly associated both with the electron delocalization effect to a π^* orbital of the conjugate 4-amino-3-penten-2-onato-*N,O* moiety and vacant d orbitals of the phosphorus atom in the dpeap ligand and with the electron-withdrawing effect of the substituents attached to the methine group, similar to the case of $[\text{Pd}(\text{pip})(\text{CHYY})]$.⁵⁾

An attempt to isolate a dinuclear complex by the reaction between **8** and bis(acetylacetonato)palladium(II) was unsuccessful, **8** being recovered quantitatively after heating under reflux in 1,2-dichloroethane for 6.5 h. The methine proton of the diacetylmethyl moiety in **8** is strongly bonded to the methine carbon, and does not give rise to tautomerism leading to 4-hydroxy-3-palladio-3-penten-2-one moiety, in contrast to the case of (2,2'-bipyridine)chloro(2,4-dioxopentyl)palladium(II).¹⁵⁾

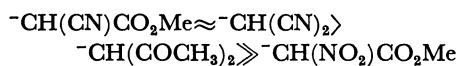
In contrast to the rapid reaction of **3** with $\text{Tl}(\text{acac})$, **3** reacted slowly with a carbanion formed from acetyl-

TABLE 3. ^1H -NMR DATA^{a)}

Compound	1-Me ^{b)} , 5-Me ^{b)}	3-CH ^{b)}	1'-CH ₂ N ^{c)}		2'-CH ₂ P ^{c)}		Others	
	δ/ppm	δ/ppm	δ/ppm	$^3J(\text{PH})/\text{Hz}$	δ/ppm	$^2J(\text{PH})/\text{Hz}$	δ/ppm	$^3J(\text{PH})/\text{Hz}$
1	1.76, 1.92	4.92	3.43(m)	17	2.32(m)	—	10.87(b, 1H, NH)	—
2	1.78, 1.94	4.90	3.43(m)	—	2.71(m)	—	10.79(b, 1H, NH)	—
3	1.98, 2.03	4.91	3.50(dt)	29	2.32(dt)	11	—	—
4	2.02, 2.06	4.95	3.51(dt)	30	2.40(dt)	11	—	—
5	1.98, 2.07	4.96	3.59(dt)	26	2.51(dt)	10	3.51(s, 3H, OMe)	—
6	2.02, 2.16	5.04	3.69(dt)	28	2.62(dt)	11	7.21(s, 5H, Ph)	—
7	1.95, 2.09	4.90	3.50(dt)	26	2.48(dt)	10	0.56(t, 3H, 6''-Me) ^{c,d)}	—
							2.13(t, 2H, 3''-CH ₂) ^{c)}	—
8	1.98, 2.02	4.98	3.33(dt)	26	2.25(dt)	10	3.82(d, 1H, CH)	5
							2.02(s, 6H, Me)	—
9	2.03, 2.06	5.04	3.04(dt)	25	2.51(dt)	10	2.81(d, 1H, CH)	2
10	1.99, 2.03	4.98	3.33(dt)	23	2.47(dt)	10	3.02(d, 1H, CH)	3
							3.38(s, 3H, OMe)	—

a) In CDCl_3 . b) Appearing as a singlet. c) $^3J(\text{H,H})=ca. 6\text{ Hz}$. d) A multiplet near $\delta\ 1.1(4\text{H})$ for 4''- and 5''-CH₂ protons was observed.

acetone and sodium methoxide, and gave a nearly 1 : 1 mixture of **3** and **8** after treatment with the carbanion in THF at room temperature for 24 h. However, **3** did not react with methyl nitroacetate in the presence of an equimolar amount of sodium methoxide. The reactivities of the carbanions toward **3** were ordered as follows.



This order is consistent with that of the nucleophilicity of the carbanions.^{13,17)}

Reaction of 3 with Dimethyldithiocarbamate.

Complex **3** reacted with $\text{Na}(\text{S}_2\text{CNMe}_2) \cdot 2\text{H}_2\text{O}$ in dichloromethane, giving yellow powders. The IR spectrum of the powders lacked the bands characteristic of the dpeap ligand, and newly showed two bands at 1545 and 970 cm^{-1} , assignable to $\nu(\text{C}=\text{N})$ and $\nu(\text{S}=\text{C})$ frequencies, respectively. Accordingly, the powders were assigned to bis(dimethyldithiocarbamato)-palladium(II).⁹⁾ It is noteworthy that the tridentate dpeap ligand in **3** is substituted virtually quantitatively by bidentate dimethyldithiocarbamato ligands, which are soft themselves and are expected to be coordinated strongly to soft palladium(II) ion.

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References

- 1) H. Kanatomi, "Kirehto Kagaku," ed by K. Ueno, Nankodo, Tokyo (1975), Vol. 5, pp. 251—265, and literatures cited therein.
- 2) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, "Progress in Inorganic Chemistry," ed by F. A. Cotton, Interscience Publishers, New York (1966), Vol. 7, pp. 176—195, and literatures cited therein.
- 3) L. Wolf and E. G. Jaeger, *Z. Chem.*, **5**, 317 (1965).
- 4) E. Uhlig and E. Gottschling, *Z. Anorg. Allg. Chem.*, **376**, 113 (1970).
- 5) K. Hiraki, M. Onishi, and H. Matsuo, *J. Organomet. Chem.*, **185**, 111 (1980).
- 6) K. Issleib and H. Oehme, *Chem. Ber.*, **100**, 2685 (1967).
- 7) W. H. Perkin and J. L. Simonsen, *J. Chem. Soc.*, **91**, 833 (1907).
- 8) W. H. Nelson, W. J. Randall, and D. F. Martin, *Inorg. Synth.*, IX, 53 (1971).
- 9) C. G. Sceney and R. J. Magee, *Inorg. Nucl. Chem. Lett.*, **10**, 323 (1974).
- 10) K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, **1977**, 291.
- 11) E. S. Petrov, M. I. Terekhova, A. I. Shatenshtein, and B. A. Trofimov, *Dokl. Akad. Nauk SSSR*, **211**, 1393 (1973).
- 12) O. A. Reutov, I. P. Belestskaya, and K. P. Butin, "CH-Acids," translated by T. R. Crompton. Pergamon Press, New York (1978), p. 11.
- 13) K. Hiraki, Y. Fuchita, and Y. Morita, *Bull. Chem. Soc. Jpn.*, **51**, 2012 (1978).
- 14) Y. Fuchita, Y. Morita, K. Hiraki, and K. Misono, Unpublished data.
- 15) Y. Tohda, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, **1975**, 54.
- 16) a) S. Okeya, N. Yanase, Y. Nakamura, and S. Kawaguchi, *Chem. Lett.*, **1978**, 699; b) N. Yanase, Y. Nakamura and S. Kawaguchi, *Inorg. Chem.*, **17**, 2874 (1978).
- 17) Ref. 12, pp. 59 and 62.