

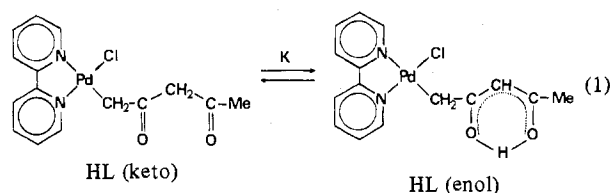
Contribution from the Department of Chemistry,
Faculty of Science, Osaka City University, Sumiyoshiku, Osaka 558, Japan**Di- and Trinuclear Metal Complexes Containing a 2,4-Pentanedionate Dianion as a Bridging Ligand**

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The terminal-carbon-bonded 2,4-pentanedione moiety in the Pd(II) complex PdCl(acac-C¹)(bpy) (HL) still has an acidic proton and reacts with Cu(acac)₂, VO(acac)₂, and Pd(tfac)₂ to afford insoluble trinuclear complexes of the type ML₂. Similar reactions of HL with an excess amount of Be(acac)₂, Pd(acac)₂, and Pd(tfac)₂ gave soluble dinuclear complexes of the type M(β-dik)L. The ligand substitution reactions of [Cu(acac)(bpy)]ClO₄ and [Pd(hfac)(bpy)](hfac) with HL also produced [CuL(bpy)]ClO₄ and [PdL(bpy)](hfac), respectively. IR and ¹H NMR data available suggest that in these new complexes, the 2,4-pentanedione moiety in L retains the Pd-C bond and is coordinated to another metal atom via the two oxygen atoms, thus functioning as a bridging ligand.

Chloro(2,4-pentanedionato-C¹)(2,2'-bipyridine)palladium(II) (HL), which was prepared recently, attains a tautomatization equilibrium in organic solvents, *K* being 0.7 in CDCl₃.¹



Although the PdCl(bpy) substituent in the 2,4-pentanedione is electron donating as is indicated by the ¹H NMR spectra, the compound HL still retains the acidic character, suggesting the capability of O, O' chelation to another metal ion. If this be the case, the pentanedionate dianion will act as a bridging ligand connecting the palladium(II) and another metal ion in the product compounds.

Experimental Section

Syntheses. Bis[1-(chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato]copper(II), CuL₂. A dichloromethane solution (5 mL) of HL (0.100 g, 0.252 mmol) was added to a dichloromethane solution (5 mL) of bis(2,4-pentanedionato)copper(II), Cu(acac)₂ (0.033 g, 0.126 mmol), with stirring at room temperature. After several minutes the solution began to deposit a yellow-green precipitate, but stirring was continued for about 1 h. The product was filtered, washed twice with 5-mL portions of dichloromethane, and dried in vacuo. The yield was 0.074 g (69%).

Bis[1-(chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato]oxovanadium(IV), VO(L)₂. The reaction between VO(acac)₂ (0.033 g, 0.124 mmol) and HL (0.100 g, 0.252 mmol) in a similar fashion as above gave a yellow-green product (0.1016 g) in a 94% yield.

Bis[1-(chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato]palladium(II), PdL₂. A chloroform solution (15 mL) containing bis(1,1,1-trifluoro-2,4-pentanedionato)palladium(II), Pd(tfac)₂ (0.054 g, 0.131 mmol), and HL (0.104 g, 0.262 mmol) was refluxed for 2 h. After cooling of the system, a yellow precipitate was filtered, washed twice with 5-mL portions of chloroform, and dried in vacuo. The yield was 0.044 g (37%).

2,4-Pentanedionato[1-(chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato]beryllium(II), Be(acac)L. A benzene solution (20 mL) containing Be(acac)₂ (0.618 g, 2.78 mmol) and HL (0.040 g, 0.100 mmol) was refluxed for 10 h. After cooling of the system, a yellow precipitate was filtered off and washed with benzene (5 mL). The filtrate was concentrated by evaporation and gave an additional precipitate on addition of ethyl ether. The product was gathered, recrystallized from chloroform-ethyl ether, and dried in vacuo. The yield of the crude product was 0.039 g (78%).

2,4-Pentanedionato[1-(chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato]palladium(II), Pd(acac)L. A solution in 1,2-dichloroethane (75 mL) of Pd(acac)₂ (1.500 g, 4.92 mmol) and HL (0.201 g, 0.506 mmol) was refluxed for 3 h to afford a yellow precipitate, which was worked up in a similar manner as above. The yield was 0.195 g (65%).

1,1,1-Trifluoro-2,4-pentanedionato[1-(chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato]palladium(II), Pd(tfac)L. A chloroform solution (30 mL) containing Pd(tfac)₂ (0.288 g, 0.553 mmol) and HL (0.107 g, 0.269 mmol) was refluxed for 9 h. After filtration, the filtrate was evaporated to dryness under reduced pressure in a rotary evaporator. The residue was washed three times with benzene (20 mL) to remove the residual Pd(tfac)₂ and then recrystallized from tetrahydrofuran-ethyl ether. The yield was 0.097 g (55%).

[1-(Chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato](2,2'-bipyridine)copper(II) Perchlorate, [CuL(bpy)]ClO₄. When a dichloromethane solution (5 mL) of HL (0.112 g, 0.282 mmol) was added dropwise with stirring to a suspension of [Cu(acac)(bpy)]ClO₄² (0.118 g, 0.282 mmol) in dichloromethane (5 mL) at room temperature, the solid particle changed gradually from dark blue to yellow-green. After stirring for 2 h, the precipitate was filtered off, washed twice with 2-mL portions of dichloromethane, and dried in vacuo. The yield was 0.171 g (84%).

[1-(Chloro(2,2'-bipyridine)pallada(II))-2,4-pentanedionato](2,2'-bipyridine)palladium(II) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, [PdL(bpy)](hfac). [Pd(hfac)(bpy)](hfac)³ (0.136 g, 0.201 mmol) was allowed to react with HL (0.082 g, 0.206 mmol) in dichloromethane (10 mL) at room temperature, and the product was worked up in a similar fashion as above. The yield was 0.148 g (85%).

Measurements. IR spectra were recorded in Nujol on JASCO IR-E (4000–650 cm⁻¹) and Hitachi EPI-L (700–200 cm⁻¹) spectrometers. A JNM-PS 100 spectrometer was used to obtain ¹H NMR spectra in CDCl₃ or Me₂SO-*d*₆ containing tetramethylsilane as an internal reference. The molecular weight was determined by vapor pressure osmometry with an instrument manufactured by Knauer in Berlin, Germany. Analysis for palladium was performed by the method of atomic absorption spectroscopy on a Hitachi 208 instrument.

Results and Discussion

Preparation of Complexes. Substitution-labile complexes such as Cu(acac)₂ and VO(acac)₂ react readily with HL in dichloromethane at room temperature to afford trinuclear complexes of the ML₂ type in high yields. Pd(acac)₂ was rather inert and did not give PdL₂ in a good yield even at higher temperatures. Pd(tfac)₂ was more labile and reacted with HL in refluxing chloroform to give PdL₂ in a 37% yield. These trinuclear complexes are insoluble in the usual solvents such as benzene, chloroform, acetone, alcohols, and ethers, which precludes further characterization in solution.

With the aim of preparing soluble dinuclear complexes, ligand substitution reactions of rather inert bis(β-diketonato)metal complexes such as Be(acac)₂, Pd(acac)₂, and Pd(tfac)₂ with HL were examined. A large excess of M(β-dik)₂ was used to prevent formation of ML₂ and to afford M(β-dik)L in a good yield. (In the case of the Be(II) compound, even a 15 molar excess of Be(acac)₂ was insufficient and gave a mixture of Be(acac)L and BeL₂.) The β-diketonoate ligands in [Cu(acac)(bpy)]ClO₄ and [Pd(hfac)(bpy)](hfac) were also replaced by L in the reactions with HL in dichloromethane at room temperature to result in the complexes of the type [ML(bpy)]X in high yields.

Table I. Analytical Results and Molecular Weight Data

complex	% C		% H		% N		% Pd		mol wt	
	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
CuL ₂	42.10	41.95	3.30	3.34	6.55	6.33	24.9	24.9		
VOL ₂	41.94	42.19	3.28	3.35	6.52	6.54	24.8	25.2		
PdL ₂	40.10	39.90	3.14	3.19	6.14	6.23	35.5	34.4		
Be(acac)L	47.64	47.15	4.20	4.11	5.56	5.64	21.1	21.5	504	541 ^a
Pd(acac)L	39.93	39.75	3.52	3.58	4.66	4.46	35.4	34.8		
Pd(tfac)L	36.64	36.84	2.77	2.81	4.27	4.33	32.5	32.4		
[CuL(bpy)]ClO ₄	41.98	42.01	3.10	3.39	7.83	7.32	14.9	14.3	715	364 ^b
[PdL(bpy)](hfac)	41.62	41.33	2.68	2.73	6.47	6.28	24.6	24.5	866	419 ^b

^a Determined in chloroform (0.005 mol/L) at 37 °C. ^b Determined in *N,N*-dimethylformamide (0.01 mol/L) at 60 °C.

Table II. IR Data in Nujol (cm⁻¹)

complex	$\nu(\text{C}=\text{O}) +$	$\nu(\text{Pd}-\text{C})$	$\nu(\text{Pd}-\text{Cl})$
	$\nu(\text{C}=\text{C})$		
CuL ₂	1530, 1510	501	333
VOL ₂	1527, 1502	502	330
PdL ₂	1520, 1505	505	330
Be(acac)L	1545, 1515	498	317
Pd(acac)L	1530, 1505	507	330
Pd(tfac)L ^a	1527, 1508	511	326
[(CuL(bpy)]ClO ₄	1533, 1515	486	280
[PdL(bpy)](hfac) ^b	1530, 1510	523	325

^a The $\nu(\text{CO})$ band of the tfac ligand seems to be overlapped by the $\nu(\text{CC})$ band of bpy. ^b The hfac anion in the outer sphere exhibits the strong $\nu(\text{CO})$ band at 1670 cm⁻¹.

In these substitution reactions the 2,4-pentanedionate ligand remains in the coordination sphere of palladium(II) indicating that the Pd-C bond is strong enough in these compounds. However, reactions of HL with chlorides and bromides of beryllium(II), cobalt(II), nickel(II), copper(II), and iron(III) did not afford the desired products but gave rise to PdX₂(bpy) (X = Cl or Br) instead. Presumably the ML₂-type complex may have been produced at first, but decomposed by reacting with the hydrogen halide which arose from the reaction between HL and the metal halide.

Characterization of Complexes. In Table I are collected the analytical results and molecular weight data obtained for the newly prepared complexes. Besides the trinuclear complexes, Pd(acac)L shows a poor solubility and Pd(tfac)L is unstable in solution, undergoing a disproportionation reaction. Thus the molecular weight was determined only for the other three compounds. The value 541 observed for Be(acac)L in chloroform at 37 °C is close to the calculated value 504. On the other hand, the values found for [CuL(bpy)]ClO₄ and [PdL(bpy)](hfac) in *N,N*-dimethylformamide at 60 °C are both about half of the calculated formula weights, indicating that these compounds dissociate completely in DMF.

The parent complex HL exhibits the $\nu(\text{CO})$ bands at 1723 and 1630 cm⁻¹, which are attributed to the keto and enol tautomers, respectively, of the terminal-carbon-bonded 2,4-pentanedione. These bands are lost in IR spectra of the newly prepared complexes, and instead two strong bands are observed in the 1550-1500-cm⁻¹ region which are characteristic of the O,O'-chelated 2,4-pentanedionate ligand (Table II). The band observed at around 500 cm⁻¹ was tentatively assigned to the $\nu(\text{Pd}-\text{C})$ vibration by reference to that for HL at 530 cm⁻¹. A little decrease in frequency is noticed for either complex. On the other hand the $\nu(\text{Pd}-\text{Cl})$ frequency is almost unaltered except the case for [CuL(bpy)]ClO₄ where an unreasonably large shift is observed.

The ¹H NMR data for the β -diketonate moieties in three dinuclear complexes are shown in Table III together with those for the parent complex HL for comparison. Be(acac)L exhibits two methyl signals at 2.03 and 1.98 ppm with an area ratio of 1:2. These are unequivocally assigned to methyls in the L and acac ligands, respectively, since the tetrahedral structure

Table III. ¹H NMR Data

complex	solvent	chem shift, δ^a			
		CH ₃	CH ₂	CH	OH
HL	CDCl ₃				
enol		1.95	2.94	6.00	15.47
keto		2.29	2.87	3.96 ^b	
Be(acac)L	CDCl ₃	2.03 (a)	3.01	6.21 (a)	
		1.98 (b)		5.59 (b)	
Pd(acac)L	CDCl ₃	2.07 (a)	3.09	6.15 (a)	
		2.05		5.37 (b)	
		2.04 (b,b') ^c			
[PdL(bpy)](hfac)	(CD ₃) ₂ SO	2.04	3.02	5.97 (a)	5.27 (b)

^a Relative to internal TMS. Letters in parentheses refer to those in Figure 1. ^b Resonance of the central methylene protons in the keto tautomer. ^c Undistinguishable.

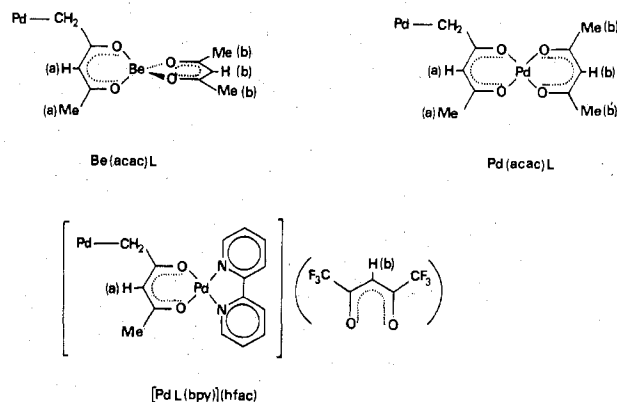


Figure 1. Proposed structures of the dinuclear complexes.

of beryllium(II) renders the two methyl groups in acac equivalent (Figure 1). The methyl and methylene protons in L resonate at slightly lower fields as compared with those in the enol tautomer of HL. Thus it seems reasonable to assign the lower field signal (6.21 ppm) of the two methine resonances to CH in L. All protons in the acac moiety in L resonate at fields a little lower than those in HL probably due to slightly increased electron donation to Be(II) as compared with donation to the proton in HL. On the other hand, the chemical shifts of the methyl (1.98 ppm) and methine (5.59 ppm) protons in the acac ligand are about 0.1 ppm higher than those in Be(acac)₂ (2.12 and 5.65 ppm, respectively). A similar situation is also noticed for the other two complexes and the upfield shift seems to be caused by the enhanced electron donation of L as compared with the 2,4-pentanedionate anion.

In the spectrum of Pd(acac)L three methyl signals are found. The lowest signal is tentatively assigned to the methyl in L. Because of the square-planar structure of Pd(II), the two methyl groups in acac (2.04, 2.05 ppm) are not equivalent but their discrimination is difficult to effect. Of the two methine resonances the lower field one at 6.15 ppm is reasonably ascribed to the methine proton in L.

[PdL(bpy)](hfac) exhibits two methine signals at 5.97 and 5.27 ppm, of which the former is assigned to CH in L by reference to the chemical shift of CH in HL. The methine proton of the hfac anion in [Pd(*n*-PrNH₂)₄](hfac)₂ and [Pd(py)₄](hfac)₂ resonates at 5.89 and 5.97 ppm, respectively, in CDCl₃.³ The value of 5.27 ppm in the present case lies at a remarkably high field. The difference of solvent might be responsible for this discrepancy. These ¹H NMR data alone may not exclude the possibility of [Pd(hfac)(bpy)]L, but the IR spectra clearly deny the latter since the 1610-cm⁻¹ band characteristic of the chelated hfac ligand in [Pd(hfac)(bpy)](hfac) disappeared after the reaction with HL, whereas the 1670-cm⁻¹ band for the hfac anion in the outer sphere is retained.

The proposed structures of the dinuclear complexes in Figure 1 are well reconciled with the IR and ¹H NMR data, and the insoluble trinuclear complexes ML₂ are also presumed to have similar structures. Metal complexes containing a β-diketonate dianion which have been reported so far are TeCl₂(C₅H₆O₂),⁴ Te(C₅H₆O₂),⁴ and Te(C₇H₁₀O₂).⁵ In these complexes the dianion is chelating to the tellurium(IV) or -(II) atom via the two terminal carbon atoms. The role of the pentanedionate anion in the present compound connecting two metal atoms

via the terminal carbon and two oxygen atoms is a novel one and is expected to be found in the future among various compounds of metals other than palladium(II) and of β-dicarbonyl ligands other than 2,4-pentanedione.

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Registry No. CuL₂, 67360-75-2; VOL₂, 67360-76-3; PdL₂, 67360-77-4; Be(acac)L, 67360-78-5; Pd(acac)L, 67360-79-6; Pd(tfac)L, 67360-80-9; [CuL(bpy)]ClO₄, 67360-82-1; [PdL(bpy)](hfac), 67360-84-3; HL, 59588-96-4; Cu(acac)₂, 13395-16-9; VO(acac)₂, 3153-26-2; Pd(tfac)₂, 63742-52-9; Be(acac)₂, 10210-64-7; Pd(acac)₂, 14024-61-4; [Cu(acac)(bpy)]ClO₄, 67360-85-4; [Pd(hfac)(bpy)](hfac), 65353-89-1.

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Tri-*tert*-butylphosphine Complexes of Silver(I). Preparation, Characterization, and Spectral Studies¹

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Tri-*tert*-butylphosphine reacts with silver salts to form complexes of the types [(*t*-Bu)₃P]₂AgX and (*t*-Bu)₃PAgX. The 2:1 complexes have been isolated for X = ClO₄, BF₄, PF₆, and NO₃ and the 1:1 complexes have been isolated for X = Cl, Br, I, CN, SCN, CH₃CO₂, and NO₃. ¹H and ³¹P NMR and vibrational spectral measurements as well as the conductance measurements show that the 2:1 complexes contain the linear cation [(*t*-Bu)₃P-Ag-P(*t*-Bu)₃]⁺ whereas the 1:1 complexes are nonionic compounds. Molecular weight measurements in 1,2-dichloroethane or chloroform show that the complexes (*t*-Bu)₃PAgX, where X = Cl, CH₃CO₂, and NO₃, are monomers whereas the bromo complex (*t*-Bu)₃PAgBr is a dimer; the thiocyanato complex (*t*-Bu)₃PAgBr has a degree of association of 1.5. Vibrational spectral data indicate that the acetato complex has a three-coordinate structure whereas the nitrate complex has a two-coordinate structure. The cyano and the thiocyanato complexes appear to contain bridging CN and SCN groups, respectively. The Ag-P stretching frequencies for the complexes occur in the 85–115-cm⁻¹ region. In contrast to the earlier reported silver(I) complexes of tertiary phosphines, the tri-*tert*-butylphosphine complexes do not undergo rapid phosphine exchange at room temperature as shown by the silver-phosphorus spin-spin coupling observed in their ³¹P NMR spectra at ambient temperatures. The ¹J(Ag-P) values for the neutral complexes follow the order NO₃ > CH₃CO₂ > Cl > SCN > Br > I > CN.

Introduction

A variety of silver(I) complexes of triarylphosphines²⁻¹¹ and mixed alkyl-aryl tertiary phosphines^{6,11,12} are known. However, most of the known silver(I) complexes of trialkylphosphines^{11,13-19} are of 1:1 stoichiometry and these complexes are indicated to have associated structures in which silver atoms are tetrahedrally coordinated. Structures of four such complexes have been determined by crystallographic studies;^{16,18,19} the complex (*n*-Pr)₃PAgSCN¹⁶ is a polymer whereas the complexes Et₃PAgCl,¹⁹ Et₃PAgBr,¹⁹ and Et₃PAgI¹⁸ are tetramers with "cubanelike" structures. The silver(I) halide complexes of triethylphosphine¹³ as well as the trimethylphosphine complexes Me₃PAgI¹⁷ and Me₃PAgNO₃¹⁷ also exist as tetramers in benzene solutions. Tetrameric structures have also been established for the 1:1 triphenylphosphine complexes of silver(I) halides by X-ray diffraction

studies.⁷⁻¹⁰ Nonionic, three- or four-coordinate complexes^{5,8} of the types (R₃P)₂AgX and (R₃P)₃AgX as well as the cationic complexes^{2,5} of the types (R₃P)₄Ag⁺, (R₃P)₃Ag⁺, and (R₃P)₂Ag⁺, where R = phenyl or *p*-tolyl, have also been reported.

To date little work has been reported on silver(I) complexes of sterically hindered phosphines. In continuation of our work on metal complexes of sterically hindered phosphines,²⁰⁻²⁵ we have investigated reactions of tri-*tert*-butylphosphine with a variety of silver(I) salts. The results of this investigation show that in contrast to less bulky phosphines, tri-*tert*-butylphosphine forms complexes which with one possible exception contain only two- or three-coordinate silver.

Experimental Section

General Procedures. Tri-*tert*-butylphosphine was prepared by the method reported²¹ previously. It was manipulated either in a glovebox