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Di- and Trinuclear Metal Complexes Containing a β-Diketonate Dianion as a Bridging Ligand[†]

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The dinuclear palladium(II) complexes $[(PP)Pd(C^1\text{—}C^3\text{-}\beta\text{-dik}(2-)\text{-}O,O')Pd(PP)](ClO_4)_2$ containing a β-diketonate dianion as a bridging ligand were prepared by the reactions of the mononuclear complexes $[Pd(\beta\text{-dik}(2-)\text{-}C^1\text{—}C^3)(PP)]$ with $[Pd(PP)(H_2O)_2](ClO_4)_2$. In the reactions of $[Pd(etac(2-)\text{-}C^1\text{—}C^3)(dpe)]$ with $[Pt(PPh_3)_2(H_2O)_2](ClO_4)_2$ and $[Ni(acac)_2]$ in the 1:1 mole ratio, similar dinuclear complexes $[(dpe)Pd(C^1\text{—}C^3\text{-etac}(2-)\text{-}O,O')Pt(PPh_3)_2](ClO_4)_2$ and $[(dpe)Pd(C^1\text{—}C^3\text{-etac}(2-)\text{-}O,O')Ni(acac)_2]$ were produced, respectively, while the reactions of $[Pd(\beta\text{-dik}(2-)\text{-}C^1\text{—}C^3)(PP)]$ with $Ni(ClO_4)_2\cdot 6H_2O$ and $Mg(ClO_4)_2$ in the 2:1 mole ratio afforded the trinuclear complexes $[M\{O,O'\text{-}\beta\text{-dik}(2-)\text{-}C^1\text{—}C^3Pd(PP)\}_2](ClO_4)_2$ (M=Ni(II) and Mg(II)). The trihapto coordination to palladium(II) and *O,O'*-chelation to another metal atom of the β-diketonate dianion in these complexes were deduced mainly by IR and NMR spectroscopy.

The terminal-carbon-bonded 2,4-pentanedionato and ethyl acetoacetato complexes with palladium(II), $[PdCl(acac\text{-}C^1)(bpy)]$ and $[PdCl(etac\text{-}C^1)(bpy)]$, were derived from the trihapto carbon-bonded complexes, $[PdCl(acac\text{-}C^1\text{—}C^3)]_2$ (**1a**)[1] and $[PdCl(etac\text{-}C^1\text{—}C^3)]_2$ (**1b**),[2] by the bridge-splitting reactions with 2,2′-bipyridine, and reacted with thallium(I) 2,4-pentanedionate to afford the trihapto complexes containing dianions of these β-dicarbonyl compounds $[Pd(acac(2-)\text{-}C^1\text{—}C^3)(bpy)]$ (**2a**) and $[Pd(etac(2-)\text{-}C^1\text{—}C^3)(bpy)]$ (**2b**).[3]

Each of dianion complexes **2a** and **2b** still possesses uncoordinated oxygen atoms, suggesting the possibility of coordination with another metal ion. In fact the reaction of **2a** with an equimolar amount of $[Pd(hfac)(bpy)](hfac)$ (hfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion) afforded a yellow precipitate which gave satisfactory analysis as $[Pd_2(acac(2-))(bpy)_2](hfac)_2$.[3] Although the IR spectral data of this compound strongly suggested that the 2,4-pentanedionate dianion is bridging two palladium(II) ions by the trihapto coordination and *O,O'*-chelation, insolubility of the compound in common organic solvents precluded satisfactory characterization. The present paper is concerned with this kind of dinuclear and trinuclear palladium(II) complexes of bridged β-dicarbonyl dianions containing phosphine ligands in place of 2,2′-bipyridine to increase solubility in organic solvents.[4] The *C,O,O'*-bridging of 2,4-pentanedionate dianions in the dinuclear and trinuclear complexes was previously reported,[5] and the second type of bridging is presented in this paper.

Experimental

Materials. Diphosphines, *cis*-1,2-bis(diphenylphosphino)ethylene(dpe), and 1,2-bis(diphenylphosphino)ethane (dppe), were purchased from Alfa division, Ventron, U.S.A. Dichloro(diphosphine)palladium(II) complexes $[PdCl_2(dpe)]$ and $[PdCl_2(dppe)]$ were prepared according to the literature method[6] (Anal. Found for $[PdCl_2(dpe)]$: C, 54.23; H, 3.86% and Found for $[PdCl_2(dppe)]$: C, 54.51; H, 4.20%). Diaquabis(triphenylphosphine)platinum(II) perchlorate $[Pt(PPh_3)_2(H_2O)_2](ClO_4)_2$ was prepared as follows:[7] a methanol solution (10 cm³) of silver(I) perchlorate (0.250 g, 1.19 mmol) was added to a suspension of *cis*-dichlorobis(triphenylphosphine)platinum(II) (0.470 g, 0.60 mmol) in chloroform at 0 °C. After stirring of the mixture for 5 min, silver(I) chloride precipitated was filtered off and the filtrate was evaporated to dryness under reduced pressure. These operations were performed at 0 °C. The crude product thus obtained was reprecipitated from dichloromethane–diethyl ether to obtain a white solid. The yield was 0.280 g (49%). Found: C, 45.05; H, 3.64%. Calcd for $C_{36}H_{34}O_{10}Cl_2P_2Pt$: C, 45.30; H, 3.59%. Perchlorate salts $Ni(ClO_4)_2\cdot 6H_2O$ and $Mg(ClO_4)_2$ were obtained from Mitsuwa Chemicals and Kishida Chemicals, respectively and used without further purification.

Mononuclear Trihapto Complexes of β-Diketonate Dianions with Palladium(II). η^3-3-Acetyl-2-oxidoallyl(2,2′-bipyridine)palladium(II) $[Pd(acac(2-)\text{-}C^1\text{—}C^3)(bpy)]$ (**2a**) and η^3-3-ethoxycarbonyl-2-oxidoallyl(2,2′-bipyridine)palladium(II), $[Pd(etac(2-)\text{-}C^1\text{—}C^3)(bpy)]$ (**2b**) were prepared by the reported method.[3] The corresponding diphosphine derivatives were prepared by simple displacement of the 2,2′-bipyridine ligand in **2a** and **2b** by diphosphines as follows.

*η^3-3-Acetyl-2-oxidoallyl{*cis*-1,2-bis(diphenylphosphino)ethylene}palladium(II) $[Pd(acac(2-)\text{-}C^1\text{—}C^3)(dpe)]$ (**3a**) and the Corresponding dppe Derivative $[Pd(acac(2-)\text{-}C^1\text{—}C^3)(dppe)]$ (**3b**):* A dichloromethane solution (20 cm³) of dpe (0.522 g, 1.32 mmol) or dppe (0.573 g, 1.46 mmol) was added drop by drop to a suspension of **2a** (0.432 g, 1.20 mmol) in dichloromethane (15 cm³) with stirring at room temperature. After being stirred for 30 min, the mixture was passed through a glass filter and the filtrate was concentrated to *ca.* 5 cm³ by evaporation under reduced pressure. Diethyl ether (20 cm³) was added to the concentrate to obtain **3a** (0.654 g) and **3b** (0.640 g) as pale yellow precipitates in 91 and 87% yields, respectively.

*$[Pd(etac(2-)C^1\text{—}C^3)(dpe)]$ (**3c**), $[Pd(etac(2-)\text{-}C^1\text{—}C^3)(dppe)]$ (**3d**), and $[Pd(etac(2-)\text{-}C^1\text{—}C^3)(PPh_3)_2]\cdot CH_2Cl_2$ (**3e**):* In a similar manner as above, η^3-3-ethoxycarbonyl-2-oxidoallyl derivatives **3c**, **3d**, and **3e** were prepared using a dichloromethane solution of **2b** instead of a suspension

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[†] In this paper, β-dik(2−) represents a dianion of 2,4-pentanedione (acac(2−)) or ethyl acetoacetate (etac(2−)) and PP a bidentate phosphine such as *cis*-1,2-bis(diphenylphosphino)ethylene(dpe) and 1,2-bis(diphenylphosphino)ethane(dppe) or two molecules of triphenylphosphine.

of **2a** in the same solvent, as pale yellow powders in 87, 93, and 86% yields, respectively. Inclusion of one mole of solvent of crystallization in **3e** was confirmed by the elemental analysis and NMR spectroscopy.

Dinuclear Complexes Containing a β-Diketonate Dianion as a Bridging Ligand between Two Palladium(II) Ions. *[(dpe)Pd(*C^1—C^3*-acac(2−)-*O,O′*)Pd(dpe)](ClO_4)$_2$ (**4a**)*: An acetone solution (10 cm^3) of silver(I) perchlorate (0.234 g, 1.13 mmol) was added to a suspension of [$PdCl_2$(dpe)] (0.322 g, 0.562 mmol) in the same solvent (20 cm^3) with stirring at room temperature. After stirring of the mixture for *ca.* 1 h, silver(I) chloride precipitated was filtered off and the filtrate was evaporated to dryness under reduced pressure, leaving diaquadiphosphinepalladium(II) perchlorate on the bottom and a trace of silver(I) chloride which had passed through the glass filter on the wall of the vessel. To obtain a transparent solution freed of silver(I) chloride, the residue was redissolved in a minimum amount of methanol (*ca.* 10 cm^3) and the solution was filtered again, and then the filtrate was added drop by drop to a solution (15 cm^3) of **3a** (0.308 g, 0.512 mmol) with stirring at 0 °C. The mixture was further stirred for 20 min and a yellow precipitate produced was filtered, washed with cold methanol and diethyl ether successively, and dried *in vacuo*. The yield was 0.380 g (57%). Crystallization from acetone–diethyl ether (1:2 by volume) gave transparent crystals which turned opaque on standing in air. Similarly, the corresponding dppe complex [(dppe)Pd(*C^1—C^3*-acac(2−)-*O,O′*)Pd(dppe)](ClO_4)$_2$ (**4b**) was obtained as a yellow precipitate in a 55% yield, using [$PdCl_2$(dppe)] as a starting material instead of [$PdCl_2$(dpe)].

[(dpe)Pd(C^1—C^3*-etac(2−)-*O,O′*)Pd(dpe)](ClO_4)$_2$ (**4c**), [(dppe)Pd(*C^1—C^3*-etac(2−)-*O,O′*)Pd(dppe)](ClO_4)$_2$ (**4d**), and [(PPh_3)$_2$Pd(*C^1—C^3*-etac(2−)-*O,O′*)Pd(dppe)](ClO_4)$_2$ (**4e**)*: These 3-ethoxycarbonyl-2-oxidoallyl derivatives **4c**, **4d**, and **4e** were produced as pale yellow powders from **3c**, **3d**, and **3e**, respectively, by the reactions with appropriate diphosphine complexes in a similar fashion as above. The yields of **4c**, **4d**, and **4e** were 83, 71, and 70%, respectively.

Dinuclear Complexes Containing an Ethyl Acetoacetate Dianion as a Bridging Ligand between Palladium(II) and Another Metal Ion. *[(dpe)Pd(*C^1—C^3*-etac(2−)-*O,O′*)Pt(PPh_3)$_2$](ClO_4)$_2$·0.72CH_3NO_2 (**5a**) and [(PPh_3)$_2$Pd(*C^1—C^3*-etac(2−)-*O,O′*)Pt(PPh_3)$_2$](ClO_4)$_2$·1.15CH_3NO_2 (**5b**)*: A nitromethane solution (20 cm^3) of [Pt(PPh_3)$_2$(H_2O)$_2$](ClO_4)$_2$ (0.372 g, 0.389 mmol) was added dropwise to a solution of **3c** (0.258 g, 0.409 mmol) or **3e** (0.340 g, 0.410 mmol) in methanol (15 cm^3) with stirring at room temperature. After being stirred for *ca.* 40 min, the solution was concentrated to *ca.* 5 cm^3 by evaporation under reduced pressure. Diethyl ether (20 cm^3) was added to the concentrate to obtain **5a** and **5b** as yellow precipitates. The yields were 0.446 g (74%) and 0.484 g (74%), respectively. Inclusion of nitromethane which could not be removed by pumping was confirmed only by nitrogen analysis of **5a** and **5b**, since these complexes were not stable in solution.

[(dpe)Pd(C^1—C^3*-etac(2−)-*O,O′*)Ni(acac)$_2$] (**6**)*: An acetone solution (5 cm^3) of [Ni(acac)$_2$] (0.140 g, 0.545 mmol) was added drop by drop to a solution of **3c** (0.320 g, 0.507 mmol) in the same solvent (10 cm^3) with stirring at room temperature, and then the solution was heated to *ca.* 50 °C. After *ca.* 30 min, a pale yellow precipitate began to appear and the amount increased with continued stirring of the mixture at 50 °C for additional 2 h. The pale yellow product was then filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 0.361 g (80%). The crude product was recrystallized from chloroform–diethyl ether.

Trinuclear Complexes Containing Bridging β-Diketonate Dianions between Two Palladium(II) Ions and Another Metal Ion. *[Ni{(*O,O′*-acac(2−)-*C^1—C^3*)Pd(dpe)}$_2$](ClO_4)$_2$ (**7a**)*: An acetone solution (7 cm^3) of Ni(ClO_4)$_2$·6H_2O (0.061 g, 0.17 mmol) was added dropwise to a solution of **3a** (0.200 g, 0.333 mmol) in dichloromethane (15 cm^3) with stirring at room temperature. The mixture was filtered after *ca.* 1 h of stirring and the filtrate was concentrated to *ca.* 3 cm^3 by evaporation under reduced pressure. Diethyl ether (15 cm^3) was added slowly to the concentrate to obtain **7a** as a pale green precipitate. The yield was 0.223 g (92%). The product was reprecipitated from dichloromethane–diethyl ether.

*[Ni{*O,O′*-etac(2−)-*C^1—C^3*)Pd(dpe)}$_2$](ClO_4)$_2$ (**7b**) and [Ni{(*O,O′*-etac(2−)-*C^1—C^3*)Pd(dppe)}$_2$](ClO_4)$_2$ (**7c**)*: In a similar manner as above, **7b** and **7c** were prepared as pale green powders by reactions of Ni(ClO_4)$_2$·6H_2O with **3c** and **3d**, respectively. The yields were 0.251 g (87%) and 0.237 g (98%), respectively.

*[Mg{(*O,O′*-acac(2−)-*C^1—C^3*)Pd(dpe)}$_2$](ClO_4)$_2$ (**8a**)*: A methanol solution (5 cm^3) of Mg(ClO_4)$_2$ (0.054 g, 0.25 mmol) was added drop by drop to a solution of **3a** (0.308 g, 0.512 mmol) in dichloromethane (20 cm^3) with stirring at room temperature. After being stirred for *ca.* 40 min, the solution was concentrated to *ca.* 4 cm^3 by evaporation under reduced pressure. Diethyl ether (10 cm^3) was added to deposit a pale yellow powder of **8a**, which was filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 0.328 g (93%). The product was reprecipitated from dichloromethane–diethyl ether. Pale yellow crystals of **8a** were obtained by careful crystallization from dichloromethane–acetone but they are not stable and turned opaque on standing in air. Similarly, the corresponding etac(2−) derivative, [Mg{(*O,O′*-etac(2−)-*C^1—C^3*)Pd(dpe)}$_2$](ClO_4)$_2$ (**8b**) was obtained as a pale yellow powder in a 93% yield by the reaction of Mg(ClO_4)$_2$ with **3c**.

Measurements. Infrared spectra were obtained in Nujol mull with a JASCO DS 701G (4000—200 cm^{-1}) infrared spectrophotometer. Absorption spectra were measured in CH_2Cl_2 with a Hitachi EPS-3T spectrophotometer. NMR spectra were recorded on JEOL JNM MH-100 (for ^{1}H), FX-60Q (for ^{13}C and ^{31}P), and FX-90Q (for ^{31}P) instruments. Molecular weights were determined with a vapor pressure osmometer manufactured by Knauer, West Berlin, West Germany. Magnetic susceptibility of **7b** was determined by the Faraday method using a balance manufactured by Shimadzu with [Cr(NH_3)$_6$]Cl_3 as a standard.

Results and Discussion

The dinuclear palladium(II) complexes of a novel type, [(PP)Pd(*C^1—C^3*-β-dik(2−)-*O,O′*)Pd(PP)](ClO_4)$_2$ (**4a—e**) containing dianions of 2,4-pentanedione and ethyl acetoacetate as a bridging ligand and diphosphines (PP), were prepared by the simple reactions of the η^3 complexes of β-diketonate dianions, [Pd(β-dik(2−)-*C^1—C^3*)(PP)] (**3a—e**) with diaquadiphosphinepalladium(II) perchlorate in methanol at 0 °C.

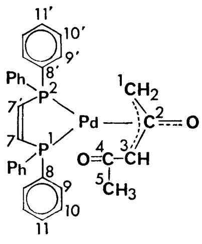
These reactions were successfully extended to obtain dinuclear and trinuclear complexes containing a β-diketonate dianion which bridges palladium(II) and platinum(II), nickel(II), or magnesium(II) ions in the same way as above. Thus the mononuclear complexes **3c** and **3e** reacted with [Pt(PPh_3)$_2$(H_2O)$_2$](ClO_4)$_2$ in a mixture of nitromethane and methanol (2:1 by volume) at room temperature to give the

Table 1. Analytical data for the newly prepared complexes

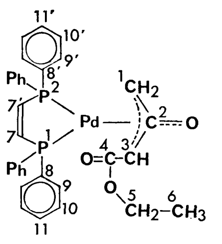
	Complex	Found(Calcd)(%) C	H	P	Mol wt[a)]
3a	[Pd(acac(2 –)-C^1—C^3)(dpe)]	61.87(61.96)	4.69(4.70)	10.31(10.31)	617(601)
3b	[Pd(acac(2 –)-C^1—C^3)(dppe)]	61.71(61.75)	5.04(5.02)		611[b)] (603)
3c	[Pd(etac(2 –)-C^1—C^3)(dpe)]	59.98(60.92)	4.73(4.79)	9.88(9.82)	638(631)
3d	[Pd(etac(2 –)-C^1—C^3)(dppe)]	59.94(60.72)	5.07(5.10)		627[b)] (633)
3e	[Pd(etac(2 –)-C^1—C^3)$(PPh_3)_2$]·CH_2Cl_2	60.83(61.19)	4.78(4.78)		779[b)] (759)
4a	[(dpe)Pd(C^1—C^3-acac(2 –)-O,O')Pd(dpe)]$(ClO_4)_2$	52.20(52.48)	3.88(4.02)	9.32(9.50)	1347(1305)
4b	[(dppe)Pd(C^1—C^3-acac(2 –)-O,O')Pd(dppe)]$(ClO_4)_2$	51.92(52.40)	4.15(4.17)	9.26(9.48)	1369(1307)
4c	[(dpe)Pd(C^1—C^3)-etac(2 –)-O,O')Pd(dpe)]$(ClO_4)_2$	52.19(52.20)	3.90(4.08)	9.46(9.28)	1379(1335)
4d	[(dppe)Pd(C^1—C^3-etac(2 –)-O,O')Pd(dppe)]$(ClO_4)_2$	51.54(52.12)	4.26(4.22)	8.58(8.47)	1445(1337)
4e	[$(PPh_3)_2$Pd(C^1—C^3-etac(2 –)-O,O')Pd(dppe)]$(ClO_4)_2$	55.75(55.83)	4.34(4.27)		1419(1463)
5a	[(dpe)Pd(C^1—C^3-etac(2 –)-O,O')Pt$(PPh_3)_2$]$(ClO_4)_2$·0.72CH_3NO_2	53.00(51.80)	4.03(3.93)	0.63[c)] (0.63)	1318(1550)
5b	[$(PPh_3)_2$Pd(C^1—C^3-etac(2 –)-O,O')Pt$(PPh_3)_2$]$(ClO_4)_2$·1.15CH_3NO_2	54.18(54.39)	4.22(4.12)	0.92[c)] (0.92)	1591(1678)
6	[(dpe)Pd(C^1—C^3-etac(2 –)-O,O')Ni$(acac)_2$]	56.49(56.82)	4.94(5.00)		841(888)
7a	[Ni{(O,O'-acac(2 –)-C^1—C^3)Pd(dpe)}$_2$]$(ClO_4)_2$	49.61(51.03)	4.03(3.87)		1992(1459)
7b	[Ni{(O,O'-etac(2 –)-C^1—C^3)Pd(dpe)}$_2$]$(ClO_4)_2$	48.97(50.93)	4.13(3.98)		1357(1519)
7c	[Ni{(O,O'-etac(2 –)-C^1—C^3)Pd(dppe)}$_2$]$(ClO_4)_2$	50.29(50.46)	4.31(4.23)		1484(1523)
8a	[Mg{(O,O'-acac(2 –)-C^1—C^3)Pd(dpe)}$_2$]$(ClO_4)_2$	51.57(52.60)	4.08(3.96)		
8b	[Mg{(O,O'-etac(2 –)-C^1—C^3)Pd(dpe)}$_2$]$(ClO_4)_2$	51.46(51.76)	4.29(4.07)		

a) In CH_2Cl_2 at 27 °C unless otherwise stated. b) In $(CH_3)_2CO$ at 45 °C. c) N%.

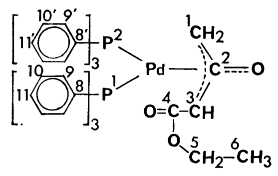
Table 2. ^{13}C NMR data for mononuclear complexes **3a**, **3c**, and **3e** in $CDCl_3$[a)]



3a



3c

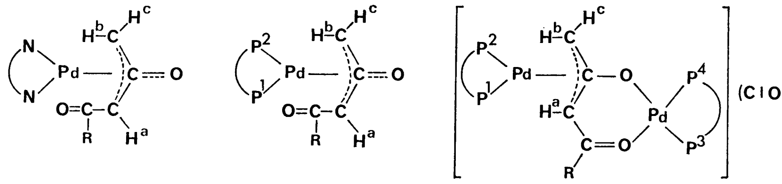


3e

		C^1	C^2	C^3	C^4	C^5	C^6	C^7,$C^{7'}$	C^8,$C^{8'}$	C^9,$C^{9'}$	C^{10},$C^{10'}$	C^{11},$C^{11'}$
3a	δ	48.4 d	177.0 t	75.9 d	203.7 dd	29.6		145.9 m		132.4 d	129.3 d 129.1 d	≈131.2
	J(P¹-C)	52.7	5.5	≈0	2	0				13.2	10.6	0
	J(P²-C)	≈0	5.5	40	5	0					10.3	
	J(C-H)	149		145		127		165		≈161	164	≈161
3c	δ	48.3 d	176.4 dd	62.5 dd	171.1 dd	58.5	14.0	146.0 m		132.5 d	129.2 d 129.0 d	≈131.1
	J(P¹-C)	52.0	6.2	1.8	1.2	0	0			13.4	10.5	0
	J(P²-C)	≈0	5.5	46.5	5.9	0	0				10.3	
	J(C-H)	150		152		146	126	165		≈161	163	≈161
3e	δ	54.1 dd	174.5 t	68.4 dd	170.1 dd	58.8	14.0		130.7 d 130.6 d	133.8 d 133.7 d	128.3 d 128.1 d	130.0 br
	J(P¹-C)	48	5	4	1	0	0		4	13	10	
	J(P²-C)	2.5	5	45	6	0	0		5			
	J(C-H)	153		155		146	126			161	163	163

a) Chemical shift (δ) in ppm from internal Me_4Si and coupling constant (J) in Hz. d = Doublet, dd = doublet of doublets, t = triplet, m = multiplet, and br = broad.

TABLE 3. ^{1}H NMR DATA FOR MONO- AND DINUCLEAR COMPLEXES[a)]



R=CH_3 (**2a**) OCH_2CH_3 (**2b**) R=CH_3 (**3a**, **3b**) OCH_2CH_3 (**3c**—**e**) R=CH_3 (**4a**) OCH_2CH_3 (**4c**)

	CH_3	CH_3——CH_2		H^a	H^b	H^c	Coupling constants in Hz
2a$^{b)}$	2.40			3.71 d	2.71 d	2.55 dd	J(bc)=4.4, J(ac)=1.5
2b$^{b)}$		1.23 t	4.07 q	3.53 d	3.02 d	2.27 dd	J(bc)=4.4, J(ac)=2.3
3a	1.78			4.27 d	≈3.0 br		J(P^2-H^a)=9.5
3b	1.70			4.35 d	2.96 m		J(P^2-H^a)=8.0
3c		0.83 t	3—4$^{c)}$	4.28 dd	3—4		J(P^2-H^a)=8.0, J(ac)=*ca.* 2.0
3d		0.81 t	3—5 br	4.38 d	3—4		J(P^2-H^a)=7.2
3e		0.86 t	3.4—3.5$^{c)}$	4.03 t	3.4—3.5	2.74 br	J(P^2-H^a)=5.4, J(ac)=5.4
4a	d)			5.25 d	d)	d)	J(P^2-H^a)=6.8
4c		0.81 t	3.78 br	4.78 d	3.7 br 3.0 br		J(P^2-H^a)=9.0

a) Same as footnote a) for Table 2. q=Quartet. In CD_2Cl_2 (**2a**, **2b**, **3a**, and **3c**) and in $(CD_3)_2CO$ (**3b**, **3d**, **3e**, **4a**, and **4c**). b) Ref. 3. c) Not assignable due to overlapping with H^b and H^c signals. d) Not assignable due to diethyl ether impurity.

ionic dinuclear mixed-metal complexes [(PP)Pd(C^1–C^3-etac(2−)-O,O')Pt(PPh_3)$_2$](ClO_4)$_2$ (**5a**, PP=dpe; **5b**, PP=2PPh_3), whereas the reaction of **3c** with [Ni(acac)$_2$] in acetone at 50 °C afforded the neutral complex [(dpe)Pd(C^1—C^3-etac(2−)-O,O')Ni(acac)$_2$] (**6**). Contrary to all these reactions in the mole ratio of 1:1, the reactions of **3a**, **3c**, and **3d** with $Ni(ClO_4)_2\cdot 6H_2O$ and of **3a** and **3c** with $Mg(ClO_4)_2$, in the 2:1 mole ratio produced the ionic trinuclear mixed-metal complexes [M{O,O'-β-dik(2−)-C^1—C^3)Pd(PP)}$_2$](ClO_4)$_2$ (**7a**—**c**, M=Ni(II); **8a** and **8b**, M=Mg(II)), which contain two bridged β-diketonate dianions connecting two different metal ions.

All of the newly prepared complexes inclusive of the trinuclear ionic complexes are moderately soluble in usual organic solvents, and their analytical and molecular weight data are listed in Table 1. Except **7a** and **7b** which give somewhat abnormal molecular weights, each of almost all complexes does not dissociate in nonpolar organic solvents such as CH_2Cl_2.

Mononuclear Trihapto Complexes of β-Diketonate Dianions with Palladium(II). The ^{13}C NMR data for the mononuclear complexes **3a**, **3c**, and **3e** in $CDCl_3$ are listed in Table 2. The dpe complexes are more stable than the corresponding dppe and PPh_3 complexes, exhibiting very good ^{13}C NMR spectra. Assignment of the three sets of higher-field signals in the spectrum of **3a** to the methyl, methylene, and methine carbons was made on the basis of the ^{1}H non-decoupled data, and other signals were assigned as listed in Table 2 by comparison with the spectra for **2a**[3)] and [Pt(acac(2−)-C^1—C^3){P(p-ClC_6H_4)$_3$}$_2$],[8)] of which the trihapto structures were confirmed by the NMR spectra. Four carbons (C^1—C^4) of the acac(2−) skeleton couple to the ^{31}P atom(s), strongly suggesting the trihapto coordination of the ligand to palladium(II). Of these, the terminal methylene (C^1) and methine (C^3) carbons couple strongly to the ^{31}P atom situated at the trans position, each resonating as a doublet, whereas the central carbonyl carbon (C^2) resonates as a triplet, indicating that the coupling constants to both ^{31}P atoms are nearly equal in spite of their environmental nonequivalence. The other carbonyl carbon (C^4) is remote from the coordination sites and weakly couples to both P^1 and P^2. The ^{13}C NMR spectral data for [Pd(etac(2−)-C^1—C^3)(Me_2bpy)][3)] (**2c**) were also helpful for signal assignment of **3c** listed in Table 2. Compared with the ^{13}C NMR signals of the allylic moiety in **2a** and **2c**,[3)] the methylene and methine carbons of **3a** and **3c** resonate at the lower field by 10—20 ppm. Such a deshielding of these carbon atoms is presumably due to the larger back-donation of palladium(II) to diphosphine than 2,2′-bipyridine. The same situation is also seen for the shielding of allylic protons (*vide infra*).

Contrary to **3a**, the terminal methylene (C^1) and methine (C^3) carbons of the allylic moiety in the PPh_3 complex **3e** resonate as a doublet of doublets due to the couplings to both P^1 and P^2. The coupling constants (Table 2) are quite similar to those in [Pt(acac(2−)-C^1—C^3){P(p-ClC_6H_4)$_3$}$_2$][8)] (J(P^1-C^1)=55, J(P^2-C^1)=5; J(P^1-C^3)=5, J(P^2-C^3)=52 Hz). Although the central carbonyl carbon (C^2) in **3e** does not discriminate both P atoms as in the case of **3a**, the environmental nonequivalence of both P atoms (*vide infra*) is shown by slightly different coupling constants of C^2 in the case of **3c**, the signal appearing as a doublet of doublets.

The ^{1}H NMR data for the mononuclear and dinuclear palladium(II) complexes containing β-diketonate dianions and diphosphines are listed in Table

TABLE 4. $^{31}P\{H\}$ NMR DATA FOR MONONUCLEAR (**3a**, **3c**, AND **3e**) AND DINUCLEAR (**4a** AND **4c**) COMPLEXES[a)]

	P^1, P^2		$J(P^1\text{-}P^2)$	P^3, P^4	
3a[b)]	52.8 d	60.2 d	11		
3c[b)]	54.0 d	59.4 d	9		
3e[b)]	24.5 d	30.3 d	27		
4a[c)]	60.9 d	66.6 d	18	66.2 br	68.2 br
4c[c)]	60.7 d	64.1 d	16	69.0 br	71.6 br

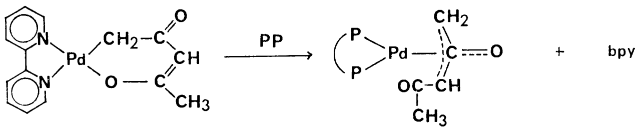
a) Chemical shift (δ) in ppm from external H_3PO_4 and coupling constant (J) in Hz. d=Doublet, br=broad. b) In $CDCl_3$. c) In $(CD_3)_2CO$ at 30 °C.

3, and compared with those for the analogous 2,2′-bipyridine complexes **2a** and **2b**.[3)] Complexes **2a** and **2b** showed four and five signals with the area ratios of 3:1:1:1 and 3:1:1:1:2, respectively and these signals were reasonably interpreted on the basis of the trihapto structures of acac(2−) and etac(2−) as listed in Table 3.

On the other hand, the ^1H NMR spectra of the newly prepared diphosphine complexes are not conclusive for such a structure assignment, since the signals ascribable to H^b and H^c overlap with each other and with other signals. However, the signal from H^a is useful. Thus, H^a of complex **3c** resonates at 4.28 ppm from internal Me_4Si in $CDCl_3$ as a doublet of doublets due to coupling to P^2 (J=8 Hz) in the trans position and to H^c (J=2 Hz). The latter interaction between H^a and H^c appears as a coupling across four bonds constituting a planar zig-zag configuration (the so-called W rule),[9)] suggesting the anti structure of the η-allylic etac(2−) ligand in **3c**. The H^a signal of the diphosphine complexes other than **3c** looks just like a doublet, but this may be attributed to low sensitivity of the NMR instrument used for the measurements. In the case of the triphenylphosphine complex **3e**, the 4.03-ppm signal probably assignable to H^a appears as a triplet, indicating same coupling constants (J=5.4 Hz) of H^a to each of H^c and P^2, accidentally. When one drop of D_2O was added to a $CDCl_3$ solution of **3e** and the mixture was left to stand for 30 min, the signal diminished remarkably, confirming assignment of the signal to an exchangeable unique proton H^a. The fact that the ^{13}C signal from the methine carbon (C^3) at 68.4 ppm decreased by the D_2O treatment also certifies that the methine proton was deuterated. The downfield shift of the H^a signal is generally observed in the present case for displacement of the 2,2′-bipyridine ligand in **2a** and **2b** by diphosphines, again indicating the difference in back-donation of palladium(II) to diphosphines and 2,2′-bipyridine (*vide supra*).

The $^{31}P\{H\}$ NMR spectra of the mononuclear (**3a**, **3c**, and **3e**) and dinuclear (**4a** and **4c**) complexes are recorded and listed in Table 4. The spectra of the mononuclear complexes in $CDCl_3$ are quite simple; for example, complex **3a** shows two signals as an AB quartet at 52.8 and 60.2 ppm downfield from external H_3PO_4 with $J(P^1\text{-}P^2)$=11 Hz. The spectrum indicates that the two phosphorus atoms are not equivalent and the difference in their environments is larger than that of two phosphorus atoms in [Pt(acac(2−)-C^1-C^3)-$\{P(p\text{-}ClC_6H_4)_3\}_2$],[8)] of which signals appeared at 18.6 and 19.3 ppm as an AB quartet. In the platinum case, the signal at 19.3 ppm with larger ^1J(Pt-P) was assigned to P situated at the site trans to the allylic methine carbon, since the dangling acetyl moiety was thought to be electron attracting and the acetyl-substituted methylene group to exert slightly smaller trans influence than the unsubstituted methylene end. Although unequivocal discrimination of phosphorus atoms is not possible in the present case, the lower-field signal at 60.2 ppm might be assigned to P^2 situated at the site trans to the methine carbon (C^3). Other complexes **3c** and **3e** also give two doublets with $J(P^1\text{-}P^2)$=9 and 27 Hz, respectively. For two cis couplings of ^{31}P atoms in [PdCl(dppe){P(n-Pr)$_3$}]$^+$, similar values 11 and 21 Hz were reported, in contrast to 408 Hz for trans coupling.[10)]

Here, it should be noticed that [Pd(acac(2−)-C^1—C^3)(NN)] (NN=bpy (**2a**), 4,4′-Me_2bpy, and phen) were always contaminated with the C,O-chelated acac(2−) complexes [Pd(acac(2−)-C,O)(NN)] in 20—25% proportions which were determined by ^1H NMR spectra.[3)] However, none of NMR data in the present diphosphine complexes **3a** and **3b** show evidence for contamination with the C,O-chelated acac(2−) complex with diphosphinepalladium(II). Moreover, **3a** and **3b** are produced in high yields of 87—91% which exceed contents of **2a** (75—80%) in the starting complex. These facts suggest that the transformation of the bonding mode from C,O-chelation to trihapto coordination occurrs during the preparation. Other complexes [Pt(tfac(2−)-C,O)L_2] which contain a C,O-chelated 1,1,1-trifluoro-2,4-pentanedionate dianion with PPh_3, $P(p\text{-}ClC_6H_4)_3$, or $AsPh_3$ as L were isolated and characterized.[11)]

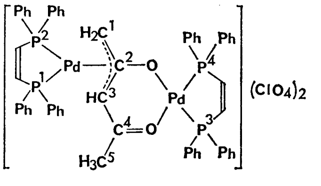


PP = dpe (**3a**)
dppe (**3b**)

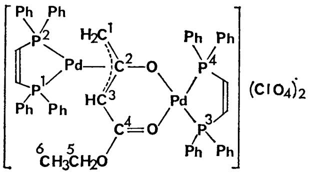
Infrared spectra of the mononuclear complexes **3a**—**e** in the 1500—1700 cm^{-1} region are quite similar to those of **2a** and **2b**, exhibiting a medium ν(C=O) band at 1630—1670 cm^{-1} and a very strong and broad band at 1530—1560 cm^{-1} assignable to the ν(C$\overset{\dots}{=}$O) and/or ν(C$\overset{\dots}{=}$C) vibration. The weak bands due to δ(CCC) of the allylic skelton are not discernible owing to overlapping with strong bands from the diphosphine ligands in the region of 500—600 cm^{-1}.

Dinuclear Complexes Containing a β-Diketonate Dianion as a Bridging Ligand between Two Palladium(II) Ions. Only the ketonic carbonyl band at higher frequency (1633—1667 cm^{-1}) mentioned above is lost and the ν(C$\overset{\dots}{=}$O) and/or ν(C$\overset{\dots}{=}$C) band is shifted to higher frequency (1550—1590 cm^{-1}) more or less in the dinuclear complexes **4a**—**e** without noticeable change in the other part, suggesting that the free carbonyl oxygens coordinated to another palladium ion by O,O'-chelation to make dinuclear complexes.

Table 5. ^{13}C NMR data for β-diketonate dianions in dinuclear complexes **4a** and **4c** in $(CD_3)_2CO$



4a



4c

		C^1	C^2	C^3	C^4	C^5	C^6
4a	δ	53.4 d, br	166.7 t	76.9 d	208.4	≈29.4	
	$\Delta\delta$	+5.0	−10.3	+1.0	+4.7	≈+0.2	
	$J(P^1\text{-}C)$	43	6	≈0	≈0	≈0	
	ΔJ	−10	0	0	−2	0	
	$J(P^2\text{-}C)$	≈0	6	28	≈0	≈0	
	ΔJ	0	0	−12	−5	0	
	$J(C\text{-}H)$	≈153		158		≈131	
4c	δ	53.5 d, br	170.1 t	63.7 d	180.5 br	64.7	13.7
	$\Delta\delta$	+5.2	−6.3	+1.2	+9.4	+6.2	−0.3
	$J(P^1\text{-}C)$	43	6	0	≈0	0	0
	ΔJ	−9	≈0	−2	−1	0	0
	$J(P^2\text{-}C)$	≈0	6	33	≈0	0	0
	ΔJ	≈0	≈0	−14	−6	0	0
	$J(C\text{-}H)$	154		157		150	127

a) Same as footnote a) for Table 2. $\Delta\delta=\delta(\mathbf{4a})-\delta(\mathbf{3a})$, $\delta(\mathbf{4c})-\delta(\mathbf{3c})$. $\Delta J=J(\mathbf{4a})-J(\mathbf{3a})$, $J(\mathbf{4c})-J(\mathbf{3c})$.

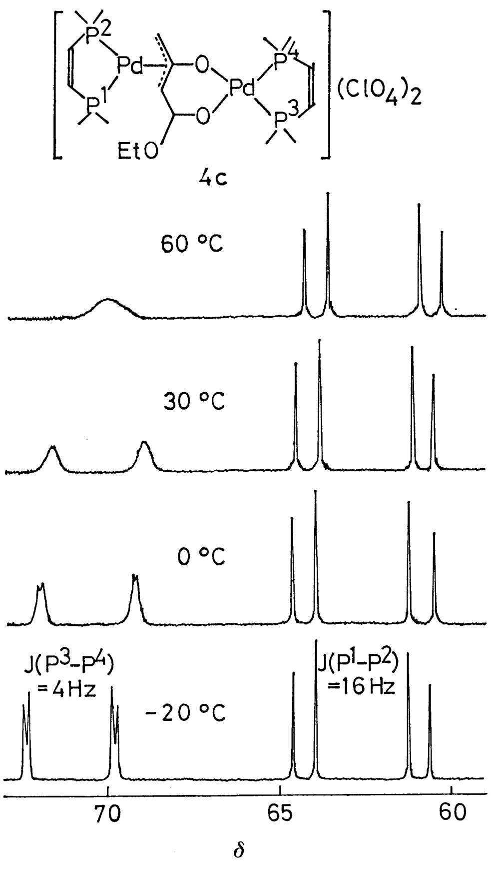


Fig. 1. Temperature dependence of the 24.2 MHz $^{31}P\{H\}$ NMR spectrum of $[(dpe)Pd(O,O'\text{-etac}(2-)\text{-}C^1\text{—}C^3)Pd(dpe)](ClO_4)_2$ (**4c**) in $(CD_3)_2CO$ with H_3PO_4 as an external reference.

Similarly, ^{1}H NMR spectrum of **4c** (Table 3) resembles as a whole that of the mononuclear complex **3c**, except the H^a signal which appears as a doublet at 4.78 ppm with $J(P^2\text{–}H^a)=9$ Hz. The downfield shift seems to be caused by coordination to the second palladium ion *via* the oxygen atoms and loss of coupling to H^c by violence of the W rule due to transposition of H^a from syn in **3c** to anti in **4c**.

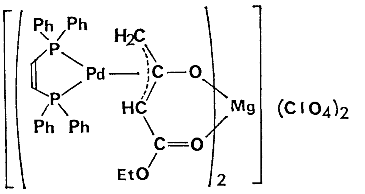
The $^{31}P\{H\}$ NMR spectrum of **4a** in $(CD_3)_2CO$ at 30 °C shows two broader signals at 66.2 and 68.2 ppm besides two doublets at 60.9 and 66.6 ppm with $J(P^1\text{–}P^2)=18$ Hz (Table 4). A similar situation also appears in the spectrum of **4c** which shows two broader signals at 69.0 and 71.6 ppm apart from the two sharp doublets at 60.7 and 64.1 ppm with $J(P^1\text{–}P^2)=16$ Hz. The latter doublets are assigned to P^1 and P^2 by reference to the spectra of **3a** and **3c**. As Fig. 1 shows, the former signals which are assigned to P^3 and P^4, become broader with increasing temperature and coalesce at about 60 °C, indicating occurrence of the coordination site exchange between P^3 and P^4. On the other hand, these two signals sharpen as the temperature is lowered, giving two doublets with $J(P^3\text{–}P^4)=4$ Hz at −20 °C. This also reflects unsymmetric coordination of the etac(2−) anion to another palladium ion *via* oxygen atoms, although individual assignment of the signals to P^3 and P^4 is not possible. The coordination-site exchange may be assisted by solvent molecules.[12]

Table 5 lists the ^{13}C NMR data for the dinuclear complexes **4a** and **4c** in $(CD_3)_2CO$. It can be seen from Tables 2 and 5 that the trihapto coordination of the β-dik(2−) ligands with palladium(II) in the mononuclear complexes is still retained in the dinuclear complexes. Again, C^1 and C^3 signals in the dinuclear complexes **4a** and **4c** appear as doublets due to coupling to ^{31}P situated at the trans position. However, the coupling constants are smaller than those in the mononuclear complexes **3a** and **3c** as shown by ΔJ in Table 5, indicating that the allylic carbons-palladium bond became weaker on chelation to another metal ion *via* oxygen atoms. Each carbonyl carbon (C^2) in **4a** and **4c** resonates as a triplet like that in **3a** and **3e**. Contrary to couplings of these allylic carbons, the double doublet of ketonic carbonyl carbon (C^4) signal in the mononuclear complexes disappears in the dinuclear complexes and the C^4 carbon in **4a** and **4c** resonates as a broad singlet. Loss of the couplings indicates the transposition of the carbonyl group from the anti to syn position far apart from P^1 and P^2 in order to coordinate with another metal atom.

It is also worth noting that signals from C^1, C^3, and C^4 are shifted downfield more or less on chelation, while only C^2 shows substantial upfield shift, as shown by $\Delta\delta$ in Table 5. It might be caused by the change in the bonding mode around C^2 from $\gg C{=}O$ to $\gg C{-}O\diagdown$. In the case of neat 2,4-pentanedione, the carbonyl carbon of keto tautomer resonates at 202.6 ppm, while that of enol one resonates at 191.8 ppm,[13] making the upfield shift by $\Delta\delta = -10.8$ ppm from $>C{=}O$ to $\gg C{-}O\diagdown$ which is comparable to $\Delta\delta(C^2) = -10.3$ ppm from **3a** to **4a**.

Di- and Trinuclear Complexes Containing a β-Diketonate Dianion as a Bridging Ligand between Palladium(II) and Another Metal Ion. Except **6** which shows a ν(C=O) band at 1677 cm^{-1} and four strong to medium bands in the region of 1510—1610 cm^{-1}, IR spectra of **5a**–**8b** again exhibit no ketonic carbonyl band at higher frequency but only a strong and broad band assignable to the ν(C$\doteq$O) and/or ν(C$\doteq$C) vibration in the region of 1560—1640 cm^{-1}. Although the spectral region is a little higher than 1550—1590 cm^{-1} for **4a**—**e**, these features resemble those of dipalladium(II) complexes **4a**—**e**, suggesting that the bonding mode of β-dik(2−) ligands in **5a**–**8b** is similar to that in **4a**—**e**.

Contrary to dipalladium(II) complexes **4a**—**e**, these mixed-metal dinuclear and trinuclear complexes with palladium(II) and platinum(II), nickel(II), or magnesium(II) are less stable in usual organic solvents, and do not give good ^1H and ^{13}C NMR spectra. For instance, the dinuclear complex with platinum(II), **5a**, decomposes in $CDCl_3$ gradually during the spectral measurement, exhibiting free-ester signals and depositing a white precipitate on the wall of the NMR tube. The trinuclear complex with magnesium(II), **8b**, is rather stable in haloalkanes and gives somewhat broad ^{13}C signals in $CDCl_3$. However, signal assignment is unequivocal: C^1 (terminal methylene), 51.6d ($J(P^1\text{–}C) = ca.$ 51 Hz); C^2 (central carbonyl), 172.3; C^3 (methine), 60.0d ($J(P^2\text{–}C) = ca.$ 53); C^4 (ester carbonyl), 177.6; C^5 (ethoxy methylene), 60.5 and C^6 (ethoxy methyl), 13.3 ppm from internal Me_4Si. These chemical shifts are comparable to those for **4c**, suggesting that the etac(2−) ligands in **8b** are working as a bridging ligand through trihapto bonding to palladium(II) and *O,O'*-chelation to magnesium(II) as follows.



8b

Although the NMR data for all nickel(II) complexes, unfortunately, can not be obtained because of their paramagnetic characters, nickel(II) complexes **7a**—**c** seem to contain the β-dik(2−) ligands of bonding mode analogous to that in **8b** on the basis of the similarity of IR spectra between nickel(II) and magnesium(II) complexes. The above-mentioned higher-frequency shift of the ν(C$\doteq$O) and/or ν(C$\doteq$C) vibrations in **5a**–**8b** by *ca.* 10—50 cm^{-1} compared with those in **4a**—**e** might reflect the weaker metal-oxygen bonds in the mixed-metal complexes in conformity with instability of these complexes in solution.

In this connection, it is meaningful to remember that the dinuclear complex with $Ni(acac)_2$, **6**, shows a ν(C=O) band at 1677 cm^{-1} in addition to bands in the 1510—1610-cm^{-1} region, The absorption spectrum of **6** in CH_2Cl_2 exhibits two bands at 9100 cm^{-1} ($^3A_{2g} \rightarrow {}^3F_{2g}$, $\varepsilon = 7.7$) and at 15200 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $\varepsilon = 8.6$), typical of the octahedral arrangement around the nickel(II) ion, although the third band is obscured by a higher-intensity ligand band. Hence, the higher-frequency carbonyl band in the IR spectrum of **6** might suggest the very weak bonding of the ketonic carbonyl oxygen to occupy the sixth coordination site around the nickel(II) ion, presumably due to the simple adduct formation between neutral molecules in this special case. In the addition compound, $[NiBr_2(C_5H_8O_2)_2]$, of anhydrous nickel bromide with two molecules of 2,4-pentanedione,[14] the ν(C=O) band appeared at 1693 cm^{-1} very near to 1677 cm^{-1}.

On the other hand, the stereochemistry around the nickel(II) ion in **7a**—**c** and the magnesium(II) ion in **8a** and **8b** seems to be tetrahedral and not planar. For instance, complex **7b** is paramagnetic as shown by the $\mu_{\text{eff}}^{\text{corr}}$ value of 3.3 BM, and shows a shoulder band assignable to a spin-allowed transition ($^3T_1(F) \rightarrow {}^3T_1(P)$) at 22200 cm^{-1} ($\varepsilon = ca.$ 65) together with two weak bands at 16100 ($\varepsilon = 9.3$) and 8900 cm^{-1} ($\varepsilon = 5.5$).

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