Molecular Structures of *HT*-[MM'Cl_2(μ-Me_2Ppy)$_2$] (MM'=Pd_2, PdPt, and Pt_2; Me_2Ppy=2-(Dimethylphosphino)pyridine) and *HT*-[Pd_2Cl_2(μ-Ph_2Ppy)$_2$] (Ph_2Ppy=2-(Diphenylphosphino)pyridine)

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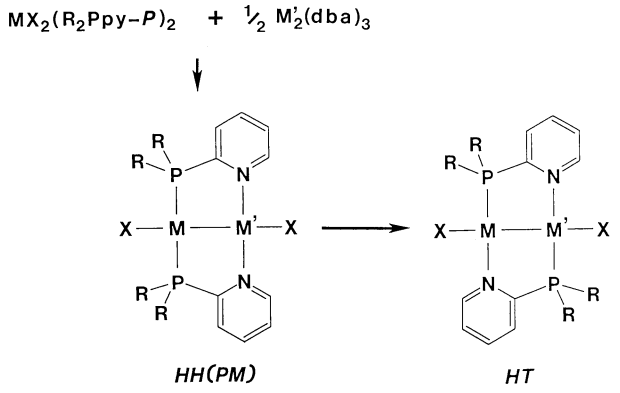
Crystal structures of Pd(I) and Pt(I) dinuclear complexes, [MM'Cl_2(μ-Me_2Ppy)$_2$] (MM'=Pd_2 (**1**), PdPt (**2**), and Pt_2 (**3**)) and [Pd_2Cl_2(μ-Ph_2Ppy)$_2$] (**4**), were determined by the single crystal X-ray diffraction method. Crystal data and final R values are: **1**, triclinic, $P\bar{1}$, a=10.019(2), b=10.902(2), c=9.062(1) Å, α=97.75(2), β=102.45(2), γ=82.64(2)°, V=952.7(3) Å^3, Z=2, and R=0.047; **2**, monoclinic, $P2_1/n$, a=16.532(2), b=19.205(3), c=13.260(2) Å, β=93.86(2)°, V=4200(1) Å^3, Z=8, and R=0.043; **3**, monoclinic, $P2_1/n$, a=16.515(5), b=19.095(10), c=13.233(4) Å, β=93.15(3)°, V=4167(3) Å^3, Z=8, and R=0.047; **4**, monoclinic, $C2/c$, a=30.505(4), b=17.896(2), c=12.983(1) Å, β=98.52(1)°, V=7009(1) Å^3, Z=8, and R=0.041. All of the complexes were found to be the head-to-tail isomer of a side-by-side type dinuclear structure. The metal–metal bond distances of 2.584(1) Å in **1**, 2.561(1) Å in **2**, 2.573(1) Å in **3**, and 2.594(1) Å in **4** are relatively short compared with those in the analogous dinuclear complexes bridged by diphosphine ligands. All of the M–P, M–N, and M–Cl distances in Me_2Ppy complexes become shortened in the order of the Pd_2>PdPt>Pt_2 complexes.

In a previous paper,[1] we have reported the preparation and characterization of Pd(I) and Pt(I) dinuclear complexes bridged by 2-(dimethylphosphino)pyridine (Me_2Ppy) or its diphenyl analogue (Ph_2Ppy), [MM'X_2(μ-R_2Ppy)$_2$] (M,M'=Pd, Pt; X=Cl, Br, I; R=Me, and Ph), together with reaction profiles in formation of these dinuclear complexes from [MX_2(R_2Ppy-*P*)$_2$] and [M'$_2$(dba)$_3$] (dba=1,5-diphenyl-1,4-pentadien-3-one). These conproportionation reactions were found to proceed in two steps by studies of ^{31}P NMR spectra; the first step is the dimerization to form the head-to-head isomer, and then it isomerizes to the head-to-tail isomer at the second step (Scheme 1). Rates of these dimerization and isomerization reactions vary largely with the kinds of metal, phosphine and halide ligands.

In this paper we report structures of [MM'Cl_2(μ-Me_2Ppy)$_2$] (MM'=Pd_2 (**1**), PdPt (**2**), and Pt_2 (**3**)) and [Pd_2Cl_2(μ-Ph_2Ppy)$_2$] (**4**) determined by the X-ray diffraction method to confirm their geometrical structures assigned on the basis of NMR spectra, and comparisons of the results with those of the related Pd(I) and Pt(I) dinuclear complexes.[2-8] X-ray structure analyses have been reported on a number of dinuclear complexes bridged by Ph_2Ppy.[9-15] However, no report has been published on the present [M_2X_2(μ-Ph_2Ppy)$_2$]-type complex. For the dinuclear Me_2Ppy complexes, only [Au_2(μ-Me_2Ppy)$_2$](BF_4)$_2$ has been known so far.[16]



Scheme 1.

Experimental

The title complexes were prepared by methods reported previously.[1] Crystals of *HT*-[MM'Cl_2(μ-Me_2Ppy)$_2$] (MM'=Pd_2, PdPt, and Pt_2) were obtained by recrystallization from methanol or ethanol. Crystals of *HT*-[Pd_2Cl_2(μ-Ph_2Ppy)$_2$] were grown by slow evaporation of a dichloromethane solution mixed with hexane.

Crystal data, experimental conditions and refinement information are listed in Table 1. The X-ray intensities were measured using graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) on an automated Rigaku four-circle diffractometer AFC-5R for **1** and AFC-5 for others. The θ–2θ scan technique was employed at a scan rate of 4—6° min^{-1} in θ. The lattice constants were determined from 24—49 2θ values ($20°<2\theta<30°$). Absorption corrections were made by the Gauss numerical integration method[17] except for **1**, because the crystal of **1** was cut and the outside could not be indexed. In order to avoid systematic error by the heavy absorption for the Pt_2 complex, **3**, symmetry-related reflections were also measured for $2\theta\leqslant40°$. The space groups of **2** and **3** were uniquely determined by systematic absences. Refinements for **1** and **4** succeeded by assuming the centrosymmetric space groups. The structures were solved by Patterson–Fourier methods and non-H atoms were refined anisotropically. The H atoms for Pd_2 complexes, **1** and **4**, were located by difference syntheses and refined with isotropic thermal parameters. Coordinates of all the H atoms in **2** and **3** were calculated

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

	1 $[Pd_2Cl_2(Me_2Ppy)_2]$	**2** $[PdPtCl_2(Me_2Ppy)_2]\cdot 1/2EtOH$	**3** $[Pt_2Cl_2(Me_2Ppy)_2]\cdot 1/2EtOH$	**4** $[Pd_2Cl_2(Ph_2Ppy)_2]\cdot 1/2C_6H_{14}$
Chemical formula	$C_{14}H_{20}Cl_2N_2P_2Pd_2$	$C_{14}H_{20}Cl_2N_2P_2PdPt\cdot 1/2(C_2H_6O)$	$C_{14}H_{20}Cl_2N_2P_2Pt_2\cdot 1/2(C_2H_6O)$	$C_{34}H_{28}Cl_2N_2P_2Pd_2\cdot 1/2(C_6H_{14})$
Formula weight	562.02	673.71	762.37	853.39
Solvent for crystallization	Methanol	Ethanol	Ethanol	Dichloromethane/hexane
Color and shape of crystals	Dark-red prism	Red prism	Yellow prism	Dark-red prism
Space group and Z	$P\bar{1}$, 2	$P2_1/n$, 8	$P2_1/n$, 8	$C2/c$, 8
Cell dimentions				
a/Å	10.019(2)	16.532(2)	16.515(5)	30.505(4)
b/Å	10.902(2)	19.205(3)	19.095(10)	17.896(2)
c/Å	9.062(1)	13.260(2)	13.233(4)	12.983(1)
α/°	97.75(2)			
β/°	102.45(2)	93.86(2)	93.15(3)	98.52(1)
γ/°	82.64(2)			
V/Å^3	952.7(3)	4200(1)	4167(3)	7009(1)
D_m[a)]/Mg m^{-3}	1.93(2)	2.08(2)	2.37(2)	1.62(2)
D_x/Mg m^{-3}	1.96	2.13	2.43	1.62
μ(Mo $K\alpha$)/mm^{-1}	2.31	7.98	14.00	1.29
Size of specimen/mm^3	0.2×0.35×0.8	0.3×0.5×0.5	0.4×0.23×0.35	0.2×0.3×0.5
$2\theta_{max}$/°	60	55	55	55
Range of h, k, and l	$-14\leq h\leq 14$ $-15\leq k\leq 15$ $0\leq l\leq 12$	$-21\leq h\leq 21$ $0\leq k\leq 24$ $0\leq l\leq 17$	$-15\leq h\leq 21$ $-24\leq k\leq 0$ $-17\leq l\leq 17$	$-39\leq h\leq 39$ $0\leq k\leq 23$ $0\leq l\leq 16$
Systematic absences	None	$h0l$, $h+l$ odd; $0k0$, k odd	$h0l$, $h+l$ odd; $0k0$, k odd	hkl, $h+k$ odd; $h0l$, h or l odd
Possible space groups	$P1$ or $P\bar{1}$	$P2_1/n$	$P2_1/n$	Cc or $C2/c$
Variation in standard reflections	0.990—1.010	0.994—1.011	0.990—1.004	0.993—1.008
$\Sigma(\lvert F_o\rvert/\lvert F_o\rvert_{initial})/n$	n=3	n=5	n=4	n=5
Number of reflections measured	5899	10073	10443	8421
Number of reflections observed [$\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$]	5222	4697	6244	5298
Transmission factor, A	No correction	0.158—0.249	0.025—0.077	0.685—0.805
Number of unique reflections	5222	4482	3626	5055
$R(F)$	0.047	0.043	0.047	0.041
$R_w(F)$	0.067	0.052	0.046	0.058

a) Measured by flotation in a ZnI_2 aqueous solution.

Table 2. Fractional Coordinates ($\times10^4$, $\times10^5$ for Pd and Pt) and Equivalent Thermal Parameters ($\times10$)

Atom	x	y	z	$B_{eq}/(Å^2)$
		1		
Pd1	22306(5)	10322(5)	5973(6)	22
Pd2	26899(5)	29119(5)	−6112(6)	22
Cl1	2154(3)	−354(2)	2474(3)	39
Cl2	3094(3)	4585(2)	−1918(3)	41
P1	770(2)	2563(2)	1296(2)	25
P2	2674(2)	1447(2)	−2525(2)	24
N1	2547(6)	4168(5)	1426(7)	24
N2	3357(6)	−359(6)	−687(7)	26
C11	1661(8)	3888(7)	2251(8)	26
C12	1553(11)	4570(10)	3648(11)	44
C13	2368(13)	5539(11)	4193(12)	54
C14	3268(11)	5815(9)	3352(11)	44
C15	3331(9)	5116(7)	1960(9)	32
C16	−236(10)	2256(9)	2624(12)	42
C17	−557(9)	3218(8)	−170(10)	35
C21	3436(7)	−112(7)	−2095(9)	27
C22	3954(10)	−1016(9)	−3111(11)	41
C23	4406(11)	−2185(9)	−2683(12)	44
C24	4303(8)	−2438(8)	−1274(11)	36
C25	3793(8)	−1512(7)	−305(10)	31
C26	3579(10)	1761(9)	−3972(10)	41
C27	943(9)	1164(9)	−3594(10)	37
		2		
M1[a]	77831(4)	18679(4)	88114(6)	30
M2[a]	69024(4)	29529(4)	90221(6)	28
M3[a]	77498(4)	23012(4)	42142(6)	26
M4[a]	66870(4)	13970(4)	36275(6)	27
Cl1	8736(3)	920(2)	8777(4)	58
Cl2	5965(2)	3895(2)	9302(3)	43
Cl3	8744(2)	3130(2)	4889(3)	39
Cl4	5546(2)	695(2)	2989(3)	38
P1	8672(2)	2695(2)	8663(3)	30
P2	6090(2)	2285(2)	8066(3)	26
P3	8304(2)	1347(2)	4841(3)	24
P4	6764(2)	2038(2)	2272(3)	28
N1	7845(6)	3473(5)	9882(8)	25
N2	6796(7)	1158(5)	8925(8)	34
N3	6820(5)	824(5)	4997(7)	20
N4	7083(6)	3121(5)	3461(8)	32
C11	8622(7)	3307(6)	9692(9)	24
C12	9270(8)	3562(7)	10297(11)	32
C13	9117(9)	4026(7)	11082(11)	38
C14	8336(9)	4204(7)	11233(10)	36
C15	7717(8)	3940(7)	10625(10)	32
C16	9726(8)	2443(8)	8715(13)	46
C17	8583(9)	3248(7)	7549(10)	36
C21	6051(8)	1395(7)	8559(9)	27
C22	5379(8)	984(7)	8574(10)	35
C23	5468(10)	307(8)	8942(12)	52
C24	6206(10)	74(7)	9292(11)	43
C25	6840(9)	517(7)	9281(11)	41
C26	5035(8)	2542(7)	7888(12)	38
C27	6364(9)	2146(7)	6777(10)	37
C31	7574(7)	817(6)	5461(9)	21
C32	7740(8)	445(7)	6359(10)	31
C33	7109(8)	68(7)	6776(10)	33
C34	6368(8)	90(7)	6299(11)	35
C35	6229(7)	461(6)	5385(10)	26
C36	9132(8)	1454(8)	5778(11)	42
C37	8694(8)	727(7)	3968(12)	38
C41	6647(7)	2960(7)	2589(10)	31
C42	6163(8)	3425(7)	2066(11)	37
C43	6109(9)	4086(8)	2439(13)	49
C44	6560(10)	4261(8)	3345(15)	55
C45	7033(9)	3770(7)	3852(13)	44
C46	6009(8)	1896(8)	1234(11)	41
C47	7708(9)	2014(8)	1648(11)	41
O1	4416(14)	3999(10)	6181(15)	154
C101	5813(16)	4038(11)	6058(26)	145
C102	5157(15)	4347(12)	6367(23)	117
		3		
Pt1	78005(5)	18729(4)	87734(6)	31
Pt2	69016(5)	29626(4)	89779(6)	28
Pt3	77454(5)	23073(4)	42188(6)	28
Pt4	66787(5)	14068(4)	35949(6)	27
Cl1	8719(4)	900(3)	8707(5)	55
Cl2	5989(3)	3928(3)	9243(5)	51
Cl3	8728(3)	3158(3)	4852(4)	45
Cl4	5583(3)	674(3)	2957(4)	44
P1	8711(3)	2682(3)	8657(4)	35
P2	6081(3)	2318(3)	8023(4)	33
P3	8306(3)	1358(3)	4840(4)	29
P4	6740(3)	2048(3)	2243(4)	36
N1	7838(9)	3469(8)	9844(11)	31
N2	6792(9)	1205(8)	8865(11)	35
N3	6818(8)	838(7)	4954(10)	21
N4	7071(9)	3126(9)	3479(12)	37
C11	8610(11)	3301(9)	9705(13)	27
C12	9254(11)	3574(10)	10293(15)	35
C13	9100(13)	4014(11)	11111(15)	40
C14	8316(13)	4182(11)	11236(14)	42
C15	7703(12)	3941(10)	10596(14)	32
C16	9763(13)	2420(11)	8761(19)	53
C17	8648(13)	3244(11)	7536(13)	38
C21	6055(11)	1413(10)	8519(13)	31
C22	5361(12)	1013(12)	8560(15)	41
C23	5459(14)	336(12)	8957(16)	49
C24	6197(15)	99(11)	9302(17)	53
C25	6844(14)	541(11)	9275(17)	50
C26	5027(12)	2596(11)	7863(16)	42
C27	6377(13)	2198(11)	6708(16)	44
C31	7555(11)	830(9)	5441(13)	26
C32	7718(12)	440(11)	6324(15)	38
C33	7082(12)	65(11)	6726(15)	39
C34	6335(12)	91(10)	6242(15)	37
C35	6216(11)	485(9)	5331(14)	28
C36	9104(12)	1453(12)	5820(17)	47
C37	8718(13)	742(10)	3951(16)	41
C41	6653(12)	2970(12)	2622(16)	44
C42	6168(12)	3468(11)	2080(16)	42
C43	6104(14)	4117(13)	2530(21)	62
C44	6546(16)	4275(13)	3406(25)	80
C45	7019(15)	3754(12)	3926(18)	55
C46	5990(13)	1921(10)	1214(15)	39
C47	7692(11)	2005(11)	1604(14)	36
O1	4376(18)	3998(17)	6102(24)	167
C101	6149(32)	4173(30)	6404(40)	191
C102	5283(35)	4255(34)	6151(46)	217
		4		
Pd1	40291(2)	33047(3)	29281(4)	24
Pd2	37696(2)	20598(3)	36654(4)	27
Cl1	4192(1)	4515(1)	2229(1)	38
Cl2	3437(1)	1009(1)	4417(2)	49

a) M is Pd or Pt with 50% probability each. b) Occupation factor is 0.5.

Table 2. (Continued)

Atom	x	y	z	$B_{eq}/(Å^2)$	Atom	x	y	z	$B_{eq}/(Å^2)$
P1	3449(1)	3003(1)	1778(1)	25	C63	2893(3)	3978(4)	−968(6)	44
P2	3953(1)	2695(1)	5119(1)	28	C64	3253(3)	4134(4)	−1434(6)	49
N1	3593(2)	1574(3)	2185(4)	34	C65	3661(3)	3962(5)	−954(6)	48
N2	4532(2)	3489(3)	4217(4)	27	C66	3723(2)	3628(4)	25(5)	37
C11	3442(2)	2014(4)	1384(5)	27	C71	3528(2)	3346(4)	5360(5)	30
C12	3317(3)	1721(4)	396(5)	38	C72	3109(3)	3052(5)	5335(8)	58
C13	3345(3)	991(4)	209(6)	45	C73	2752(3)	3523(5)	5534(8)	59
C14	3502(3)	546(5)	1019(7)	57	C74	2834(3)	4250(5)	5744(6)	47
C15	3621(3)	840(4)	2004(6)	47	C75	3251(3)	4529(4)	5774(6)	41
C21	4454(2)	3262(4)	5169(5)	30	C76	3599(2)	4091(4)	5581(6)	38
C22	4729(3)	3473(5)	6064(5)	48	C81	4077(2)	2158(4)	6327(5)	34
C23	5084(3)	3939(5)	5995(6)	48	C82	3988(3)	2427(5)	7258(6)	45
C24	5169(2)	4155(4)	5022(6)	37	C83	4096(3)	2023(6)	8164(6)	62
C25	4890(2)	3916(4)	4149(5)	33	C84	4285(4)	1357(7)	8136(7)	75
C51	2928(2)	3179(4)	2247(5)	29	C85	4380(3)	1052(5)	7203(8)	71
C52	2865(3)	3858(4)	2680(7)	50	C86	4271(3)	1462(5)	6303(6)	52
C53	2450(3)	4039(5)	2947(8)	63	C101[b]	4989(6)	607(9)	4259(14)	54
C54	2099(3)	3553(5)	2832(7)	52	C102[b]	4872(13)	816(19)	3579(28)	154
C55	2166(3)	2883(5)	2424(7)	54	C103[b]	5063(10)	1452(15)	3608(22)	109
C56	2580(3)	2671(4)	2136(6)	45	C104[b]	5359(6)	1900(9)	4005(13)	48
C61	3363(2)	3468(3)	510(5)	29	C105[b]	5425(5)	2117(9)	3693(13)	47
C62	2939(2)	3645(4)	0(6)	37	C106[b]	5077(29)	2098(17)	2645(75)	184

theoretically and fixed in the refinement. The function, $\sum w||F_o|-|F_c||^2$, was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by the block-diagonal least-squares method. Complex neutral-atom scattering factors were used.[18] The calculations were carried out on a HITAC M-680 computer at Institute for Molecular Science and on a FACOM M780/10 computer at Keio University using the computation program system UNICS-III.[19] The atomic parameters are listed in Table 2, and selected bond lengths and bond angles in Table 3.[20]

Crystals of **2** and **3** are isostructural and the lattice constants are nearly the same. The electron-densities at the metal atoms in **2** were almost the same, although it is a mixed-metal complex. Since the complex has pseudo-twofold symmetry as shown in Fig. 1 (2), the equivalent electron-densities were attributed to the orientational disorder, i.e. the complex has two possible orientations, Pd–Pt and Pt–Pd, with 50% probability each. This assumption was supported by the following observations. Colors of the crystals of Pd_2 (**1**), PdPt (**2**), and Pt_2 (**3**) complexes are dark-red, red, and yellow, respectively. The presence of the Pd–P and Pt–P bonds in (**2**) were confirmed by the ^{31}P NMR spectrum in solution. The spectrum showed a pattern assignable on the basis of $^1J_{(P,Pt)}$, $^2J_{(P,Pt)}$, and $^3J_{(P,P)}$ coupling constants and was different from those of **1** and **3**.[1] By an electron probe micro analyzer (EPMA), both Pd $L\alpha$ (λ=4.368 Å) and Pt $M\alpha$ (λ=6.047 Å) were observed. These results, in particular, the ^{31}P NMR spectral data indicate that **2** is the Pd–Pt complex and not a mixture of the Pd–Pd and Pt–Pt complexes. Metal atoms in **2** were treated as the same atom with an averaged scattering factor for Pd and Pt, assuming that the thermal vibrations of the Pd and Pt atoms at the same position in unit cells are identical. This approximation is proper, since the B_{eq} values of the metal atoms in **2** and **3** are 2.6—3.0 Å^2 and 2.7—3.1 Å^2, respectively as listed in Table 2. Metal atoms and non-H atoms in the ligands of **2** were refined anisotropically without any difficulty.

Large thermal parameters of the ethanol molecule in **2** and **3** suggest positional disorder. In **4**, hexane molecule lies near the centre of symmetry at (1/2 0 1/2), indicating positional disorder.

Results and Discussion

Perspective drawings of the complexes are presented in Fig. 1 together with the numbering schemes. In each unit cell of **2** and **3**, there are two crystallographically independent dinuclear complexes, but they are quite similar in geometries and chemically equivalent. While crystals of **2** and **3** are isostructural, the crystal structure of **1** is different from those of **2** and **3**. Solvents used for crystallization were ethanol for the former two, and methanol for the latter. However, crystals of **1** grown from an ethanol solution had the same cell constants as those from methanol.

The head-to-tail (*HT*) isomers of **1**—**4**, which were assigned on the basis of NMR and electronic spectra,[1] have been confirmed. Except for Pd1 in **1**, each metal ion is square-planarly coordinated by the other metal ion, and P, N, and Cl donor atoms. The coordination around Pd1 in **1** is appreciably distorted towards tetrahedral geometry. Table 4 shows dihedral angles between the plane formed by M, M′, and P atoms and the plane by M, Cl, and N atoms to estimate the tetrahedral distortion of coordination geometry. Only Pd1 in **1** has the dihedral angle of 21.7°. The angles for all other metal ions are less than 8.4°. The two coordination planes around each of two metal ions are twisted for all the complexes, and the dihedral angles between them range 38—43°. Table 5 lists these angles together with those found in analogous Pd(I) and Pt(I) dinuclear complexes bridged by bidentate phosphine ligands.[2-8] Similar twisted angles are seen in these phosphine

Table 3. Selected Bond Lengths (l/Å) and Bond Angles (ϕ/°)[a)]

	1	2	3	4		1	2	3	4
M1–M2	2.584(1)	2.568(1)	2.579(1)	2.594(1)	M2–M1–C11	161.6(1)	172.4(1)	174.7(2)	174.0(1)
M3–M4		2.554(1)	2.566(1)		M1–M2–C12	175.9(1)	173.8(1)	175.5(1)	171.5(1)
M1–C11	2.441(3)	2.410(4)	2.403(6)	2.428(2)	M4–M3–C13		176.0(1)	178.3(1)	
M2–C12	2.423(3)	2.427(4)	2.419(6)	2.411(2)	M3–M4–C14		170.9(1)	173.5(1)	
M3–C13		2.416(4)	2.413(5)		M2–M1–P1	75.4(1)	79.0(1)	80.7(1)	77.4(1)
M4–C14		2.424(4)	2.404(5)		M1–M2–P2	79.1(1)	78.0(1)	80.0(1)	79.6(0)
M1–P1	2.195(2)	2.182(4)	2.167(5)	2.207(2)	M4–M3–P3		78.9(1)	80.4(1)	
M2–P2	2.192(2)	2.197(4)	2.182(5)	2.203(2)	M3–M4–P4		77.9(1)	79.9(1)	
M3–P3		2.188(4)	2.176(6)		M2–M1–N2	96.5(2)	93.9(3)	91.2(4)	93.8(1)
M4–P4		2.189(4)	2.175(6)		M1–M2–N1	92.4(2)	92.2(3)	91.0(4)	93.9(1)
M1–N2	2.140(6)	2.140(11)	2.107(15)	2.122(5)	M4–M3–N4		92.1(3)	90.7(4)	
M2–N1	2.165(6)	2.118(10)	2.108(15)	2.106(5)	M3–M4–N3		93.6(3)	91.7(4)	
M3–N4		2.131(10)	2.127(16)		C11–M1–P1	98.3(1)	95.9(1)	96.1(2)	98.8(1)
M4–N3		2.122(9)	2.103(13)		C12–M2–P2	96.9(1)	98.7(1)	98.2(2)	97.1(1)
P1–C11	1.815(8)	1.807(12)	1.837(18)	1.842(7)	C13–M3–P3		98.9(1)	99.5(2)	
P2–C21	1.828(8)	1.833(14)	1.850(20)	1.828(7)	C14–M4–P4		96.5(1)	96.1(2)	
P3–C31		1.817(12)	1.815(19)		C11–M1–N2	93.3(2)	91.3(3)	92.1(4)	89.5(1)
P4–C41		1.833(14)	1.838(24)		C12–M2–N1	91.6(2)	91.2(3)	90.9(4)	88.9(2)
P1–C16	1.814(11)	1.805(14)	1.806(22)		C13–M3–N4		90.3(3)	89.4(5)	
P1–C17	1.815(9)	1.817(14)	1.829(19)		C14–M4–N3		92.5(3)	92.6(4)	
P2–C26	1.837(10)	1.813(14)	1.821(20)		P1–M1–N2	164.4(2)	172.7(3)	171.7(4)	170.2(2)
P2–C27	1.836(10)	1.817(14)	1.847(22)		P2–M2–N1	171.2(2)	170.0(3)	170.8(4)	173.3(1)
P3–C36		1.797(14)	1.807(21)		P3–M3–N4		170.7(3)	170.9(5)	
P3–C37		1.809(15)	1.822(21)		P4–M4–N3		170.3(3)	170.6(4)	
P4–C46		1.815(14)	1.806(21)		M1–P1–C11	110.6(3)	109.9(4)	108.2(6)	113.5(3)
P4–C47		1.816(16)	1.828(19)		M2–P2–C21	117.4(3)	111.9(5)	110.3(6)	114.9(2)
P1–C51				1.812(7)	M3–P3–C31		111.5(4)	110.0(6)	
P1–C61				1.829(6)	M4–P4–C41		110.0(5)	107.9(8)	
P2–C71				1.804(7)	M1–P1–C16	116.9(3)	117.1(5)	117.7(7)	
P2–C81				1.830(7)	M1–P1–C17	118.1(3)	118.7(5)	117.8(6)	
N1–C11	1.363(10)	1.363(15)	1.337(24)	1.331(8)	M2–P2–C26	114.3(3)	117.5(5)	117.5(7)	
N2–C21	1.359(10)	1.371(17)	1.337(23)	1.355(9)	M2–P2–C27	113.8(3)	116.6(5)	115.3(7)	
N3–C31		1.353(14)	1.346(22)		M3–P3–C36		116.5(5)	117.8(7)	
N4–C41		1.356(16)	1.329(26)		M3–P3–C37		117.8(5)	117.4(7)	
N1–C15	1.352(10)	1.359(17)	1.370(24)	1.339(9)	M4–P4–C46		117.6(5)	118.9(7)	
N2–C25	1.342(11)	1.319(17)	1.380(26)	1.346(9)	M4–P4–C47		117.3(5)	115.8(6)	
N3–C35		1.332(15)	1.321(23)		M1–P1–C51				112.7(2)
N4–C45		1.355(17)	1.342(29)		M1–P1–C61				119.4(2)
					M2–P2–C71				112.6(2)
					M2–P2–C81				117.2(2)
					M2–N1–C11	115.1(5)	117.3(8)	119.4(12)	118.8(4)
					M1–N2–C21	116.6(5)	115.8(8)	120.5(12)	117.9(5)
					M4–N3–C31		115.7(7)	118.0(11)	
					M3–N4–C41		117.4(8)	117.5(14)	
					M2–N1–C15	124.8(5)	123.8(8)	123.6(12)	123.4(4)
					M1–N2–C25	124.5(6)	126.6(9)	123.1(13)	122.4(4)
					M4–N3–C35		124.5(7)	122.5(11)	
					M3–N4–C45		122.9(9)	119.9(14)	
					P1–C11–N1	110.7(5)	112.5(8)	112.6(13)	111.3(5)
					P2–C21–N2	113.4(6)	112.6(9)	111.1(13)	113.1(4)
					P3–C31–N3		114.1(8)	113.9(12)	
					P4–C41–N4		110.9(9)	113.8(15)	

a) M denotes (**1**) Pd, (**2**) Pd or Pt with 50% probability each, (**3**) Pt, and (**4**) Pd, respectively.

complexes. For the R_2Ppy complexes, the P–C–N–M moiety of the bridge is fixed coplanar, and the dihedral angle of the coordination planes is determined by the M–P–C–N torsion angles, which are listed in Table 4. The tetrahedral distortion observed for Pd1 in **1** may be the result from the imbalance in two M–P–C–N torsion angles, which is caused by molecular packing in the crystal. The ^{31}P NMR spectrum of **1** in solution indicates equivalent coordination geometry around two Pd atoms.

All of the M–P, M–N, and M–Cl lengths in the Me_2Ppy complexes **1**, **2**, and **3** become slightly short in the order of Pd_2 (**1**)>PdPt (**2**)>Pt_2 (**3**). It is known that metal–ligand bond lengths are in general shorter in Pt(0)

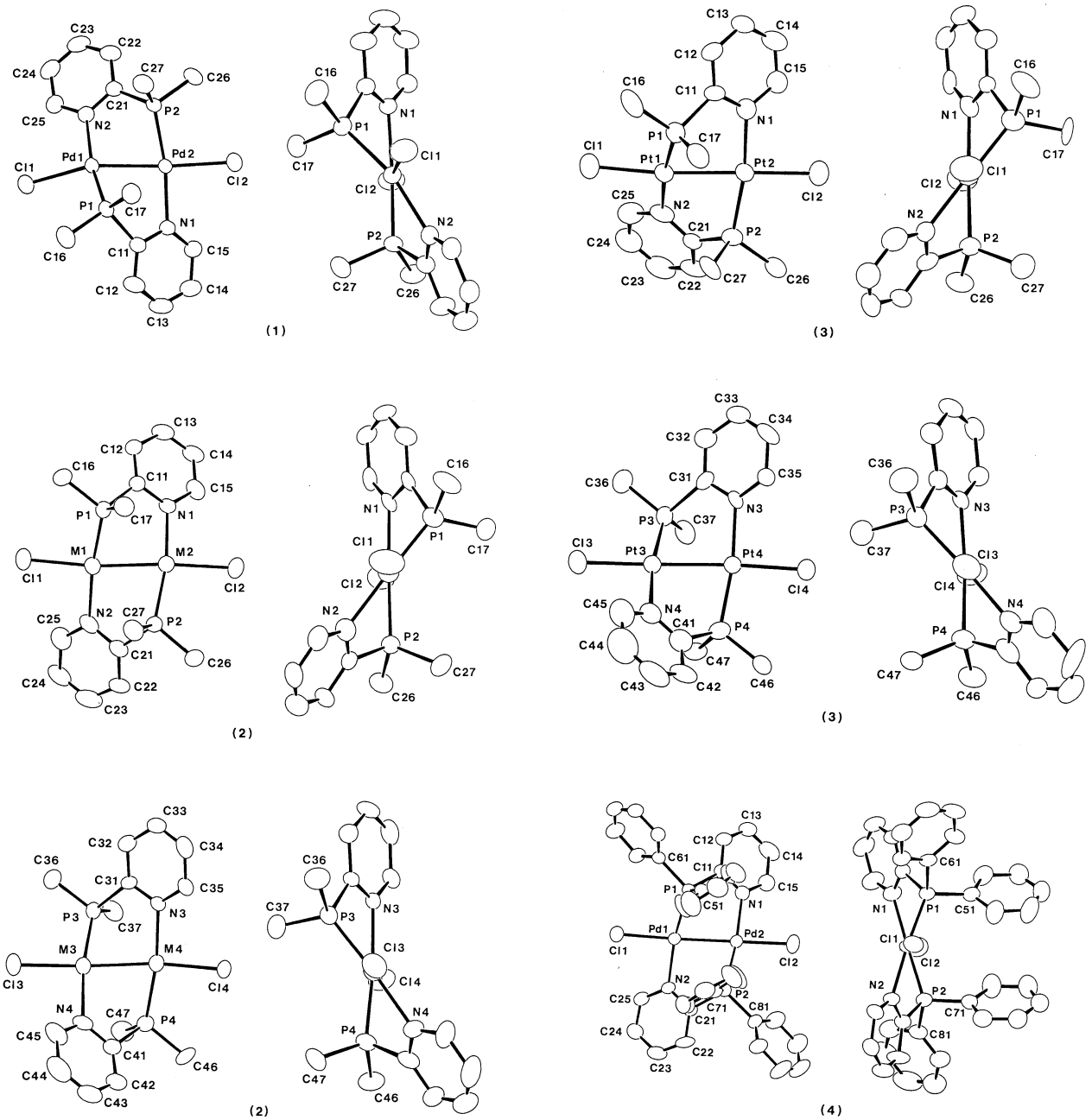


Fig. 1. Perspective views of the complexes and projections along the metal–metal bond. (**1**) *HT*-[$Pd_2Cl_2(\mu\text{-}Me_2Ppy)_2$], (**2**) *HT*-[$PdPtCl_2(\mu\text{-}Me_2Ppy)_2$], (**3**) *HT*-[$Pt_2Cl_2(\mu\text{-}Me_2Ppy)_2$], and (**4**) *HT*-[$Pd_2Cl_2(\mu\text{-}Ph_2Ppy)_2$].

and Pt(II) complexes than in the corresponding Pd(0) and Pd(II) complexes.[21] The same relation in metal–ligand bond length is seen between the Pd(I) and Pt(I) complexes. Direct comparisons of the Pd(I)–ligand and Pt(I)–ligand bond lengths in **2** were not possible because of disorder in the positions of these two metal ions. For the metal–metal bond lengths, the average value (2.561(1) Å) of two kinds of hetero-metal dinuclear complex in **2** is a little smaller than those of **1** (2.584(1) Å) and **3** (av 2.573(1) Å). The differences in these values seem to be too small to discuss more. However, it is noted that the metal–metal bond lengths in **1**—**4** are fairly short compared with those of structurally known Pd(I) and Pt(I) dinuclear complexes shown in Table 5.[2-8] The short M–M bond lengths in the R_2Ppy (R=Me, Ph) complexes may be related to the shorter distance between the P and N donor atoms in these ligands than those between two donor atoms of other bridging ligands given in Table 5. The P···N distances (2.627—2.677 Å) of R_2Ppy are considerably shorter than the distances of

Table 4. Dihedral Angles (ϕ/°) Showing Tetrahedral Distortions and Torsion Angles (ϕ/°) of the Bridge

Complex	Metal	Plane (M, M', P) vs. plane (M, Cl, N)[a]	M–P–C–N[b]
1	Pd1	21.7	48.9
	Pd2	2.8	28.9
2	M1	6.0	−44.0
	M2	5.8	−40.3
	M3	4.1	36.8
	M4	8.4	43.5
3	Pt1	4.5	−44.1
	Pt2	4.5	−38.9
	Pt3	2.5	37.2
	Pt4	6.7	41.3
4	Pd1	6.5	37.5
	Pd2	8.2	28.1

a) The value shows tetrahedral distortion of square planar coordination around the metal. b) For M(n) row, the value shows the torsion angle of M(n)–P(n)–C(n1)–N(n).

P···P (2.880—2.970 Å) of diphosphines and P···S (2.883 and 2.937 Å) of btmp.

The M–P bond lengths in the present R$_2$Ppy complexes are remarkably shorter (by ca. 0.1 Å) than those in the complexes with bridging diphosphine ligands given in Table 5. The lengthening of M–P bond lengths in the diphosphine complexes is attributable to the mutual trans influence of two phosphino donor groups in the trans positions as observed on a large number of phosphine complexes. The Pd–P bond length (2.207(2) and 2.203(2) Å) in **4** is slightly longer than that (2.195(2) and 2.192(2) Å) in **1**. On the other hand, the Pd–N bond length (2.122(5) and 2.106(5) Å) in **4** is fairly shorter than that (2.165(6) and 2.140(6) Å) in **1**. The result would indicate the stronger trans influence of the -PMe$_2$ group than the –PPh$_2$ group towards the M(I) ion. In the previous paper,[1] we reported that the Me$_2$Ppy complexes isomerized from the *HH*- to *HT*-isomers more rapidly than did the Ph$_2$Ppy complexes. The rapid isomeriza-

Table 5. Comparisons of Structural Parameters of M(I) Dinuclear Complexes Bridged by Phosphinopyridines, Diphosphinomethanes, and Phosphinomethylthioethers[a]

Complex	M–M / Å	P···E[b] / Å	M–P / Å	Twist angle of coord. planes/°	Ref.
HT-[Pd$_2$Cl$_2$(μ-Me$_2$Ppy)$_2$] (**1**)	2.584(1)	2.627	2.195(1)	43.11	
		2.677	2.192(2)		
HT-[PdPtCl$_2$(μ-Me$_2$Ppy)$_2$] (**2**)	2.568(1)	2.648	2.182(4)	39.3	
	2.554(1)	2.677	2.197(4)	40.1	
		2.672	2.188(4)		
		2.642	2.189(4)		
HT-[Pt$_2$Cl$_2$(μ-Me$_2$Ppy)$_2$] (**3**)	2.579(1)	2.656	2.167(5)	38.4	
	2.566(1)	2.644	2.182(5)	39.7	
		2.662	2.176(6)		
		2.667	2.175(6)		
HT-[Pd$_2$Cl$_2$(μ-Ph$_2$Ppy)$_2$] (**4**)	2.594(1)	2.635	2.207(2)	38.75	
		2.669	2.203(2)		
[Pd$_2$Br$_2$(μ-dmpm)$_2$]	2.603(1)	2.931	2.291(3)	50.5	2
			2.275(3)		
[Pd$_2$Br$_2$(μ-dppm)$_2$]	2.699(5)	c)	2.26(1)	39	3
			2.28(1)		
			2.29(1)		
			2.32(1)		
[Pt$_2$Cl$_2$(μ-dppm)$_2$]	2.652(2)	2.930	2.293	38.5	4
		2.964	2.263		
			2.259		
			2.251		
[Pd$_2$(OCOCF$_3$)$_2$(μ-dppm)$_2$]	2.594(2)	c)	2.309(2)	44.5	5
			2.296(2)		
[Pd$_2$Cl(SnCl$_3$)(μ-dppm)$_2$]	2.644(2)	2.880	2.295(4)	41.3	6
		2.960	2.307(4)		
			2.343(4)		
			2.296(4)		
[Pd$_2$Cl$_2$(μ-Medppm)$_2$]	2.6639(7)	2.955	2.297	37	7
		2.970	2.297		
			2.294		
			2.294		
[Pd$_2$Cl$_2$(μ-btmp)$_2$]	2.590(2)	2.883	2.226(3)	51.6	8
		2.937	2.243(3)		

a) The abbreviations used in this table are; dmpm=(CH$_3$)$_2$PCH$_2$P(CH$_3$)$_2$, dppm=(C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$, Medppm=(C$_6$H$_5$)$_2$PCH(CH$_3$)P(C$_6$H$_5$)$_2$, and btmp=(C$_6$H$_5$)$_2$PCH$_2$SCH$_2$C$_6$H$_5$. b) E denotes N, P, and S for phosphinopyridine, diphosphinomethane, and phosphinomethylthioether, respectively. c) No data are available in the references.

tion may be the result from the stronger trans influence (effect) of the $-PMe_2$ group.

For the bond angles around the metal ion, the angles of M–M–N (90.7—96.5°) and Cl–M–N (88.9—93.3°) are roughly the right angle, while those of Cl–M–P (95.9—99.5°) and M–M–P (75.4—80.7°) deviated fairly largely from the right angle. Other structural parameters of the Me_2Ppy and Ph_2Ppy moieties are normal and very close to those of unidentate phosphorus donating Me_2Ppy in *cis*-$[PdCl_2(Me_2Ppy\text{-}P)_2]$.[22]

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References

1) T. Suzuki and J. Fujita, *Bull. Chem. Soc. Jpn.*, **65**, 1016 (1992).

2) M. L. Kullberg, F. R. Lemke, D. R. Powell, and C. P. Kubiak, *Inorg. Chem.*, **24**, 3589 (1985).

3) R. G. Holloway, B. R. Penfold, R. Colton, and M. J. McCormick, *J. Chem. Soc., Chem. Commun.*, **1976**, 485.

4) M. P. Brown, R. J. Puddephatt, M. Rashidi, Lj Manojlović-Muir, K. W. Muir, T. Solomun, and K. R. Sedden, *Inorg. Chim. Acta*, **23**, L33 (1977).

5) T. E. Krafft, C. I. Hejna, and J. S. Smith, *Inorg. Chem.*, **29**, 2682 (1990).

6) M. M. Olmstead, L. S. Benner, H. Hope, and A. L. Balch, *Inorg. Chim. Acta*, **32**, 193 (1979).

7) C.-L. Lee, Y.-P. Yang, S. J. Rettig, B. R. James, D. A. Nelson, and M. A. Lilga, *Organometallics*, **5**, 2220 (1986).

8) Y. Fuchita, K. I Hardcastle, K. Hiraki, and M. Kawatani, *Bull. Chem. Soc. Jpn.*, **63**, 1961 (1990).

9) J. P. Farr, M. M. Olmstead, and A. L. Balch, *Inorg. Chem.*, **22**, 1229 (1983).

10) A. Maisonnet, J. P. Farr, M. M. Olmstead, C. T. Hunt, and A. L. Balch, *Inorg. Chem.*, **21**, 3961 (1982).

11) J. P. Farr, M. M. Olmstead, C. H. Hunt, and A. L. Balch, *Inorg. Chem.*, **20**, 1182 (1981).

12) J. P. Farr, M. M. Olmstead, N. M. Rutherford, F. E. Wood, and A. L. Balch, *Organometallics*, **2**, 1758 (1983).

13) L. J. Tortorelli, C. A. Tucker, C. Woods, and J. Bordner, *Inorg. Chem.*, **25**, 3534 (1986).

14) E. Lastra, M. P. Gamasa, J. Gimeno, M. Lanfranchi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, **1989**, 1499.

15) C. G. Arena, E. Rotondo, F. Faraone, M. Lanfranchi, and A. Tiripicchio, *Organometallics*, **10**, 3877 (1991); S. L. Schiavo, E. Rotondo, G. Bruno, and F. Faraone, *ibid.*, **10**, 1613 (1991).

16) Y. Inoguchi, B. Milewski-Mahrla, and H. Schmidbaur, *Chem. Ber.*, **115**, 3085 (1982).

17) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

18) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV. (Present distributor D. Reidel, Dordrecht.)

19) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

20) Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the observed and calculated structure factors are deposited as Document No. 9011 at the Office of the Editor of Bull. Chem. Soc. Jpn.

21) For example; *cis*-$[PdCl_2(PMePh_2)_2]$ (Pd–Cl=2.338(2), 2.344(2) Å; Pd–P=2.262(2), 2.267(2) Å) (N, W. Alcock and J. H. Nelson, *Acta Crystallogr., Sect. C*, **41**, 1748 (1985).) and *cis*-$[PtCl_2(PMePh_2)_2]$ (Pt–Cl=2.345(1)—2.359(2) Å; Pt–P=2.245(1)—2.250(2) Å) (H. Kin-Chee, G. M.McLaughlin, M. McPartlin, and G. B. Robertson, *Acta Crystallogr., Sect. B*, **38**, 421 (1982).). $[Pd(phen)_2](ClO_4)_2$ (Pd–N=2.043(4), 2.059(4) Å) (J. V. Rund and A. C. Hazell, *Acta Crystallogr., Sect. B*, **36**, 3103 (1980)) and $[Pt(phen)_2]Cl_2 \cdot 3H_2O$ (Pt–N=2.026(8), 2.039(8) Å) (A. Hazell and A. Mukhopadhyay, *Acta Crystallogr., Sect. B*, **36**, 1647 (1980)). $[Pd(PPhBu^t_2)_2]$ (Pd–P=2.285(2) Å) and $[Pt(PPhBu^t_2)_2]$ (Pt–P=2.252(1) Å) (S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98**, 5850 (1976).

22) T. Suzuki, M. Kita, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 3434 (1990).