Table III. Comparative MLCT Energies (μm^{-1})[a]

complex	$d_\sigma \rightarrow L$[b]	$d_\pi \rightarrow L$[c]	$\Delta_{\pi-\sigma}$
Pt(II) Complexes			
$Pt(P(OEt)_3)_4{}^{2+}$	3.71	4.80	1.09
$[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$	3.74	4.80	1.06
$[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$	3.76[d]	4.80[d]	1.04
$Pt(DEPE)_2{}^{2+}$	3.68	4.69	1.01
trans-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$			
P	3.81	*h*	
CN	4.01	*h*	
cis-$[Pt(PEt_3)_2(CH_3)_2]$[e]	3.66	4.63	0.97
$Pt(CNEt)_4{}^{2+}$[f]	3.93[d]	4.83[d]	0.90
$Pt(CN)_4{}^{2-}$[g]	3.85[d]	4.55[d]	0.70
Pd(II) Complexes			
$Pd(DEPE)_2{}^{2+}$	4.18	4.76	0.58
trans-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$			
P	4.45	*h*	
$Pd(CNEt)_4{}^{2+}$[f]	4.56[d]	5.16[d]	0.60

[a] From MCD data. [b] $1A_{2u}(^1A_{2u})$ in D_{4h} or $1B_{1u}(^1B_{1u})$ in D_{2h}. [c] $2E_u(^1E_u)$ in D_{4h} or $3B_{2u},2B_{3u}(^1B_{2u},{}^1B_{3u})$ in D_{2h}. [d] From absorption data. [e] $B_1(^1B_1)$ and $B_2,A_1(^1B_2,{}^1A_1)$ in C_{2v}.[10] [f] Reference 7b. [g] Reference 7a. [h] Band location uncertain.

component of the energy difference due to the spin-orbit splitting of the A_{2u} and E_u states, which of course is larger for Pt(II) than Pd(II). Thus for Pd(II) $\Delta_{\pi-\sigma}$ is about the same for PR_3 and CNEt, implying comparable π-acceptor ability.

It is interesting that separate $nd \rightarrow$ P donor and $nd \rightarrow CN^-$ transitions could be resolved in the cyanophosphine complexes studied here. This resolution indicates separate configurations involving the different ligand-based orbitals. However, the energy difference between these ligand-based orbitals is quite small, being less than ~0.2 μm^{-1} for Pt(II) and Pd(II) and slightly larger for Ni(II). Furthermore, the change in energy of the MLCT spectrum, as judged by the $d_\sigma \rightarrow L$ transition, and the change in spread of the spectrum, as judged by $\Delta_{\pi-\sigma}$, over a range of ligands is not very large. For example, the Pt(II) the $d_\sigma \rightarrow L$ transition shifts less than 0.36 μm^{-1} while $\Delta_{\pi-\sigma}$ changes only by 0.39 μm^{-1} for the complexes of Table III. The lack of strong dependence of transition energies on the nature of the ligand, which is apparent here, has been cited[6,9] as an indication of considerable $(n + 1)p_z$ character in the "ligand" LUMO. We believe this is a valid point but should not be taken to the extreme of minimizing the ligand contribution to the LUMO. There is a nonnegligible ligand contribution as clearly evidenced by the resolution of separate transitions to the CN^- and PR_3 ligands of the D_{2h} complexes investigated here. Thus it is reasonable to view the LUMO's in these P-donor M(II) complexes, and probably also the Rh(I) and Ir(I) complexes investigated previously,[1,2,5,6,8,9] as having significant contributions of *both* metal $(n + 1)p_z$ and ligand orbitals and consequently the LUMO as being extensively delocalized over both metal and ligands.

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Registry No. $[Pt(P(OEt)_3)_4](ClO_4)_2$, 88212-05-9; $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$, 30053-63-5; $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$, 32324-65-5; $[Pt(DEPE)_2](ClO_4)_2$, 88657-18-5; $[Pt(DEPE)_2](PF_6)_2$, 88657-19-6; $[Pd(DEPE)_2](PF_6)_2$, 88657-21-0; $[Ni(DEPE)_2](PF_6)_2$, 88657-22-1; *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$, 15390-91-7; *trans*-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$, 88657-23-2; *trans*-$[Ni(PEt_3)_2(CN)_2]$, 14523-37-6.

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Preparation, Structure, and Properties of Central-Carbon-Bonded Diethyl Malonato Complexes of Palladium(II) with Bis(μ-chloro) and μ-Oxalato Bridges

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cis-Bis(diethyl malonato-*C*)palladium(II) complexes have been prepared by the reaction of diethyl malonate with a tetrachloropalladate ion in an alkaline solution. During the preparation of the complex Pd-induced oxidative decomposition of the ligand occurs to yield a (μ-oxalato)palladium(II) complex, whose structure has been determined by a single-crystal X-ray study. The compound, $Na_2[(Pd(C_7H_{11}O_4)_2)_2Cl_2]K_2[(Pd(C_7H_{11}O_4)_2)_2(C_2O_4)]\cdot 4H_2O$, crystallizes in the monoclinic space group *Cc*, with cell constants $a = 28.331$ (3) Å, $b = 16.212$ (1) Å, $c = 22.510$ (2) Å, $\beta = 122.21$ (1)°, and $Z = 4$. The structure has been solved by heavy-atom methods, and least-squares refinements have led to $R = 0.056$ and $R_w = 0.076$ for 4691 reflections with $F_o > 2\sigma(F_o)$. The crystal consists of two kinds of dimeric complexes held together by interaction of the carbonyl oxygen atoms and alkali-metal ions. The bridging oxalate group is approximated to be of D_{2h} symmetry, exhibiting $\nu_{CO}(B_{2u})$ at 1618 cm^{-1}. The (diethyl malonato-*C*)palladium(II) compounds react with methanol to give diethyl bis(hydroxymethyl)malonate in a moderate isolated yield.

Introduction

Since the first synthesis of a carbon-bonded β-diketonato Pd(II) complex by Kawaguchi and co-workers,[1a] extensive work has been carried out on such a type of Pd(II) compounds with β-diketones and β-ketoacetic esters.[1] In contrast, only a limited number of Pd(II) compounds with malonic esters have been isolated and characterized so far,[2] although diethyl malonate is a very useful reagent for C-C bond formation in reactions with organopalladium compounds.[3] Our attention was thus drawn to the neglected Pd(II) compounds with un-

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substituted diethyl malonate and led us to investigate basic reactions between the ligand and a chloropalladate ion and characterize the resultant complexes. In this paper we wish to report the preparation of the (diethyl malonato-*C*)palladium(II) compounds, the X-ray crystal structure of the compound possessing a (μ-oxalato)palladium(II) moiety that might be produced by Pd-induced oxidative decomposition of diethyl malonate, and the reaction of the Pd–malonate-*C* compounds with methanol for C–C bond formation.

Experimental Section

General Comments. The cited yield data were based on isolated pure components and are not maximized. All melting points were taken in capillary tubes with a Shibata melting point apparatus. Proton NMR spectra were determined on a Hitachi R-24 spectrometer by using $CDCl_3$ solutions with Me_4Si as the internal standard. Infrared spectra were recorded on a Hitachi 295 infrared spectrophotometer. The elemental analyses were performed by the Service Center of Elemental Analyses in Kyushu University.

Preparation of Palladium Complexes 1 and 2 with Central-Carbon-Bonded Diethyl Malonato Ligands. A mixture of diethyl malonate (0.96 g, 6 mmol), sodium tetrachloropalladate (0.88 g, 3 mmol), and potassium hydroxide (0.37 g, 6.6 mmol) in water (6 mL) was stirred at room temperature for 1 day during which time yellow product appeared along with a dark brown precipitate; the product was then extracted with several 50-mL portions of CH_2Cl_2. The organic layer was concentrated in vacuo until yellow crystals in a small quantity of orange solution was obtained. After standing of the mixture at ambient temperature for 1 day, yellow crystals, $Na_2[(Pd(C_7H_{11}O_4)_2)_2Cl_2]$ (**1**), were filtered, washed with a small quantity of CH_2Cl_2, and dried at 50 °C in vacuo: yield 0.20 g (14%); mp ca. 200 °C dec. Anal. Calcd for $C_{28}H_{48}Cl_2Na_2O_{16}Pd_2$: C, 34.80; H, 4.60. Found: C, 34.71; H, 4.56. IR (KBr): 1730 sh and 1703 vs cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ 1.25 (t, $J = 7.2$ Hz, 24 H, CH_3), 4.20 (q, $J = 7.2$ Hz, 16 H, CH_2).

After the collection of the crystals of **1**, the resulting orange filtrate was allowed to stand over 2 weeks to give yellow bricks; these were picked up on a sintered-glass frit, washed with CH_2Cl_2, and dried at 20 °C in vacuo. These crystals, $Na_2[(Pd(C_7H_{11}O_4)_2)_2Cl_2]K_2[(Pd(C_7H_{11}O_4)_2)_2(C_2O_4)]\cdot 4H_2O$ (**2**), were suitable for X-ray study: yield 0.025 g (4.9%); mp ca. 200 °C dec. Anal. Calcd for $C_{58}H_{96}Cl_2Na_2K_2O_{40}Pd_4$: C, 33.92; H, 4.71. Found: C, 33.88; H, 4.58. IR (KBr): 1730 sh, 1710 vs, and 1618 s cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ ca. 1.25 (m, CH_3), ca. 4.1 (m, CH_2).

Disodium [Bis(μ-chloro)bis(bis(diethyl malonato-*C*)dipalladate)] (1) and Its Dipotassium and Dilithium Analogues, 3 and 4. Sodium hydroxide (0.36 g, 9 mmol) was used in place of KOH for the preparation of **1**; otherwise the procedure was similar to those of the above reaction to give yellow crystals (0.32 g, 22%). This sample was identical with the sample (**1**) prepared above. The dipotassium and dilithium analogues, **3** and **4**, were prepared similarly by using corresponding alkali-metal salts of tetrachloropalladate(II) and hydroxide in the yields of 4.7 and 42%, respectively. The IR spectra of these products were identical with that of **1**.

Reaction of the (Diethyl malonato-*C*)palladium(II) Compounds with Methanol. A suspension of **1** or a solution of **4** (0.04 mmol) in warm methanol (10 mL) was stirred for 30 min until a complete precipitation of palladium metal and a decoloration of the yellow solution took place. The methanol of the filtrate was distilled off in vacuo to yield a mixture of a white precipitate (NaCl) and a viscous oil, which was separated by dissolution in chloroform followed by evaporation of the solvent in vacuo. The product (0.03 g, 85%) was identical with known diethyl bis(hydroxyethyl)malonate. IR (neat): 3520 (OH), 1628 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ 1.27 (t, $J = 7.0$ Hz, 6 H, CH_3), ca. 2.9 (bs, 2 H, OH), 4.10 (s, 4 H, CH_2), 4.26 (q, $J = 7.0$ Hz, 4 H, CH_2).

Table I. Crystallographic Data

formula	$Pd_4K_2Cl_2Na_2O_{40}C_{58}H_{96}$
fw	2054.07
space group	*Cc*
a, Å	28.331 (3)
b, Å	16.212 (1)
c, Å	22.510 (2)
β, deg	122.21 (1)
V, $Å^3$	8747.7 (12)
Z	4
F(000)	4138
d(calcd), g cm^{-3}	1.560
d(measd), g cm^{-3}	1.571 (at 25 °C)
cryst size, mm	0.33 (in diameter)
μ(Mo Kα), cm^{-1}	10.45
2ϑ range, deg	$2\vartheta < 44$
no. of data	5375
$\lvert F_o\rvert > 2\sigma(\lvert F_o\rvert)$	4691
$R = \Sigma\lvert\Delta\lvert F\rvert\rvert/\Sigma\lvert F_o\rvert$	0.056
$R_w = [\Sigma w(\Delta\lvert F\rvert)^2/\Sigma w(F_o)^2]^{1/2}$	0.076

In the case where care was taken in handling insoluble materials in the above procedure, yields of Pd(0) and NaCl were found to be almost theoretical.

X-ray Crystal Structure Determination of 2. The crystal used was ground to a sphere of 0.33 mm in diameter, and the density was measured by flotation in a CCl_4–hexane mixture. The preliminary Weissenberg (Cu) X-ray photographs gave approximate cell dimensions, showing monoclinic symmetry; the systematic absences led to *Cc* or *C*2/*c* as possible space groups. Data collection was carried out on a Rigaku AFC-5 automated four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 20 ± 0.5 °C. The accurate unit-cell parameters were determined by a least-squares refinement using 23 reflections in the range of $28° < 2\vartheta < 32°$. The diffracted intensities were measured by the 2ϑ–ω scan technique with a scan rate of 10° min^{-1}. The summary of crystallographic data is presented in Table I. Three check reflections were monitored every 100 measurements throughout the data collection and showed no significant variation. Of a total of 5375 independent reflections, the intensities of 4691 reflections with $F_o > 2\sigma(F_o)$ were used for the solution and refinement of the structure. The intensity data were corrected for Lorentz and polarization effects, but no corrections for absorption or extinction were made because of the low absorption coefficient.

The presence of Cl atoms in the crystals was confirmed qualitatively. By consideration of the reaction conditions to prepare the complex and the ionic charge to be balanced, both K and Na as well as Pd atoms were assumed to be present in the crystal. The preliminary scale and overall temperature factors were estimated by the Wilson method.[4] The statistical distribution of the normalized structure factors gave equivocal indication for the presence of a center of symmetry. A Patterson synthesis gave clear indications of the presence of four "equally" heavy atoms assumed to be Pd atoms, whose positions corresponded to be centrosymmetric. At this stage, space group *C*2/*c* was assumed to be correct and the structure was solved by successive Fourier syntheses and refined by the block-diagonal least-squares method, initially with isotropic thermal parameters. The function minimized was $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where equal weights were initially adopted. After several cycles of refinement the convergence stopped at $R = 0.18$. At this stage, a difference Fourier synthesis showed some peaks at unreasonable positions probably due to echoes of the actual structure. These facts indicated that the correct choice was *Cc* for the space group, in which the structure was refined to a lower *R* factor (<0.1). Because of pseudosymmetry, consideration of the possible geometry and steric hindrance between the atoms, together with a laborious trial-and-error process, were needed to sort out the true structure from its image. In the later stages of refinement Cruickshank's weighting scheme was introduced.[5] Anisotropic thermal parameters were employed for the non-hydrogen atoms except for the water oxygen atoms, which were refined isotropically. This model

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Table II. Fractional Atomic Coordinates[a]

atom	x	y	z	atom	x	y	z
(a) Positional Parameters ($\times 10^4$) for Non-Hydrogen Atoms of the Complexes							
Pd(1)	0	−350 (1)	0	O(3)	3429 (5)	−3394 (7)	947 (6)
Pd(2)	1411 (1)	219 (1)	954 (1)	O(4)	4007 (5)	−2392 (7)	1079 (6)
Cl(1)	719 (2)	−83 (4)	−225 (3)	C(1)	3041 (7)	−2256 (10)	140 (9)
Cl(2)	721 (2)	−144 (4)	1208 (2)	C(2)	3529 (7)	−2705 (9)	768 (9)
C(11)	−597 (7)	−560 (11)	−1065 (8)	C(51)	1712 (7)	−3885 (13)	−319 (10)
C(12)	−477 (8)	−64 (12)	−1480 (10)	C(52)	1619 (8)	−4042 (14)	−1026 (13)
C(13)	−542 (7)	−1446 (12)	−1122 (9)	C(53)	1485 (7)	−3132 (12)	−229 (10)
C(14)	−510 (18)	1507 (31)	−1801 (20)	C(54)	1387 (22)	−4962 (31)	−1873 (29)
C(15)	−1016 (23)	1631 (35)	−2439 (28)	C(55)	969 (24)	−5642 (33)	−2362 (30)
C(16)	−835 (14)	−2773 (17)	−958 (19)	C(56)	1334 (17)	−2257 (22)	549 (21)
C(17)	−1071 (24)	−3150 (24)	−609 (25)	C(57)	947 (20)	−2606 (30)	695 (26)
O(11)	−678 (7)	714 (9)	−1538 (8)	O(51)	1522 (8)	−4766 (11)	−1225 (11)
O(12)	−275 (6)	−220 (9)	−1820 (7)	O(52)	1621 (7)	−3514 (11)	−1439 (9)
O(13)	−218 (6)	−1808 (10)	−1237 (8)	O(53)	1275 (5)	−2577 (9)	−651 (7)
O(14)	−899 (6)	−1885 (8)	−1019 (8)	O(54)	1492 (8)	−3109 (12)	332 (11)
C(21)	−609 (7)	−539 (11)	222 (10)	C(61)	2637 (7)	−4837 (11)	779 (10)
C(22)	−838 (8)	321 (12)	171 (10)	C(62)	2925 (8)	−4627 (13)	1540 (10)
C(23)	−368 (7)	−931 (13)	919 (10)	C(63)	2953 (9)	−5350 (12)	562 (12)
C(24)	−1513 (11)	1257 (18)	−660 (15)	C(64)	2789 (17)	−4224 (29)	2463 (18)
C(25)	−1948 (16)	1411 (23)	−1370 (18)	C(65)	2355 (19)	−3936 (29)	2557 (21)
C(26)	−113 (16)	−2161 (23)	1575 (19)	C(66)	2826 (15)	−6402 (20)	−306 (20)
C(27)	142 (20)	−2912 (35)	1522 (28)	C(67)	3048 (20)	−7154 (28)	49 (27)
O(21)	−1288 (6)	452 (9)	−477 (7)	O(61)	2553 (7)	−4491 (13)	1711 (10)
O(22)	−630 (6)	860 (8)	610 (7)	O(62)	3419 (6)	−4593 (10)	1961 (8)
O(23)	−241 (6)	−611 (10)	1467 (7)	O(63)	3454 (6)	−5308 (8)	809 (9)
O(24)	−315 (7)	−1725 (10)	872 (9)	O(64)	2635 (7)	−5865 (10)	75 (9)
C(31)	2024 (7)	492 (12)	725 (9)	C(71)	3866 (7)	−34 (10)	223 (10)
C(32)	1757 (8)	880 (13)	2 (11)	C(72)	3563 (8)	418 (12)	479 (12)
C(33)	2283 (10)	−287 (14)	809 (12)	C(73)	3566 (9)	−191 (12)	−545 (12)
C(34)	1317 (15)	2061 (18)	−666 (17)	C(74)	3624 (18)	1198 (21)	1363 (23)
C(35)	1304 (23)	2968 (26)	−391 (22)	C(75)	4078 (19)	1191 (28)	2125 (23)
C(36)	2888 (15)	−1346 (22)	1514 (17)	C(76)	3665 (11)	−701 (20)	−1479 (13)
C(37)	3438 (20)	−1234 (29)	2067 (25)	C(77)	3532 (16)	−1546 (23)	−1535 (18)
O(31)	1633 (7)	1659 (10)	28 (8)	O(71)	3911 (7)	833 (11)	1057 (9)
O(32)	1650 (7)	523 (11)	−525 (8)	O(72)	3073 (7)	368 (9)	246 (9)
O(33)	2110 (7)	−819 (10)	330 (9)	O(73)	3055 (6)	−218 (9)	−983 (7)
O(34)	2725 (6)	−404 (9)	1432 (8)	O(74)	3915 (6)	−363 (10)	−740 (8)
C(41)	2012 (7)	545 (11)	2004 (8)	C(81)	4794 (7)	−902 (12)	1381 (10)
C(42)	1870 (8)	1411 (12)	1988 (9)	C(82)	5115 (8)	−1070 (13)	1041 (12)
C(43)	1947 (7)	7 (11)	2495 (8)	C(83)	5007 (8)	−1382 (14)	2033 (12)
C(44)	2064 (13)	2756 (16)	1787 (16)	C(84)	5454 (13)	−490 (24)	354 (18)
C(45)	2467 (20)	3173 (26)	1708 (27)	C(85)	5997 (16)	−130 (32)	750 (27)
C(46)	2154 (13)	−1294 (15)	3011 (13)	C(86)	5057 (11)	−1421 (19)	3114 (13)
C(47)	1659 (14)	−1811 (22)	2733 (17)	C(87)	5089 (15)	−761 (26)	3595 (16)
O(41)	2191 (6)	1890 (9)	1880 (8)	O(81)	5202 (8)	−350 (11)	788 (10)
O(42)	1489 (6)	1704 (9)	2045 (8)	O(82)	5235 (7)	−1722 (11)	908 (9)
O(43)	1728 (6)	208 (9)	2822 (7)	O(83)	5209 (6)	−2075 (10)	2146 (8)
O(44)	2144 (6)	−743 (9)	2509 (7)	O(84)	4895 (6)	−988 (10)	2448 (8)
Pd(3)	2565 (1)	−3716 (1)	312 (1)	K(1)	2233 (2)	−624 (4)	−771 (3)
Pd(4)	3975 (1)	−1199 (1)	668 (1)	K(2)	4262 (2)	−4392 (3)	1784 (3)
O(1)	2581 (5)	−2576 (7)	−135 (6)	Na(1)	740 (3)	−1173 (4)	−1304 (4)
O(2)	3154 (4)	−1582 (7)	−22 (6)	Na(2)	321 (3)	1735 (4)	1407 (5)
(b) Positional Parameters ($\times 10^3$) for Water Oxygen Atoms in the Crystal							
O(101)	146 (1)	−178 (1)	−171 (1)	O(103)	−18 (1)	169 (2)	248 (1)
O(102)	57 (1)	50 (1)	246 (1)	O(104)	527 (1)	308 (2)	507 (2)

[a] Estimated standard deviations are given in parentheses in this and all subsequent tables.

converged at final $R = 0.056$ and $R_w = 0.076$. The final difference Fourier synthesis showed no significant residual features other than small ones near the Na, Cl, and Pd sites, giving no clear indications on the positions of H atoms. No attempt was made to locate the H atoms.

The atomic scattering factors and anomalous dispersion corrections for Pd, K^+, Cl^-, Na^+, O, and C_{cov} were taken from ref 6. Those for H atoms were adopted from the table of Stewart et al.[7] All calculations were carried out on a FACOM M-200 computer in the Computer Center of Kyushu University with the locally modified versions of the UNICS III system of crystallographic programs.[8] The drawings were made by the use of the ORTEP program.[9] The final atomic parameters are listed in Table II.

Results and Discussion

Preparation of the Pd(II) Complexes. Prepraration of the (diethyl malonato-*C*)palladium(II) compounds was accomplished by mixing diethyl malonate, $Na_2[PdCl_4]$, and KOH in H_2O. The yields were poor but pure samples of two Pd(II) compounds, **1** and **2**, were obtained. The similarity of IR and

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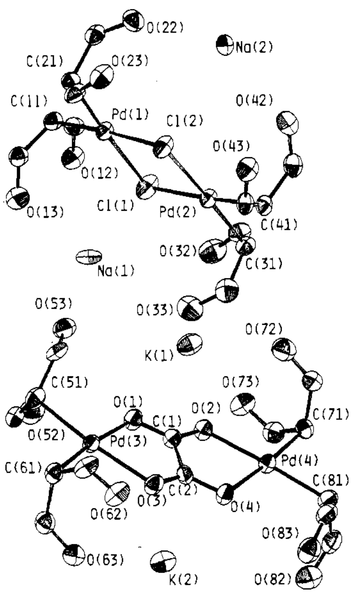

Figure 1. Molecular structure of **2**, showing the atomic numbering. Ethoxy groups have been omitted for clarity. Atoms are represented by 25% thermal ellipsoids.

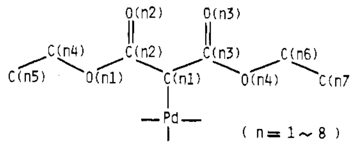

Figure 2. Atomic numbering of diethyl malonate ligands.

^{1}H NMR spectra between **1** and **2** indicated that both components consisted of a common structure unit. From the reaction mixture a considerable amount of diethyl malonate was recovered unchanged. Residual material exhibited IR absorption peaks at around 1700 cm^{-1} due to the malonic ester and gave metallic Pd(0) on treatment with $NaBH_4$. These facts suggested that some other Pd(II) compounds with diethyl malonate might be prepared as a mixture that was not extracted in organic solvents; we did not attempt to identify these products.

Analogously to the case for Pd(II) compounds of acetylacetone and ethyl acetoacetate, malonic esters are commonly considered to give central-carbon-bonded Pd(II) compounds.[1,2] The first crystallized compound (**1**) from CH_2Cl_2 extraction of the reaction mixture was reasonably assumed to be disodium [bis(μ-chloro)bis(bis(diethyl malonato-*C*)dipalladate(II))], $Na_2[(Pd(C_7H_{11}O_4)_2)_2Cl_2]$, by spectral and microanalytical data and reaction conditions for the synthesis of the complex as described later. The second component (**2**) was a minor product and exhibited a characteristic IR band at 1618 cm^{-1}, which was suggestive of the presence of a carbonyl oxygen–metal ion interaction. In order to obtain structural information on this compound, single-crystal X-ray analysis was undertaken.

Molecular Structure of 2. A view of the complex molecule(s) with partial atomic numbering is shown in Figure 1, in which all the ethoxy groups are omitted for clarity. The atoms in diethyl malonate moieties are numbered as shown in Figure 2. Water molecules in the crystal are also omitted in the drawing since they are present as lattice water. The crystal is found to contain two independent dimers that include two symmetric bridges involving Cl atoms and two symmetric ones involving an oxalate group between the Pd atoms. Stereoscopic views of the dimeric complex dianions with their countercations (K$^+$ and Na$^+$) are given as supplementary material (Figures 3 and 4). Each midpoint of the Pd atoms in each dimer is the pseudo inversion center, and these dimers are arranged with a pseudosymmetry of *C*2/*c*. In contrast, the Na atoms as well as some of the terminal C atoms of the malonate ligands are clearly out of the symmetry to impose a space group *Cc* on the crystal. From the standpoint of the crystal-packing arrangement, the two different dimers are connected by electrostatic interactions with the K$^+$ and Na$^+$ ions.

Table III. Selected Bond Lengths (Å) and Angles (deg)

(a) Chloro-Bridged Unit			
Pd(1)–Cl(1)	2.386 (8)	Pd(2)–Cl(1)	2.362 (5)
Pd(1)–Cl(2)	2.399 (4)	Pd(2)–Cl(2)	2.385 (7)
Pd(1)–C(11)	2.10 (1)	Pd(2)–C(31)	2.11 (2)
Pd(1)–C(21)	2.06 (3)	Pd(2)–C(41)	2.12 (1)
Cl(1)–Pd(1)–Cl(2)	84.7 (2)	Cl(1)–Pd(2)–Cl(2)	85.6 (2)
Cl(1)–Pd(1)–C(11)	92.7 (7)	Cl(1)–Pd(2)–C(31)	93.9 (5)
Cl(1)–Pd(1)–C(21)	177.6 (5)	Cl(1)–Pd(2)–C(41)	177.2 (5)
Cl(2)–Pd(1)–C(11)	176.8 (6)	Cl(2)–Pd(2)–C(31)	177.8 (6)
Cl(2)–Pd(1)–C(21)	93.6 (5)	Cl(2)–Pd(2)–C(41)	93.9 (6)
C(11)–Pd(1)–C(21)	89.1 (8)	C(31)–Pd(2)–C(41)	86.8 (8)
Pd(1)–Cl(1)–Pd(2)	95.2 (3)	Pd(1)–Cl(2)–Pd(2)	94.3 (2)
Pd(1)–C(11)–C(12)	109 (1)	Pd(2)–C(31)–C(32)	110 (1)
Pd(1)–C(11)–C(13)	102 (1)	Pd(2)–C(31)–C(33)	102 (2)
Pd(1)–C(21)–C(22)	103 (1)	Pd(2)–C(41)–C(42)	100 (1)
Pd(1)–C(21)–C(23)	110 (1)	Pd(2)–C(41)–C(43)	110 (1)
(b) Oxalato-Bridged Unit			
Pd(3)–O(1)	2.12 (1)	Pd(4)–O(2)	2.09 (1)
Pd(3)–O(3)	2.14 (1)	Pd(4)–O(4)	2.13 (1)
Pd(3)–C(51)	2.07 (2)	Pd(4)–C(71)	2.08 (2)
Pd(3)–C(61)	2.05 (2)	Pd(4)–C(81)	2.05 (2)
O(1)–C(1)	1.22 (2)	O(2)–C(1)	1.25 (2)
O(3)–C(2)	1.27 (2)	O(4)–C(2)	1.25 (2)
C(1)–C(2)	1.54 (2)		
O(1)–Pd(3)–O(3)	78.3 (4)	O(2)–Pd(4)–O(4)	79.9 (4)
O(1)–Pd(3)–C(51)	95.9 (7)	O(2)–Pd(4)–C(71)	95.2 (5)
O(1)–Pd(3)–C(61)	173.9 (7)	O(2)–Pd(4)–C(81)	176.0 (7)
O(3)–Pd(3)–C(51)	173.5 (7)	O(4)–Pd(4)–C(71)	174.8 (6)
O(3)–Pd(3)–C(61)	96.2 (6)	O(4)–Pd(4)–C(81)	96.0 (6)
C(51)–Pd(3)–C(61)	89.7 (8)	C(71)–Pd(4)–C(81)	88.8 (7)
Pd(3)–O(1)–C(1)	115 (1)	Pd(4)–O(2)–C(1)	113.7 (9)
Pd(3)–O(3)–C(2)	111.8 (9)	Pd(4)–O(4)–C(2)	110.0 (9)
Pd(3)–C(51)–C(52)	103 (2)	Pd(4)–C(71)–C(72)	103 (2)
Pd(3)–C(51)–C(53)	104 (1)	Pd(4)–C(71)–C(73)	105 (1)
Pd(3)–C(61)–C(62)	103 (1)	Pd(4)–C(81)–C(82)	107 (1)
Pd(3)–C(61)–C(63)	104 (2)	Pd(4)–C(81)–C(83)	110 (1)
O(1)–C(1)–O(2)	127 (1)	O(2)–C(1)–C(2)	116 (1)
O(1)–C(1)–C(2)	117 (2)	O(3)–C(2)–O(4)	122 (1)
O(3)–C(2)–C(1)	118 (1)	O(4)–C(2)–C(1)	120 (2)

Table III shows the important bond lengths and angles. The Pd atoms exhibit square-planar coordination. Each dihedral angle between two coordination planes in each dimer is small (supplementary material, Table VI); thus, the best-plane calculation indicates that the eight atoms C(11), C(21), Pd(1), Cl(1), Cl(2), Pd(2), C(31), and C(41) form an approximate plane with the maximum deviation of 0.153 Å (Cl(2)); while the twelve atoms C(51), C(61), Pd(3), O(1), O(3), C(1), C(2), O(2), O(4), Pd(4), C(71), and C(81) are nearly coplanar as shown by the maximum deviation of 0.189 Å (C(51)). These two "planes" make an angle of 62.0°. The Pd–C and Pd–Cl bond lengths are in good agreement with those of Pd(II)–C(sp^3) bond[1e–h,2b,c] and bis(μ-chloro) bridging systems[10] in analogous Pd(II) compounds, respectively. The bond angles made by *cis*-bis(malonato) coordination (C–Pd–C) are close to or slightly smaller than the expected square-planar value (90°). The oxalate group is essentially planar, exhibiting the maximum deviation of 0.013 Å (O(1)), and it completes two condensed five-membered rings with the Pd atoms, which are displaced 0.027 and 0.190 Å from the "plane". The Pd–O

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Table IV. Distances (Å) between Alkali-Metal Atoms and Carbonyl Oxygen Atoms[a] or Chlorine Atoms

Na(1)–O(12)	2.91 (2)	Na(2)–O(22)	2.71 (1)
Na(1)–O(13)	2.98 (2)	Na(2)–O(42)	2.82 (2)
Na(1)–O(53)	2.70 (1)	Na(2)–O(82)^{ii}	2.70 (2)
		Na(2)–O(83)^{ii}	2.67 (2)
Na(1)–Cl(1)	3.03 (1)	Na(2)–Cl(2)	3.36 (1)
K(1)–O(2)	2.72 (1)	K(2)–O(3)	2.65 (1)
K(1)–O(32)	2.73 (2)	K(2)–O(12)^{iii}	2.76 (2)
K(1)–O(33)	2.70 (2)	K(2)–O(22)^{ii}	2.85 (2)
K(1)–O(43)^{i}	2.78 (2)	K(2)–O(23)^{ii}	2.73 (2)
K(1)–O(72)	2.77 (1)	K(2)–O(62)	2.64 (2)
K(1)–O(73)	2.70 (2)	K(2)–O(63)	2.63 (1)

[a] Symmetry codes: no superscript, x, y, z; (i) $x, -y, 0.5 + z$; (ii) $0.5 + x, 0.5 + y, z$; (iii) $0.5 + x, 0.5 - y, 0.5 + z$.

bond lengths range from Pd(4)–O(2) = 2.087 (9) Å to Pd(3)–O(3) = 2.140 (12) Å, being marginally longer than those (1.98 (2) and 2.02 (2) Å) of $K_2[Pd(C_2O_4)_2]$.[11] The C–O bond lengths (minimum 1.22 (2) Å, maximum 1.27 (2) Å) of the oxalate group are regarded to be equal within the limit of the significance. This equivalence is supported by the lack of correlation between the C–O and Pd–O bond lengths, because a set of long and short C–O bonds in a metal carboxylate is generally attributed to the partial localization of negative charge on one oxygen atom, affecting the metal–oxygen bond length. The oxalate C–O bond lengths are in good agreement with those (1.236 (7)–1.257 (8) Å) of Cu,[12a] Ni,[12b,c] and Ti[12d] complexes with symmetric μ-oxalato bridges. The bond angles within the oxalate group are normal as compared with those of the analogous μ-oxalato metal complexes[12] described above and do not show any asymmetry. From these results the oxalate group is assigned to be of approximately D_{2h} symmetry. There are no unusual bond distances or angles within the remainder of the structure.

Molecular Packing of 2 and Alkali Metal Ion Effects. Particular interest centers on the packing mode of the two different molecules in **2**. All the β-dicarbonyl moieties of the ligands take a syn conformation (U shape), which is ascribed to the result of electrostatic interactions between the oxygen atoms and the alkali-metal ions. In other words, two kinds of cavities are formed by the U-shaped β-dicarbonyl groups and the Na^+ and K^+ ion sites in the fitting oxygen environments, connecting the two different dimers in such a way as to form pseudopolymeric structure. The K atoms are surrounded by six carbonyl oxygen atoms with maximum and minimum bond lengths of 2.85 (2) and 2.63 (1) Å; the Na atoms are surrounded by three or four carbonyl oxygens with maximum and minimum bond lengths of 2.98 (2) and 2.67 (2) Å (Table IV). The atom O(52) is the only carbonyl oxygen not used in close interaction with the cations. The smaller size of an alkali-metal ion is generally responsible for the shorter distances of alkali-metal–oxygen bonds. The assignment of the K and Na atoms in the crystal was carried out carefully by the thermal parameters in the least-squares refinement of the structure. We do not know the exact reason of the selection of alkali-metal ions included in the crystal, but it seems likely that the Cl^- ions play an important role in attracting closely the smaller Na^+ ions; the distances of Na(1)–Cl(1) and Na(2)–Cl(2) are 3.03 (1) and 3.36 (1) Å, respectively.

As was expected from the structural information, NaOH was a better base for the preparation of **1** than KOH. The reaction of $K_2[PdCl_4]$ and diethyl malonate with KOH gave a low isolated yield of an analogous potassium salt of the Pd complex **3**. The (μ-oxalato)palladium(II) complex could not be isolated under these experimental conditions. When $Li_2[PdCl_4]$ was used in place of the Na^+ or K^+ salt, yields of the Pd(II) compound(s) extracted in CH_2Cl_2 were increased. It is worthwhile to note that a fraction of the products, when $Li_2[PdCl_4]$ and KOH were employed, exhibited an IR peak at 1680 cm^{-1} in addition to a peak at around 1710 cm^{-1} due to the ester carbonyl groups. An unambiguous assignment for **2** can only be made by the X-ray structure investigation. So far, the Pd(II) compounds from $Li_2[PdCl_4]$ have resisted attempts to grow single crystals suitable for X-ray analyses so that we did not pursue the new characteristic band further and did not identify the complex. In every case where the quantity of an alkali hydroxide was less than 2 equiv/Pd ion, the yields of the Pd(II) compounds decreased extremely and the diethyl malonate was recovered as an oil.

Spectra. Since the molecular structure of **2** has been established, it is possible to interpret the spectral data. The characteristic IR band of **2** at 1618 cm^{-1} is assigned to the vibration of the B_{2u} mode of the oxalate group (D_{2h}), whose value is significantly smaller than those of μ-oxalato ligands in $[(Cu(NH_3)_2)_2(C_2O_4)_2]$ (1625 cm^{-1})[12a] and $[(Ni(C_2H_8N_2)_2)_2(C_2O_4)](NO_3)_2$ (1645 cm^{-1})[13] as well as that of a free oxalate ion (1627 cm^{-1});[14] in such a case the oxalate group has been assigned to be of D_{2h} symmetry. Strong absorption bands overlapping at around 1710 cm^{-1} are assigned to the ν(CO) vibrational mode of the ester groups. Low-wavenumber shifts in ν(CO) of ca. 30–40 cm^{-1} for **2**, relative to the value found in the free ligand, are consistent with weaker C=O bond character resulting from the Pd—C bond formation and the interaction with the alkali-metal ions in part. These shifts are smaller than those (ca. 65 cm^{-1}) found in a related system with a pyridyl-substituted diethyl malonate as a ligand,[2b,c] in which the β-dicarbonyl moieties exhibit an anti conformation (sickle shape), contrary to the case in our system. The IR spectral pattern of **1** is very similar to that of **2** except for a little difference at around 1410 cm^{-1} and the absence of the characteristic peak due to oxalate carbonyl groups. Moreover, all the IR peaks of **1** appear in the IR spectrum of **2**. The peak of maximum of carbonyl stretching bands due to the ester groups appears at 1703 cm^{-1}, which is a slightly lower value than that of **2**.

The pure crystals studied in this report are hardly soluble in pure $CHCl_3$ and CH_2Cl_2 but are soluble in those solvents containing drops of water, whose oxygen atoms probably coordinate to the alkali-metal ions to break the pseudopolymeric structure of the crystals. ^1H NMR spectra of **1** and **2** were measured in $CDCl_3$ mixed with a drop of water. The multiple NMR peaks of **2** are easily rationalized by two different chemical environments for the diethyl malonates due to two different bridging systems. The NMR spectrum of **1** shows a simple absorption pattern attributable to the equivalent diethyl malonate moieties. Thus, it exhibits a triplet at δ 1.25 and a quartet at δ 4.20 due to the ethyl protons. The peak positions of the methine protons were not discernible because of low solubility of the compounds in common organic solvents.

Reactions. The preparation of the crystals **2** includes a route to obtain the oxalato ligand from diethyl malonate. As in so many reactions of transition-metal organometallic compounds, it would be most obvious that carbon atoms coordinated to a metal ion would react with nucleophiles. Thus, the Pd(II) ion accepts a total of two electrons and is converted into Pd(0) and the coordinated C atom undergoes OH^- attack simultaneously followed by oxidation to give diethyl ketomalonate,

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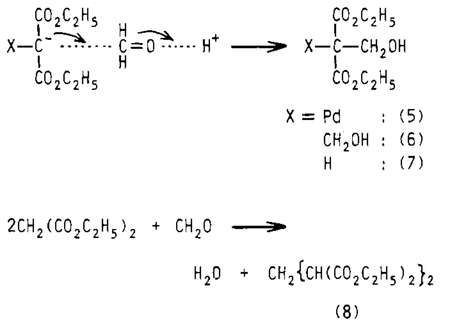
Scheme I



which would give the oxalate ligand under basic conditions via hydrolysis, loss of CO_2 (as carbonate), and autoxidation.

In order to examine the reactivity of diethyl malonate coordinated to a Pd(II) ion via the central carbon atom, **1** and **4** were treated with methanol to give a moderate isolated yield (85%) of diethyl bis(hydroxymethyl)malonate (**6**) along with almost theoretical yields of Pd(0) and NaCl. A reasonable mechanism for the reaction is outlined in Scheme I. In the reaction mixture formaldehyde is produced by a Pd-induced oxidation of methanol. By reaction of diethyl malonate and formaldehyde two different products are obtainable. With a 1:2 ratio of the aldehyde to the ester and diethylamine as catalyst, the product is tetraethyl propane-1,1,3,3-tetracarboxylate (**8**).[15] With a 2:1 ratio and potassium bicarbonate as catalyst, the product is **6**.[16] Compared with those reactions, the reaction in this study was conducted under mild conditions. A more than 50% yield of **6** suggests that autoxidation of methanol catalyzed by Pd(0) metal yields enough formaldehyde in the reaction mixture. Diethyl 2-(hydroxymethyl)malonate (**7**) was not obtained from this reaction.

In contrast to our study a reaction of palladium bis(hexafluoroacetylacetonate), $[Pd(F_6acac)_2]$, with methanol has been reported to produce an alkoxide–Pd(II) complex, $[Pd_2(\mu\text{-}CH_3O)_2(F_6acac)_2]$,[17] in which the oxygen atoms of the β-diketone anions are coordinated to the Pd(II) ions. A similar Pd(II) complex with methoxy bridges has been isolated as an intermediate in the formation of bis(2,2,6,6-tetramethylheptane-3,5-dionato)palladium(II) in methanol.[18] From these results, the formation of **6** in this study is ascribed to the active Pd–C bonds in the diethyl malonato complexes.

Conclusions

A Pd–malonate-*C* ester complex was suggested to be a very reactive species, although reactions of diethyl malonate with a chloropalladate(II) ion in an alkaline solution was not useful for preparative methods of such a complex because yields were low and mixtures of two or more products were obtained. Such reactions were significant, however, in indicating that products of such a simple organopalladation could be controlled by alkali-metal ions coexisting in the reaction mixture. Thus, studies are currently under way for a selective incorporation of metal ions into organic compound possessing coordination sites whose conformation is controlled by a Pd(II) ion and for an exploration of the synthetic utility of some Pd–malonate-*C* derivatives.

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Registry No. **1**, 88610-53-1; **2**, 88610-55-3; **3**, 88610-56-4; **4**, 88610-57-5.

Supplementary Material Available: Stereoscopic views of the dimeric complexes (Figures 3 and 4) and tables of bond lengths and angles, selected least-squares planes, thermal parameters, and observed and calculated structure factors (Tables V–VIII) (33 pages). Ordering information is given on any current masthead page.

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