framework of the polyhedral skeletal electron pair theory.[19] According to this theory the Os_4S_2 core of the compounds would have the form of a nido pentagonal bipyramid. This polyhedron would possess eight cluster valence orbitals into which 16 electrons could be placed. In fact, according to this theory compounds 1 and 3 do contain exactly 16 cluster valence electrons. Although the PSEP theory thus predicts a stable structure with five metal–metal bonds, it does not indicate where selective bond lengthening should occur. As indicated above, this may be a natural consequence of further considerations that include the effects of the ligand dispositions.

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Registry No. 1, 82093-50-3; **2a**, 91281-77-5; **2b**, 91281-78-6; **3a**, 91281-79-7; **3b**, 91281-80-0.

Supplementary Material Available: Tables of structure factor amplitudes for all four structural analyses are available (47 pages). Ordering information is given on any current masthead page.

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Carbon–Palladium(II) Complexes of Dialkyl Malonates: Synthesis, ^{1}H and ^{13}C NMR Spectroscopy, and Single-Crystal Structure Analyses[1,2]

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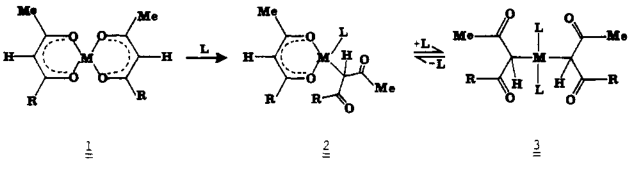
Novel square-planar palladium(II) complexes [PdL(dialkyl malonato)$_2$] having Pd–C(malonato) σ bonds were prepared by the intermolecular exchange of chloro ligands with dialkyl malonate. The bidentate ligand (L) is 2,2′-bipyridine, 1,10-phenanthroline, 2,2-bis(2-pyridyl)-1,3-dioxolane, di-2-pyridylmethane, or 1,2-bis(2-pyridyl)ethane, whereas dialkyl malonate behaves as a unidentate ligand coordinating through the central carbon atom. Treatment of bis metalated complexes with 1,3-dibromopropane under basic conditions did not result in the expected cyclization via C–C bond formation, but rather one of the malonates is replaced by bromide. The ^{1}H and ^{13}C NMR and IR spectra, novel chemistry, and structural aspects of ring size in the organometallics are discussed. Single-crystal X-ray structure analyses were conducted on bis(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II), $PdC_{27}H_{34}N_2O_{10}$, and bromo(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II), $PdBrC_{20}H_{23}N_2O_6$. Both the crystals are monoclinic and crystallize in space group $P2_1/c$. The cell constants for the former are a = 9.837 (2) Å, b = 21.647 (4) Å, c = 14.089 (2) Å, β = 95.45 (1)°, and Z = 4. Bond lengths involving palladium average 2.110 (3) Å for Pd–N and 2.095 (4) Å for Pd–C bonds. For the latter compound the cell constants are a = 8.982 (1) Å, b = 14.318 (3) Å, c = 17.368 (4) Å, β = 101.71 (2)°, and Z = 4. Bond lengths in the coordination sphere average 2.086 (4) Å for Pd–N, 2.107 (4) Å for Pd–C, and 2.404 (1) Å for Pd–Br bonds. All the pyridine rings are planar and produce an intramolecular dihedral angle of 72.6° in former and 67.3° in the latter. The palladium coordination is slightly tetrahedrally distorted from square-planar geometry.

Introduction

Usually β-dicarbonyl ligands, e.g., acetylacetonate anion, O,O-coordinate a metal ion to form a six-membered chelate ring (1). Rearrangement of the bidentate O ligands to an unidentate central carbon atom bond with Pd(II) and Pt(II) has been reported by Okeya et al.[3] and others.[4,5] Thus, the bis(acetylacetonate)palladium(II) complex on treatment with Lewis bases such as pyridine, triphenylphosphine, or diethylamine afford the C–Pd complexes 2 and 3. C-Metalated complexes of ethyl acetoacetate have been obtained in a similar manner, via the rearrangement of the corresponding O,O′-bonded chelate complexes.[3-5]

Scheme I



R = Me or OEt; M = Pd(II) or Pt(II); L = Py, PPh_3, HNR_2 etc.

Since dialkyl malonates do not exist in appreciable amounts as the enol tautomer[6] and due to the limited number of established examples of their C-bonded organometallics, we synthesized a series of unidentate (malonate-*C*)palladium(II) complexes.[7,8] We herein expand

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our original communication and describe a convenient one-step C-palladation with malonates. 2,2′-Bipyridine (4), 1,10-phenanthroline (5), 2,2-bis(2-pyridyl)-1,3-dioxolane (6), di-2-pyridylmethane (8), and 1,2-bis(2-pyridyl)ethane (7) have been utilized as the bidentate ligand, which can form either five-, six-, and seven-membered chelate rings with palladium(II). The effect of ring size on C–Pd bond formation has been evaluated. Single-crystal X-ray analyses of two of these square-planar palladium(II) complexes are also reported. Complexes 17 and 21 did not give suitable crystals for X-ray analysis; however, the corresponding ethyl ester complexes 18 and 23 afforded excellent single crystals.

Experimental Section

A. General Comments. All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on an IBM Bruker NR/80 spectrometer using $CDCl_3$ as solvent, with Me_4Si, as the internal standard. Mass spectral (MS) data (70 eV) were determined by Mr. D. Patterson on a Hewlett-Packard HP 5985 GC mass spectrometer and reported (assignment, relative intensity). For preparative thick-layer chromatography (ThLC), 2-mm silica gel PF-254-366 plates were used. IR spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer. X-ray diffraction data were collected with graphite-monochromatized Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer. Elemental analyses were obtained commercially.

B. Ligands. 2,2′-Bipyridine (4) and 1,10-phenanthroline (5) were obtained from Aldrich. 2,2-Bis(2-pyridyl)-1,3-dioxolane (6) was prepared by a known procedure.[9] 1,2-Bis(2-pyridyl)ethane (7) was prepared (76%) by the hydrogenation of the corresponding ethene[10] in absolute ethanol at 25 °C over 5% Pd/C catalyst: colorless oil; ^{1}H NMR δ 3.23 (s, CH_2, 4 H), 6.96–7.16 (m, 3,5-pyH, 4 H), 7.52 (dt, 4-pyH, J = 7.5, 1.8 Hz, 2 H), 8.51 (ddd, 6-pyH, J = 5.7, 1.8, 0.8 Hz, 2 H); ^{13}C NMR δ 37.6 (CH_2), 120.9 (C3), 122.8 (C5), 136.2 (C4), 149.0 (C6), 160.9 (C2); MS, m/e 184 (M^+, 26), 106 (M^+ − py, 100); IR (neat) 1584, 1562, 1470, 1430 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.56; N, 15.20. Found: C, 78.14; H, 6.71; N, 15.11.

Di-2-pyridylmethane (8) was prepared (80%) by Wolff–Kishner reduction of di-2-pyridyl ketone (obtained from Aldrich) with hydrazine and base in a bomb at 150 °C:[11] colorless oil; 80%; ^{1}H NMR δ 4.33 (s, CH_2, 2 H), 7.06 (2dd, 5-pyH, $J_{5,6}$ = 4.8, $J_{5,4}$ = 7.4, $J_{5,3}$ = 1.4 Hz, 2 H), 7.22 (dd, 3-pyH, $J_{3,4}$ = 7.7, $J_{3,5}$ = 1.4, $J_{3,6}$ 0.9 Hz, 2 H), 7.54 (dt, 4-pyH, $J_{4,3}$ = 7.7, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.8 Hz, 2 H), 8.52 (ddd, 6-pyH, $J_{6,5}$ = 4.8, $J_{6,4}$ = 1.8, $J_{6,3}$ = 0.9 Hz, 2 H); ^{13}C NMR δ 46.5 (CH_2), 120.7 (C3), 122.8 (C5), 135.8 (C4), 148.8 (C6), 158.9 (C2); MS, m/e 170 (M^+, 22), 169 (M^+ − 1, 100); IR (neat) 1583, 1562, 1470, 1430 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.56; H, 6.02; N, 16.38.

C. Dichloropalladium(II) complexes reported herein were prepared by the following general procedure. To a stirred solution of the appropriate bidentate ligand (1 mmol) in MeCN (20 mL) was added $PdCl_2$ (1 mmol) in warm MeCN (30 mL), followed by stirring at 25 °C for 2 h. The yellow crystalline precipitate was filtered and washed with MeCN to afford (90–95%) the desired complex. With ligand 6, the solution was concentrated to 10 mL before filtration, since the corresponding palladium complex is MeCN soluble. Complete details of characterization of these complexes are **dichloro(2,2′-bipyridine)palladium(II) (9)**,[8,12-14] **dichloro(1,10-phenanthroline)palladium(II) (10)**,[8,12] and **dichloro[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (11)**.[15]

Dibromo[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (12) was prepared from $PdBr_2$: orange-red crystals; mp >250 °C; ^{1}H NMR δ 4.34–4.45 (m, CH_2, 4 H), 7.31 (2dd, 5-pyH, $J_{5,4}$ = 7.2, $J_{5,6}$ = 5.5, $J_{5,3}$ = 1.8 Hz, 2 H), 7.84–7.94 (m, 3,4-pyH, 4 H), 9.42 (ddd, 6-pyH, $J_{6,5}$ = 5.5, $J_{6,4}$ = 1.8, $J_{6,3}$ = 0.9 Hz, 2 H); IR (CsI) 1590, 1455, 1435, 1290, 1270, 1215 cm^{-1}. Anal. Calcd for $C_{13}H_{12}N_2O_2PdBr_2$: C, 31.58; H, 2.45; N, 5.67. Found: C, 31.42; H, 2.56; N, 5.61.

Dichloro[1,2-bis(2-pyridyl)ethane]palladium(II) (13): yellow microcrystals; mp >250 °C; ^{1}H NMR δ 3.48 (m, CH_2, 4 H), 7.10–7.40 (m, 3,5-pyH, 4 H), 7.68 (2dd, 4-pyH, J = 7.5, 1.8 Hz, 2 H), 9.04 (dd, 6-pyH, J = 5.6, 1.8 Hz, 2 H); IR (CsI) 1590, 1470, 1427 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2PdCl_2$: C, 39.87; H, 3.35; N, 7.75. Found: C. 39.70; H, 3.40; N, 7.64.

Dichloro(di-2-pyridylmethane)palladium(II) (14): yellow crystals; mp >250 °C; IR (CsI) 1590, 1460, 1430 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2PdCl_2$: C, 38.02; H, 2.90; N, 8.06. Found: C, 37.92; H, 3.06; N, 7.92.

D. General Preparation of (Malonate-*C*)palladium(II) Complexes. A mixture of dialkyl malonate (5 mmol), the dichloropalladium(II) complex (**9**, **10**, **11**, **13**, or **14**) (1 mmol) and anhydrous K_2CO_3 (500 mg) in anhydrous *N*,*N*-dimethylformamide (DMF, 40 mL)[16] was stirred at 25 °C for 20 h. With complex **11** purified MeCN[17] was used as the solvent. The solid was filtered and washed with CH_2Cl_2; the yellow solution was concentrated in vacuo and chromatographed (ThLC) on silica, eluting with $MeOH/CHCl_3$ (1:20) to afford the desired C–Pd complexes.

Bis(dimethyl malonato-*C*)(2,2′-bipyridine)palladium(II) (15) and bis(dimethyl malonato-*C*)(1,10-phenanthroline)palladium(II) (16) were characterized in our preliminary communication.[7]

Bis(dimethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (17) was prepared (85%) from **11**: yellow crystals; mp 76–77 °C and decomp at 108–110 °C; ^{1}H NMR δ 3.39, 3.69 (2s, CH_3, 6 H ea), 3.85 (s, CH, 2 H), 4.17–4.38 (m, CH_2, 4 H), 7.37 (2dd, 5-pyH, J = 7.5, 5.4 Hz, 2 H), 7.75–7.84 (m, 3,4-pyH, 4 H), 9.36 (ddd, 6-pyH, J = 5.4, 1.2 Hz, 2 H); ^{13}C NMR δ 50.2, 50.7 (CH_3), 52.3 (CH), 65.5, 66.5 (CH_2), 106.4 (C), 120.8 (C3), 124.9 (C5), 138.5 (C4), 154.0 (C6), 155.1 (C2), 174.7, 175.2 (C=O); IR (CsI) 1700 (C=O), 1590, 1460, 1430 cm^{-1}. Anal. Calcd for $C_{23}H_{26}N_2O_{10}Pd$: C, 46.28; H, 4.39; N, 4.69. Found: C, 46.18; H, 4.56; N, 4.51.

Bis(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (18) was generated (88%) from **11**: yellow crystals; mp 171–172 °C dec; ^{1}H NMR δ 1.08, 1.31 (t, CH_3, J = 7.1 Hz, 6 H ea), 3.67–3.98 (m, CH_2CH_2, 4 H), 3.87 (s, CH, 2 H), 4.05–4.43 [m (8 lines), CH_2CH_3, 8 H], 7.35 (2dd, 5-pyH, J = 7.3, 5.3 Hz, 2 H), 7.74–7.82 (m, 3,4-pyH, 4 H), 9.27 (ddd, 6-pyH, J = 5.3, 1.1 Hz, 2 H); IR (CsI) 1690 (C=O), 1585, 1430, 1365, 1335 cm^{-1}. Anal. Calcd for $C_{27}H_{34}N_2O_{10}Pd$: C, 49.66; H, 5.25; N, 4.29. Found: C, 49.61; H, 5.11; N, 4.14.

Bis(dimethyl malonato-*C*)[1,2-bis(2-pyridyl)ethane]palladium(II) (19) was prepared (76%) from **13**: yellow microcrystals; mp 69–70 °C; ^{1}H NMR δ 3.37, 3.63 (s, CH_3, 6 H ea), 3.67 (s, CH, 2 H), 4.49–4.79 (m, CH_2, 4 H), 7.02–7.21 (m, 3,5-pyH, 4 H), 7.57 (2dd, 4-pyH, J = 7.3, 1.6 Hz, 2 H), 8.72 (ddd, 6-pyH, J = 4.9, 1.6, 0.8 Hz, 2 H); ^{13}C NMR δ 33.1 (CH_2), 49.9, 50.2 (CH_3), 52.0 (CH), 122.5 (C3), 125.2 (C5), 138.0 (C4), 151.1 (C6), 159.2 (C2), 174.1, 174.9 (C=O); IR (CsI) 1710 (C=O), 1600, 1475, 1430 cm^{-1}. Anal. Calcd for $C_{22}H_{26}N_2O_8Pd$: C, 47.80; H, 4.74; N, 5.07. Found: C, 47.60; H, 4.82; N, 4.99.

Bis(dimethyl malonato-*C*)(di-2-pyridylmethane)palladium(II) (20) was obtained (74%) from **14**: mp 84–86 °C; ^{1}H NMR δ 3.31, 3.69 (s, CH_3, 6 H ea), 3.75 (s, CH, 2 H), 4.39, 5.15 (d, CH_2, J = 12.2 Hz, 1 H ea), 7.31 (2dd, 5-pyH, J = 7.5, 5.4, 1.7 Hz, 2 H), 7.51 (dd, 3-pyH, J = 7.5, 1.7 Hz, 2 H), 7.79 (dt, 4-pyH, J = 7.5, 1.7 Hz, 2 H), 9.11 (ddd, 6-pyH, J = 5.4, 1.7 Hz, 2 H); IR (CsI)

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Table I. Crystal Data and Data Collection Parameters

	18	23
formula	$PdC_{27}H_{34}N_2O_{10}$	$PdBrC_{20}H_{23}N_2O_6$
fw	653.0	573.7
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	9.837 (2)	8.982 (1)
b, Å	21.647 (4)	14.318 (3)
c, Å	14.089 (2)	17.368 (4)
β, deg	95.45 (1)	101.71 (2)
V, Å^3	2987 (2)	2187 (1)
d, g cm^{-3}	1.452	1.742
Z(formulas/cell)	4	4
$\mu_{MoK\alpha}$, cm^{-1}	6.7	26.8
min rel transmissn, %	85.16	89.26
crystal size, mm	0.20 × 0.44 × 0.48	0.32 × 0.44 × 0.52
θ limits, deg	$1 < \theta < 25$	$1 < \theta < 25$
scan rates, deg min^{-1}	0.61–10.0	0.59–10.0
precisn	$I \cong 25\sigma(I)$	$I \cong 25\sigma(I)$
max scan time, s	90	120
unique data	5257	3842
obsd data	3507	2783
variables	361	271
R	0.043	0.046
R_w	0.049	0.073
max residual, e Å^{-3}	0.53	0.85
color	yellow	orange
temp, °C	23 ± 1	25 ± 4

1708 (C=O), 1595, 1480, 1430 cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_2O_8Pd$: C, 46.81; H, 4.49; N, 5.20. Found: C, 46.62; H, 4.61; N, 5.11.

E. Monometalated Complexes. Bromo(dimethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (21). A mixture of 17 (1 mmol), 1,3-dibromopropane (1 mmol), and anhydrous K_2CO_3 (500 mg) in dry MeCN[17] (40 mL) was stirred at 25 °C for 20 h. The heterogeneous mixture was filtered; the yellow solution was concentrated in vacuo and chromatographed (ThLC) on silica, eluting with MeOH/$CHCl_3$ (1:20) to afford two fractions.

Complex 21: yellow crystals (slower moving fraction, R_f 0.20); 90%; mp 159–161 °C dec; ^1H NMR δ 3.27, 3.74 (s, CH_3, 3 H ea), 4.09–4.49 (m, CH_2, 4 H), 4.39 (s, CH, 1 H), 7.21–7.58 (m, 5,5′-pyH, 2 H), 7.81–7.91 (m, 3,3′,4,4′-pyH, 4 H), 9.19 (ddd, 6-pyH, J = 5.4, 1.2 Hz, 1 H), 9.75 (ddd, 6′-pyH, J = 5.5, 1.4, 0.9 Hz, 1 H); IR (CsI) 1695 (C=O), 1585, 1420, 1350 cm^{-1}. Anal. Calcd for $C_{18}H_{19}N_2O_6PdBr$: C, 39.62; H, 3.51; N, 5.13. Found: C, 39.60; H, 3.61; N, 5.01.

Dimethyl 2-(3-bromopropyl)malonate (22): colorless oil; (74%); ^1H NMR δ 1.78–2.09 (m, 1′,2′-CH_2, 4 H), 3.31–3.51 (m, 2-CH and 3′-CH_2, 3 H), 3.75 (s, CH_3, 6 H); MS, *m/e* 223 [$M^+(^{81}Br) - OCH_3$, 22], 221 [$M^+(^{79}Br) - OCH_3$, 20], 173 ($M^+ - Br$, 48), 145 ($M^+ - CH_2CH_2Br$, 100). Anal. Calcd for $C_8H_{13}O_4Br$: C, 37.97; H, 5.18. Found: C, 37.86; H, 5.26.

Bromo(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (23) was obtained (95%) from **18** in a similar manner: yellow microcrystals; mp 138–140 °C; ^1H NMR δ 0.95, 1.36 (t, CH_3, J = 7.1 Hz, 3 H ea), 3.48–3.88 (m, CH_2CH_2, 4 H), 4.02–4.58 (m, CH_2CH_3, 4 H), 4.17 (s, CH, 1 H), 7.15–7.54 (m, 5,5′-pyH, 2 H), 7.64–8.01 (m, 3,3′,4,4′-pyH, 4 H), 9.27 (ddd, 6-pyH, J = 5.3, 1.1 Hz, 1 H), 9.93 (ddd, 6′-pyH, J = 5.5, 1.4, 0.9 Hz, 1 H); IR (CsI) 1705 (C=O), 1590, 1460, 1430 cm^{-1}. Anal. Calcd for $C_{20}H_{23}N_2O_6PdBr$: C, 41.87; H, 4.04; N, 4.88. Found: C, 41.69; H, 4.21; N, 4.71.

F. X-ray Data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator by ω–2θ scans of variable speed designed to measure all significant reflections with equal precision. Crystal data and experimental details are listed in Table I. One quadrant of data collected for each compound within the specified angular limits. Data reduction included corrections for background, Lorentz, and polarization effects, as well as an empirical absorption correction, based on ψ scans of reflections near χ = 90°.

Structures were solved by routine heavy-atom methods, and refinement was conducted by full-matrix least squares based on F, with data for which $I > 3\sigma(I)$, using the Enraf-Nonius SDP programs.[18] Non-hydrogen atoms were treated anisotropically; hydrogen atoms were fixed in calculated positions. Ethyl carbon atoms, particularly for **18**, exhibited extremely high thermal parameters, probably indicative of disorder. Although refinement of disordered models was attempted, none fit the data better than single, anisotropic atoms. Since the atomic positions of the "interesting" part of the structure are insensitive to the modelling of the ethyl groups, the single atom model was adopted. The coordinates of the non-hydrogen atoms are given in Tables II and III.

A poor crystal of **21** was also subjected to X-ray analysis. Crystal data are $PdBrC_{18}H_{19}N_2O_6$ of monoclinic space group $P2_1/c$ with a = 16.685 (4) Å, b = 8.127 (3) Å, c = 14.910 (3) Å, β = 90.16 (2)°, and Z = 4. Low-resolution and apparent systematic errors in the data prevented successful refinement to below R = 0.10, but the structure is clearly very similar to that of **23**.

Results and Discussion

A. Complex Formation. Palladium(II) chloride reacts with 1 equivalent of 2,2′-bipyridine, 1,10-phenanthroline, 2,2-bis(2-pyridyl)-1,3-dioxolane, 1,2-bis(2-pyridyl)ethane,

Table II. Coordinates for Non-Hydrogen Atoms in $PdC_{27}H_{34}N_2O_{10}$[a]

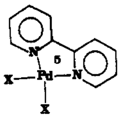
atom	x	y	z	atom	x	y	z
Pd	0.17233 (4)	0.09631 (2)	0.18496 (3)	C8	0.2785 (7)	−0.0489 (3)	0.3881 (5)
O1	0.4329 (4)	0.0757 (2)	0.2856 (3)	C9	0.1597 (8)	−0.0637 (4)	0.4266 (5)
O2	0.5154 (4)	−0.0210 (2)	0.3117 (3)	C10	0.0394 (7)	−0.0335 (4)	0.3921 (5)
O3	−0.1535 (4)	0.1178 (2)	0.2188 (4)	C11	0.0410 (6)	0.0106 (3)	0.3232 (5)
O4	−0.0968 (4)	0.2066 (2)	0.1511 (4)	C12	0.5746 (7)	0.0810 (4)	0.2815 (6)
O5	0.0028 (6)	0.1279 (3)	0.4102 (4)	C13	0.6306 (8)	0.0198 (5)	0.3118 (7)
O6	0.2060 (6)	0.1720 (3)	0.3994 (4)	C14	0.0675 (6)	0.1624 (3)	0.2588 (5)
O7	0.4516 (5)	0.1697 (3)	0.1064 (4)	C15	−0.0706 (6)	0.1590 (3)	0.2108 (5)
O8	0.3327 (5)	0.2348 (3)	0.1878 (4)	C16	0.0830 (7)	0.1515 (3)	0.3622 (5)
O9	0.2805 (6)	0.1310 (3)	−0.0603 (4)	C17	0.2046 (6)	0.1672 (3)	0.0887 (5)
O10	0.0612 (6)	0.1506 (3)	−0.0484 (4)	C18	0.1927 (7)	0.1472 (3)	−0.0126 (5)
N1	0.2729 (5)	0.0271 (2)	0.1137 (3)	C19	0.3435 (7)	0.1892 (3)	0.1256 (5)
N2	0.1606 (5)	0.0256 (2)	0.2878 (4)	C20	−0.2180 (7)	0.2036 (4)	0.0861 (7)
C1	0.2326 (7)	0.0079 (3)	0.0257 (5)	C21	−0.2352 (10)	0.2634 (5)	0.0368 (8)
C2	0.2968 (8)	−0.0398 (3)	−0.0183 (5)	C22	0.2461 (13)	0.1589 (7)	0.5003 (6)
C3	0.4082 (7)	−0.0675 (4)	0.0302 (5)	C23	0.3457 (15)	0.1221 (7)	0.5174 (9)
C4	0.4467 (7)	−0.0501 (3)	0.1232 (5)	C24	0.4658 (11)	0.2523 (6)	0.2406 (10)
C5	0.3768 (6)	−0.0035 (3)	0.1638 (5)	C25	0.4639 (15)	0.2897 (8)	0.2988 (11)
C6	0.4020 (6)	0.0126 (3)	0.2699 (5)	C26	0.0383 (11)	0.1361 (7)	−0.1526 (7)
C7	0.2768 (6)	−0.0040 (3)	0.3182 (4)	C27	−0.0928 (14)	0.1544 (8)	−0.1808 (9)

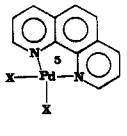
[a] Estimated standard deviations in the least significant digits are shown in parentheses.

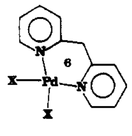
Table III. Coordinates for Non-Hydrogen Atoms in $PdBrC_{20}H_{23}N_2O_6$

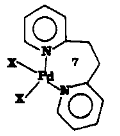
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pd	0.38543 (5)	0.30151 (4)	0.36586 (3)	C6	0.7142 (7)	0.3587 (5)	0.4341 (4)
Br	0.1947 (1)	0.40027 (7)	0.28924 (6)	C7	0.6967 (8)	0.2545 (5)	0.4522 (4)
O1	0.6091 (5)	0.4140 (4)	0.4654 (3)	C8	0.8186 (8)	0.2016 (6)	0.4898 (5)
O2	0.8603 (5)	0.3893 (4)	0.4727 (3)	C9	0.7994 (9)	0.1066 (6)	0.4973 (5)
O3	0.1900 (6)	0.0923 (4)	0.3993 (4)	C10	0.6591 (9)	0.0675 (6)	0.4681 (5)
O4	0.0135 (6)	0.1934 (4)	0.3430 (3)	C11	0.5411 (8)	0.1255 (6)	0.4329 (5)
O5	0.3409 (7)	0.1817 (4)	0.5477 (3)	C12	0.6840 (9)	0.4425 (7)	0.5412 (5)
O6	0.2964 (8)	0.3362 (4)	0.5452 (3)	C13	0.8467 (9)	0.4485 (7)	0.5381 (5)
N1	0.5490 (6)	0.3556 (4)	0.3064 (3)	C14	0.2217 (7)	0.2559 (5)	0.4288 (4)
N2	0.5590 (6)	0.2180 (4)	0.4248 (3)	C15	0.1474 (8)	0.1705 (6)	0.3914 (4)
C1	0.5189 (8)	0.3696 (6)	0.2290 (5)	C16	0.2920 (8)	0.2486 (6)	0.5110 (5)
C2	0.6284 (9)	0.3997 (6)	0.1875 (5)	C17	−0.0693 (10)	0.1164 (6)	0.2997 (5)
C3	0.7709 (9)	0.4175 (6)	0.2307 (5)	C18	−0.2202 (13)	0.1516 (8)	0.2586 (7)
C4	0.8029 (8)	0.4053 (6)	0.3105 (5)	C19	0.3663 (12)	0.3504 (8)	0.6272 (6)
C5	0.6885 (7)	0.3747 (5)	0.3487 (4)	C20	0.2568 (15)	0.3406 (10)	0.6729 (7)

and di-2-pyridylmethane in MeCN to give a quantitative yield of the dichloropalladium(II) complexes **9–14**.[8,15,19,20]





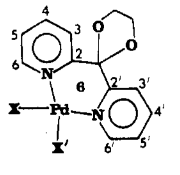




(9) X = Cl (10) X = Cl (14) X = Cl (13) X = Cl

(15) X = $CH(CO_2Me)_2$ (16) X = $CH(CO_2Me)_2$ (20) X = $CH(CO_2Me)_2$ (19) X = $CH(CO_2Me)_2$

All these complexes dissolve readily in DMF and undergo a facile ligand exchange of both the chloro ligands with excess of dialkyl potassiomalonate at 25 °C. Since complex **11** is also soluble in CH_3CN, the chloride–malonate ligand exchange can be readily conducted in this solvent.

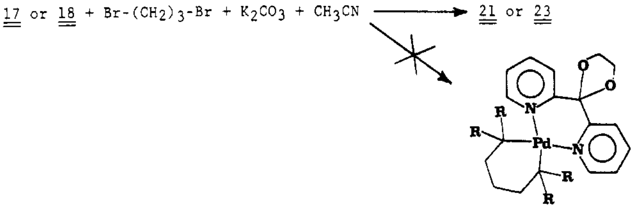


(11) X = X' = Cl
(12) X = X' = Br
(17) X = X' = $CH(CO_2Me)_2$
(18) X = X' = $CH(CO_2Et)_2$
(21) X = $CH(CO_2Me)_2$; X' = Br
(23) X = $CH(CO_2Et)_2$; X' = Br

B. Spectra Features. The ^1H and ^{13}C NMR, IR, and X-ray single-crystal data firmly establish that the malonate behaves as an unidentate ligand, forming a Pd–C bond. In the ^1H NMR, the methine proton in all malonate complexes appears as a singlet in the region δ 3.67–4.39, and there is a systematic upfield shift upon enlarging the chelate ring from five to seven members. These values fall within the δ 4.0–4.4 range for related C-bonded complexes and differ significantly from the O-bonded range (δ 4.7–5.4).[3-5] In monometalated complexes the methine proton shifts downfield by $\Delta\delta = 0.3$–0.5 ppm as compared to the corresponding bimetalated complexes. The H-6 proton of the heteroaromatic ring (H-2 in case of phenanthroline) shows a similar dramatic upfield shift trend from five- to seven-membered chelate, i.e., δ 10.07, 9.74, and 8.72 for **16**, **15**, and **19**, respectively. These trends are indicative of a diminished interaction between the H-6 proton and the methoxycarbonyl groups as one proceeds from a five- to seven-membered chelate ring. Another interesting feature shown in the ^1H as well as ^{13}C NMR spectra is the presence of two different methoxycarbonyl (or ethoxycarbonyl) groups in the six- and 7-membered ring complexes, which is indicative of a conformational stability in these rings, placing one ester group in an axial and the other in an equatorial position. Thus, the arrangement of alkoxycarbonyl group is the one shown for **24** and *not* **25**, because the monometalated complexes **21** and **23** show a similar diastereotopic character. The five-membered complexes[7] show equivalent methoxycarbonyl groups, and a similar phenomenon has been observed in five- and six-membered bis-trans-cyclopalladated complexes.[21,22] The ketal methylene protons in complex **17** appear as a symmetrical multiplet in the region δ 4.17–4.38, and the pattern becomes much more complex in the monometalated complex **21**. The corresponding ethyl ester complexes **18** and **23** show an upfield shift for these protons. The methylene protons in the six-membered ring complex **20** appear as two doublets at δ 4.39 and 5.15 with a coupling constant of 12.2 Hz, which is a typical geminal coupling, and hence the protons are in magnetically nonequivalent environments. The other ^1H and ^{13}C spectral data show the usual features, and assignments are based on the analogy with our earlier work.[8] The signal for the carbon directly bonded to palladium appears at δ 52.4 ± 0.4, which is 13 ppm downfield from free dimethyl malonate and ca. 50 ppm upfield of the related O-bonded complexes,[3-5] and further supports the assigned structures.

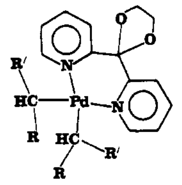
The IR spectra of these complexes exhibit a very strong carbonyl absorption at 1710–1690 cm^{-1}, which further confirms the presence of the Pd–C σ-bond formation.[5,23]

Scheme II

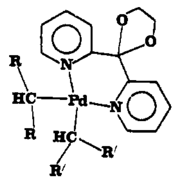


17 or 18 + $Br\text{-}(CH_2)_3\text{-}Br + K_2CO_3 + CH_3CN \longrightarrow$ 21 or 23

26



(24)



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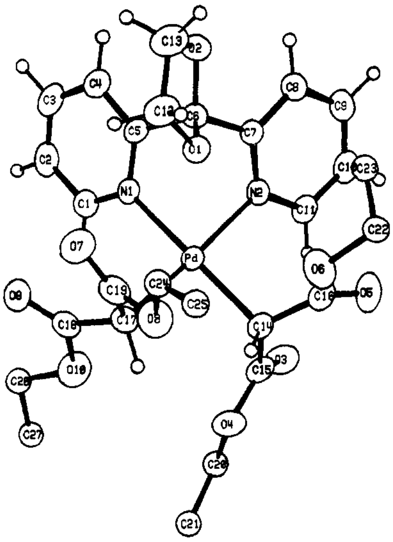
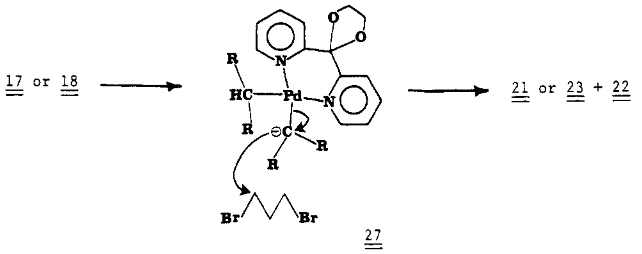


Figure 1. ORTEP drawing of bis(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II). Some of the hydrogen atoms have been omitted for clarity, and ethyl carbon atoms are represented by circles of arbitrary radius.

Scheme III



C. Monometalated Complexes. In an attempt to form the cyclometalated complex **26**, 1,3-dibromopropane was reacted with **17** or **18** and anhydrous K_2CO_3 in MeCN; however, the monometalated complexes **21** and **23**, respectively, were generated along with dimethyl 2-(3-bromopropyl)malonate (**22**). The formation of **21** or **23** can be envisioned; see Scheme II. Under the influence of the base (K_2CO_3), complex **17** or **18** generates anion **27**, which attacks 1,3-dibromopropane to afford **21** or **23** along with dimethyl 2-(3-bromopropyl)malonate. The ^{1}H NMR spectra of these monometalated complexes exhibit distinct differences in the chemical shift of the pyridine H-6 and in the multiplicity of the ketal signal. In bis(malonato-*C*) complexes **17** and **18**, H-6 appears at δ 9.36 and 9.27, respectively. In the corresponding unsymmetrical bromo malonato-*C* complexes, the two signals for H-6 and H-6′ were assigned on the basis of the spectra of the bis(malonato-*C*) complex **17** or **18** and the corresponding dibromo complex **12**. Thus in **21**, H-6 and H-6′ are observed at δ 9.19 and 9.75 while in **23**, these appear at δ 9.27 and 9.93, respectively.

D. Structure Descriptions. In order to determine the salient features and to firmly establish the structures of the Pd–C(malonato) complexes, single-crystal X-ray analyses of **18** (Figure 1) and **23** (Figure 2) were undertaken. In both complexes, the palladium atom attains the expected square-planar coordination, being bonded to two nitrogen atoms of the dipyridyl ketal ligand and σ bonded to two malonate carbon atoms in **18**. In **23**, one of the bonding sites is occupied by bromine and the other by the central malonate carbon atom. Selected bond lengths and angles of both are listed in Table IV. The Pd–N bond lengths (average 2.110 Å in **18** and 2.085 Å in **23**) are comparable to those in similar Pd(II)–pyridine complexes.[8,15,20–22] The three Pd–C bond distances range from 2.092 (4) to 2.107 (4) Å and average 2.099 Å. These distances

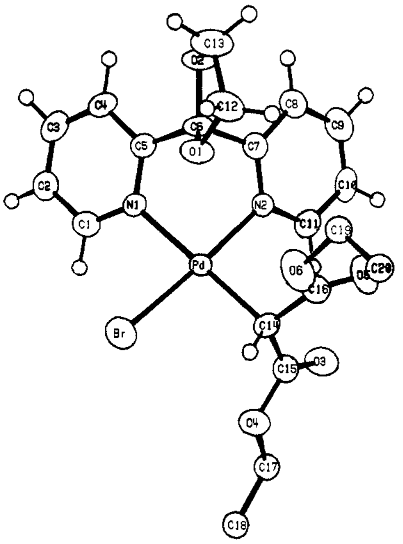


Figure 2. ORTEP drawing of bromo(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II). Some of the hydrogen atoms have been omitted for clarity, and ethyl carbon atoms are represented by circles of arbitrary radius.

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

18		23	
	Bond Lengths		
Pd-N1	2.103 (3)	Pd-N1	2.107 (4)
Pd-N2	2.117 (3)	Pd-N2	2.064 (4)
Pd-C14	2.097 (4)	Pd-C14	2.107 (4)
Pd-C17	2.092 (4)	Pd-Br	2.404 (1)
	Bond Angles		
N1-Pd-N2	82.54 (13)	N1-Pd-N2	85.66 (15)
N1-Pd-C14	177.58 (15)	N1-Pd-C14	176.28 (18)
N1-Pd-C17	96.10 (16)	N1-Pd-Br	90.11 (11)
N2-Pd-C14	95.32 (16)	N2-Pd-C14	95.72 (17)
N2-Pd-C17	174.19 (15)	N2-Pd-Br	175.48 (11)
C14-Pd-C17	86.14 (18)	C14-Pd-Br	88.60 (14)

Table V. Selected Torsion Angles (deg)[a]

atoms	18	23
Pd-N1-C5-C6	4.7	−1.8
N1-C5-C6-C7	62.0	63.6
C5-C6-C7-N2	−61.7	−62.0
C6-C7-N2-Pd	−4.8	−1.9
C7-N2-Pd-N1	51.1	44.3
N2-Pd-N1-C5	−50.4	−43.0
Pd-C14-C15-O3	74.0	82.7
Pd-C14-C16-O5	−101.0	−98.1
O3-C15-C14-C16	−48.8	−41.0
O5-C16-C14-C15	16.7	25.7
O1-C12-C13-O2	12.2	−21.8
C12-C13-O2-C6	8.1	6.1
C13-O2-C6-O1	−25.7	11.7
O2-C6-O1-C12	34.0	−25.8
C6-O1-C12-C13	−28.0	29.8
N1-C5-C6-O2	−178.0	−174.7
N2-C7-C6-O2	178.2	174.7
Pd-C17-C18-O9	−94.5	
Pd-C17-C19-O7	86.9	
O7-C19-C17-C18	−36.2	
O9-C18-C17-C19	21.6	

[a] Esd's are 0.4–0.7.

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fall within the range 2.083 (3)–2.181 (7) Å found in ten related crystal structures containing Pd(II)–C(sp^3) bonds.[8,21,22] The Pd–Br distance of 2.404 (1) Å is not unusual.[24] The chelating N–Pd–N angles of 82.54 (13)° in **18** and 85.66 (15)° in **23** differ significantly from each other as well as from that of the corresponding dichloro complex **11**, in which this angle is 87.1 (2)°.[15]

In both **18** and **23**, the six-membered chelate ring assumes a *boat conformation* (see Table V). The coordination environment around palladium in both is tetrahedrally distorted square planar. Deviations (Å) from the coordination plane are as follows: N(1), 0.054 (5); N(2), −0.070 (5); Pd, 0.034 (1); C(14), 0.052 (6); C(17), −0.069 (6). In **23**, similar deviations (Å) are as follows: N(1), 0.051 (6); N(2), 0.045 (6); Pd, 0.014 (1); Br, 0.040 (1); C(14), −0.048 (7). Each of the four pyridine rings is planar and produces intramolecular dihedral angles of 72.6° and 67.3° in **18** and **23**, respectively. Thes angles are somewhat larger than the two independent values of 64.5° and 63.4° found in **11**.[15]

The ethoxycarbonyl groups of both complexes are probably disordered, exhibiting large thermal parameters in the crystal (not illustrated in Figures 1 and 2), and leading to unrealistically short observed bond distances, particularly for C–C(ethyl) bonds.

The ketal rings of the two complexes differ in conformation (see Table V); both adopt a half-chair conformation, but C(13) lies on the local twofold axis in **18**, whereas in **23**, O(2) occupies that unique position. The Pd···O(1) distances [2.844 (3) and 2.865 (3) Å in **18** and **23**, respectively] are close to the minimum expected van der Waals distance of 3.0 Å. This contact is also observed in dichloro(dihydroxydi-2-pyridylmethane)palladium(II), in which the Pd···O distance is 2.824 (6) Å,[25] and in dichloro[2,2-bis(2-pyridyl)1,3-dioxolane]palladium(II), in which it has two independent values of 2.987 (4) and 2.935 (3) Å.[15] No intermolecular contacts less than 3.5 Å exists between the non-hydrogen atoms.

Acknowledgment. We wish to thank the National Science Foundation and Center for Energy Studies for partial support of this work.

Registry No. **7**, 4916-40-9; **8**, 1132-37-2; **9**, 14871-92-2; **10**, 14783-10-9; **11**, 91391-01-4; **12**, 91391-02-5; **13**, 91391-03-6; **14**, 91391-04-7; **15**, 84726-31-8; **16**, 84750-35-6; **17**, 91391-05-8; **18**, 91391-06-9; **19**, 91391-07-0; **20**, 91391-08-1; **21**, 91391-09-2; **22**, 29554-48-1; **23**, 91391-10-5; ethene, 74-85-1; di-2-pyridyl ketone, 19437-26-4; 1,3-dibromopropane, 109-64-8.

Supplementary Material Available: Tables of the bond distances, bond angles, hydrogen atom coordinates, and anisotropic thermal parameters and a listing of observed and calculated structure factors for **18** and **23** (49 pages). Ordering information is given on any current masthead page.

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Metathesis of Acetylenes by Triphenoxytungstenacyclobutadiene Complexes and the Crystal Structure of $W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$

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Received February 14, 1984

The reaction between W(CCMe$_3$)(1,2-dimethoxyethane)Cl$_3$ and LiO-2,6-C$_6$H$_3$(*i*-Pr)$_2$ (LiOR) yields yellow, crystalline W(CCMe$_3$)(OR)$_3$ (**1**). 3-Hexyne reacts with **1** to give Me$_3$CC≡CEt and W(C$_3$Et$_3$)(OR)$_3$ (**2**) quantitatively. W(C$_3$Et$_3$)[O-2,6-C$_6$H$_3$(*i*-Pr)$_2$]$_3$ crystallizes in the monoclinic space group $P2_1/c$ with a = 19.271 (6) Å, b = 13.000 (3) Å, c = 17.195 (6) Å, β = 96.55 (2)°, and Z = 4. Diffraction data were collected with a Syntex P2$_1$ diffractometer, and the structure was refined to R_F = 4.67% for all 3873 data with 2θ = 4.5–40.0° (Mo Kα). This sterically crowded molecule is approximately a trigonal bipyramid in which the planar tungstenacyclobutadiene ring is located in the equatorial position with the two W–C$_\alpha$ bond lengths being 1.883 (10) and 1.949 (9) Å and the W···C$_\beta$ bond distance being 2.159 (10) Å. Both **2** and an analogous W(C$_3$Pr$_3$)[O-2,6-C$_6$H$_3$(*i*-Pr)$_2$]$_3$ complex (**3**) catalyze the metathesis of 3-heptyne or 4-nonyne. They each react with 3-hexyne-d_{10} at a rate that is independent of the concentration of 3-hexyne-d_{10}, characteristic of rate limiting loss of 3-hexyne from **2** or 4-octyne from **3**: $\Delta H^{\ddagger} \simeq 26$ kcal mol^{-1} and $\Delta S^{\ddagger} \simeq 16$ eu in each case. Related studies employing O-2,6-C$_6$H$_3$Me$_2$ suggested that this ligand is not bulky enough to yield metathesis catalysts, while use of O-2,6-C$_6$H$_3$(CMe$_3$)$_2$ led to a neopentylidene complex through addition of a *tert*-butyl CH bond to the W≡C bond.

Introduction

The metathesis of dialkylacetylenes by W(CCMe$_3$)(OCMe$_3$)$_3$[2] and analogous W(CR)(OCMe$_3$)$_3$ complexes (R = Me, Et, etc.[3]) is believed to proceed by formation and decomposition of tungstenacyclobutadiene complexes. This hypothesis is supported by kinetic studies of the rate at which W(CCMe$_3$)(OCMe$_3$)$_3$ reacts with diphenylacetylene at 0 °C in ether to give W(CPh)(OCMe$_3$)$_3$ and

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