$[Pd\{CH_2C(O)Me\}Cl]_n$, a Key Product for the Synthesis of Acetonylpalladium(II) Complexes

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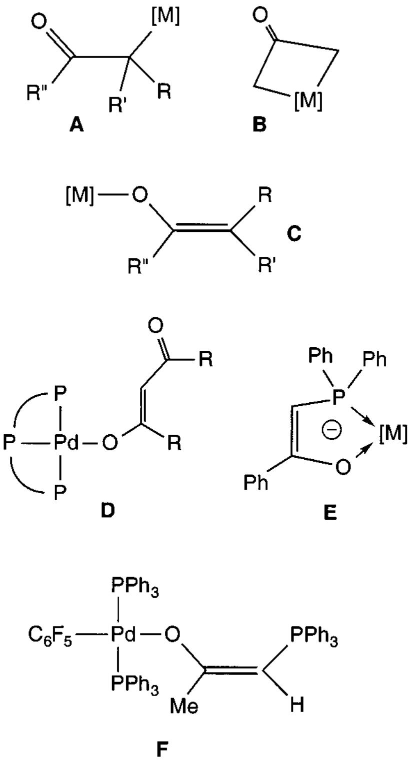
$[Hg\{CH_2C(O)Me\}_2]$ reacts with $[PdCl_2(MeCN)_2]$ (1:1) or with $(Me_4N)_2[Pd_2Cl_6]$ (2:1) to give $[Pd\{CH_2C(O)Me\}Cl]_n$, which can be used to prepare a variety of acetonyl complexes. Thus, by reacting it with the appropriate ligands, complexes $[Pd\{CH_2C(O)Me\}I]_n$, $[Pd\{CH_2C(O)Me\}ClL_2]$ [L_2 = *N*,*N*,*N′N′*-tetramethylethylenediamine, 2,2′-bipyridine, 4,4′-$(^tBu)_2$-2,2′-bipyridine, 1,10-phenathroline; L = PPh_3, dimethyl sulfoxide (dmso)], $[Pd_2\{CH_2C(O)Me\}\{\mu\text{-}\kappa^2\text{-}C,O\text{-}CH_2C(O)Me\}(\mu\text{-}Cl)Cl(dmso)_2]$, or $[Pd_2\{CH_2C(O)Me\}_2(\mu\text{-}Cl)_2(tetrahydrothiophene)_2]$ can be obtained. The crystal structures of the last two complexes and that of $[Hg\{CH_2C(O)Me\}_2]$ have been determined by X-ray crystallography.

Introduction

Palladium(II) enolates derived from monoketones have been proposed as intermediates in numerous organic transformations.[1−3] A limited number of such palladium(II) complexes have been isolated, and those well-characterized are shown to contain the σ-C-bonded carbanion $[CRR'C(=O)R'']^-$ (**A** in Scheme 1)[3−12] or the oxodimethylenemethane dianion, $[(CH_2)_2C=O]^{2-}$ (**B**).[13,14]

Scheme 1



Complexes **A** are frequently referred to as C-enolates, but, in our opinion, such designation is wrong and confusing because an enolate anion can only coordinate to a metal through the oxygen (**C**) or the π electron density. We call them ketonyls, although they have also been named 2-oxoalkyls. Among ketonylpalladium(II) derivatives, only three have been characterized by X-ray

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diffraction studies[7,13] and very few are derived from Me_2CO. These acetonyl complexes have been obtained by oxidative addition of chloroacetone to $[Pd(PPh_3)_4]$,[4,8,12] by reacting Me_2CO with $[PdCl_2(tmeda)]$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in the presence of Ag_2O,[9] or by reacting $ClCH_2C(OCH_2OMe){=}CH_2$ with Pd_2(dibenzylideneacetone)$_3$ and the resulting complex with PPh_3 and KOH.[13] Therefore, the established procedures give acetonylpalladium(II) complexes with PPh_3 or tmeda. A related family of isolated complexes containing the σ-O-bonded tautomeric enolate form (i.e., the true palladium(II) enolates) are derived from β-diketones (**D**),[15,16] carbonyl-functionalized phosphines (**E**),[17−19] carbonyl-functionalized phosphorus ylides (**F**),[20] or carbonyl-functionalized N-donor ligands.[21,22] Coordination of these ligands through oxygen is forced due to the preferred coordination of the ligand as a five-membered chelate (**E**) or the transphobia between P or C toward C-donor ligands (**D**, **F**).[23]

We report here a new method of synthesis of acetonylpalladium(II) complexes involving $[Pd\{CH_2C(O)Me\}Cl]_n$, prepared from $[Hg\{CH_2C(O)Me\}_2]$[24] as transmetallating agent, as well as the first crystal structures of acetonylpalladium(II) complexes.

Experimental Section

IR and NMR spectroscopies, elemental analyses, and melting point determinations were carried out as described elsewhere.[25] $[Hg\{CH_2C(O)Me\}_2]$,[24] $[PdCl_2(MeCN)_2]$,[26] and $(Me_4N)_2[Pd_2Cl_6]$[27] were prepared by literature methods. Single crystals of $[Hg\{CH_2C(O)Me\}_2]$ were obtained by slow diffusion of *n*-hexane into a solution of the complex in benzene.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl]_n$ (1). Method a. To a solution of $[PdCl_2(MeCN)_2]$ (0.825 g, 3.17 mmol) in Me_2CO (80 mL) was added solid $[Hg\{CH_2C(O)Me\}_2]$ (1 g, 3.17 mmol). The resulting suspension was filtered, and the solid was washed with Me_2CO and air-dried to give **1** as an orange solid. Yield: 0.621 g, 98%. Mp: 180 °C (decomp). IR (cm^{-1}): ν(C=O), 1565 (s), ν(PdCl) 354 (m), 266 (w). Anal. Calcd for C_3H_5ClOPd: C, 18.11; H, 2.53. Found: C, 17.60; H, 2.23 (on the low value of %C found, see Results and Discussion).

Method b. To a solution of $(NMe_4)_2[Pd_2Cl_6]$ (0.91 g, 1.59 mmol) in water (15 mL) was added solid $[Hg\{CH_2C(O)Me\}_2]$ (1 g, 3.18 mmol). The resulting suspension was filtered and the solid washed with water and recrystallized from MeCN/Et_2O to give **1** as an orange solid. Yield: 0.57 g, 90%.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl(tmeda)]$ (2). To a suspension of **1** (100 mg, 0.5 mmol) in Me_2CO (15 mL) was added *N*,*N*,*N*′*N*′-tetramethylethylenediamine (tmeda, 100 μL, 0.66 mmol). The reaction mixture was stirred until **1** disolved and then was filtered through Celite and concentrated (ca. 2 mL). Et_2O (10 mL) was added, the resulting suspension was filtered, and the solid was washed with Et_2O (10 mL) and air-dried to give **2** as a yellow solid. Yield: 136 mg, 86%. Mp and spectroscopic properties are the same as reported previously.[9] However, the ^1H NMR resonances at 2.56 and 2.26 ppm should be assigned to PdCH_2 and *Me*C(O), respectively.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl(PPh_3)_2]$ (3). To a suspension of **1** (80 mg, 0.4 mmol) in THF (15 mL) was added solid PPh_3 (221 mg, 0.84 mmol) under nitrogen. The reaction mixture was stirred until **1** disolved and then was filtered through Celite. The filtrate was concentrated (ca. 2 mL), Et_2O (20 mL) was added, and the resulting suspension was filtered. The solid was washed with Et_2O (10 mL) and air-dried to give **3** as a yellow solid. Yield: 240 mg, 83%. Mp and spectroscopic properties are the same as reported previously.[4,8,12]

Synthesis of $[Pd\{CH_2C(O)Me\}I]_n$ (4). To a solution of **1** (60 mg, 0.3 mmol) in MeCN (15 mL) was added NaI (47 mg, 0.31 mmol). The solution turned brown, and a white precipitate appeared. The suspension was filtered through Celite, and the solid washed with MeCN (5 mL). The combined filtrate was concentrated (2 mL), water (20 mL) was added, and the resulting suspension was filtered. The solid was washed with acetone and air-dried to give **4** as a dark brown solid. Yield: 58 mg, 66%. Mp: 214−215 °C (decomp). IR (cm^{-1}): ν(C=O), 1554 (s). ^1H NMR (DMSO-d_6): δ 2.17 (s, 3 H, *Me*CO), 2.78 (s, 2 H, PdCH_2). Anal. Calcd for C_3H_5IOPd: C, 12.41; H, 1.74. Found: C, 12.58; H, 1.76.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl(phen)]$ (5). To a solution of **1** (160 mg, 0.8 mmol) in MeCN (20 mL) was added phen·H_2O (158.6 mg, 0.8 mmol). A yellow suspension formed, which was stirred for 30 min and concentrated (10 mL), and Et_2O (10 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give **5** as a yellow solid. Yield: 274 mg, 93%. Mp: 230 °C. IR (cm^{-1}): ν(C=O), 1636 (s), ν(PdCl) 328 (m). ^1H NMR ($CDCl_3$): δ 2.43 (s, 3 H, Me), 3.14 (s, 2 H, CH_2), 7.87 (dd, 1 H, H3 or H8, $^3J_{HH} = 8.3$ Hz, $^3J_{HH} = 5.1$ Hz), 7.93 (dd, 1 H, H3 or H8, $^3J_{HH} = 8.3$ Hz, $^3J_{HH} = 5.3$ Hz), 7.95 (s, 1 H, H5 or H6), 7.96 (s, 1 H, H5 or H6), 8.49 (dd, 1 H, H4 or H7, $^3J_{HH} = 8.3$ Hz, $^5J_{HH} = 1.5$ Hz), 8.5 (dd, 1 H, H4 or H7, $^3J_{HH} = 8.3$ Hz, $^5J_{HH} = 1.2$ Hz), 9.51 (dd, 1 H, H2 or H9, $^3J_{HH} = 5.1$ Hz, $^5J_{HH} = 1.5$ Hz), 9.78 (dd, 1 H, H2 or H9, $^3J_{HH} = 5.3$ Hz, $^5J_{HH} = 1.2$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.1 (CH_2), 30.6 (Me), 125.1 (CH), 125.6 (CH), 127.0 (CH), 127.1 (CH), 129.4 (Cq), 129.9 (Cq), 137.7 (CH), 145.0 (Cq), 147.5 (Cq), 152.3 (CH), 149.5 (CH), 213.7 (CO) Anal. Calcd for $C_{15}H_{13}ClN_2OPd$: C, 47.52; H, 3.46; N, 7.36. Found: C, 47.27; H, 3.27; N, 7.40.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl(bpy)]$ (6). To a suspension of **1** (69 mg, 0.34 mmol) in Cl_2CH_2 (10 mL) was added 2,2′-bipyridine (bpy, 53.4 mg, 0.34 mmol). The resulting yellow suspension was stirred for 1 h, concentrated (6 mL), and filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give **6** as a yellow solid. Yield: 108 mg, 90%. Mp: 210 °C (decomp). IR (cm^{-1}): ν(C=O), 1634 (s), ν(PdCl) 334 (m). Anal. Calcd for $C_{13}H_{13}ClN_2OPd$: C, 43.97; H, 3.69; N, 7.89. Found: C, 43.76; H, 3.66; N, 8.17. The insolubility of **6** in organic solvents prevented NMR studies.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl(dbbpy)]$ (7). To a sus-

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Table 1. Crystal Data for Compounds 9, 10, and $[Hg\{CH_2C(O)Me\}_2]$

	9	**10**	$[Hg\{CH_2C(O)Me\}_2]$
formula	$C_{10}H_{22}Cl_2O_4Pd_2S_2$	$C_7H_{13}ClOPdS$	$C_6H_{10}HgO_2$
M_r	554.41	287.08	314.73
wavelength (Å)	0.71073	0.71073	0.71073
T (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.22 × 0.18 × 0.13	0.60 × 0.30 × 0.05	0.36 × 0.20 × 0.18
cryst syst	monoclinic	triclinic	monoclinic
space group	$P21/n$	$P\bar{1}$	$P2(1)/c$
a (Å)	10.5710(10)	5.0068(4)	8.9637(6)
b (Å)	14.4210(10)	9.0404(4)	9.0961(5)
c (Å)	12.2140(19)	11.3207(8)	9.5728(7)
α (deg)	90	70.100(5)	90
β (deg)	104.72	89.902(6)	101.194(5)
γ (deg)	90	80.671(5)	90
volume (Å^3)	1088.8(3)	474.65(5)	765.67(9)
Z	4	2	4
D_{calc} (Mg m^{-3})	2.044	2.009	2.730
F(000)	1088	2.398	568
μ (mm^{-1})	2.532	2.398	20.030
θ range (deg)	3.27−24.99	3.58−24.99	3.12−24.98
limiting indices	$-12 \leq h \leq 0$ $-17 \leq k \leq 17$ $-14 \leq l \leq 14$	$-1 \leq h \leq 5$ $-10 \leq k \leq 10$ $-13 \leq l \leq 13$	$-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $-11 \leq l \leq 0$
no. of reflns			
measd	6573	2234	2765
indep	3179	1625	1345
R_{int}	0.0230	0.0069	0.0413
abs corr	ψ-scans	ψ-scans	ψ-scans
transmissions	0.889−0.712	0.996−0.637	0.98529−0.28489
no. of data/restrains/params	3179/60/187	1625/47/101	1345/0/83
goodness-of-fit on F^2	0.917	1.081	1.015
R1^a	0.0222	0.0214	0.0273
wR2^b	0.0449	0.0567	0.0666
largest diff peak and hole (e Å^{-3})	1.523; −0.400	1.021; −0.509	1.401; −2.370

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

pension of **1** (100 mg, 0.5 mmol) in Cl_2CH_2 (15 mL) was added 4,4′-(^{t}Bu)$_2$-2,2′-bipyridine (dbbpy, 135 mg, 0.5 mmol). The reaction mixture was stirred until **1** disolved and then filtered through Celite. The resulting solution was concentrated to dryness, the residue stirred with Et_2O (15 mL), and the suspension filtered. The solid was washed with Et_2O (5 mL) and air-dried to give **7** as a yellow solid. Yield: 203 mg, 87%. Mp: 214−215 °C. IR (cm^{-1}): ν(C=O), 1636 (s), ν(PdCl) 340 (m). ^{1}H NMR (CDCl$_3$): δ 1.43 (s, 18 H, C(*Me*)$_3$) 2.36 (s, 1 H, CO*Me*), 2.92 (s, 2 H, Pd*CH$_2$*), 7.51 (dd, 2 H, H5 or H5′, $^3J_{HH}$ = 6 Hz; $^4J_{HH}$ = 1.8 Hz), 7.59 (dd, 2 H, H5 or H5′, $^3J_{HH}$ = 6 Hz; $^4J_{HH}$ = 1.8 Hz), 7.94 (d, 2 H, H3 and H3′, $^4J_{HH}$ = 1.8 Hz), 9.11 (d, 1 H, H6 or H6′, $^3J_{HH}$ = 6 Hz), 9.30 (d, 1 H, H6 or H6′, $^3J_{HH}$ = 6 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 25.3 (s, Pd*CH$_2$*), 30.1 (s, C(*Me*)$_3$), 30.2 (s, C(*Me*)$_3$), 30.4 (s, CO*Me*), 35.3 (s, *C*(Me)$_3$), 35.4 (s, *C*(Me)$_3$), 117.8 (s, CH-dbbpy), 118.5 (s, CH-dbbpy), 123.3 (s, CH-dbbpy), 124.0 (s, CH-dbbpy), 148.8 (s, CH-dbbpy), 151.4 (s, CH-dbbpy), 153.7, 156.3, 163.3, 163.8 (s, C-dbbpy), 238 (CO). Anal. Calcd for $C_{21}H_{29}ClN_2OPd$: C, 53.97; H, 6.25; N, 5.99. Found: C, 53.60; H, 6.02; N, 6.04.

Synthesis of $[Pd\{CH_2C(O)Me\}Cl(dmso)_2]$ (8). To a suspension of **1** (80 mg, 0.4 mmol) in Me_2CO (10 mL) was added dmso (150 μL, 2.1 mmol). The reaction mixture was stirred until **1** disolved and then filtered through Celite and concentrated (ca. 1 mL). Slow addition of Et_2O (10 mL) led to precipitation of a solid that was filtered, washed with Et_2O (4 mL), and air-dried to give **8** as a yellow solid. Yield: 114 mg, 80%. Mp: 81 °C. IR (cm^{-1}): ν(C=O), 1650 (s), ν(PdCl) 312 (m). ^{1}H NMR (dmso-d_6): δ 2.13 (s, 3 H, *Me*CO), 2.61 (s, 2 H, Pd*CH$_2$*). Anal. Calcd for $C_7H_{17}ClO_3PdS_2$: C, 23.67; H, 4.82; S, 18.05. Found: C, 23.64; H, 4.91; S, 17.78.

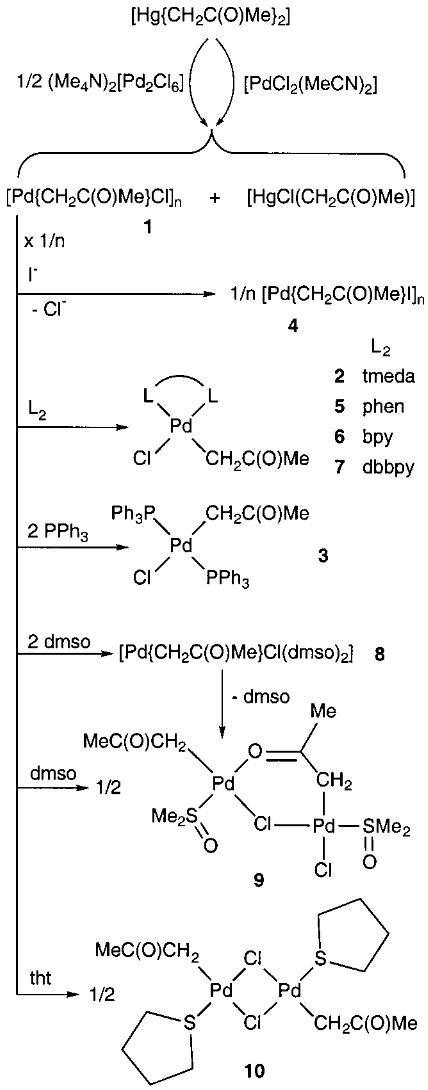
Synthesis of $[Pd_2\{CH_2C(O)Me\}\{\mu\text{-}\kappa^2\text{-}C,O-CH_2C(O)Me\}(\mu\text{-}Cl)Cl(dmso)_2]$ (9). Method a. To a suspension of **1** (80 mg, 0.4 mmol) in Me_2CO (20 mL) was added dmso (90 μL, 1.2 mmol). The reaction mixture was stirred until **1** disolved and then was filtered through Celite and concentrated (ca. 2 mL). Slow addition of Et_2O (10 mL) to the stirred solution led to precipitation of a solid, which was filtered, washed with Et_2O (4 mL), and air-dried to give **9** as a yellow solid. Yield: 90 mg, 81%. Mp: 140 °C. IR (cm^{-1}): ν(C=O), 1650 (s), 1534 (s), ν(PdCl) 294 (w), 270 (w), 242 (w). Anal. Calcd for $C_5H_{11}ClO_2PdS$: C, 21.68; H, 4.00; S, 11.57. Found: C, 21.76; H, 3.80; S, 11.60. About NMR data see Results and Discussion.

Method b. A solution of **8** in Me_2CO (11 mL) was stirred for 20 min. The solution was concentrated until a yellow solid appeared. Precipitation was completed by the addition of Et_2O (15 mL). The suspension was filtered, and the solid washed with Et_2O (5 mL) and air-dried to give **9**. Yield: 24 mg, 62%. Single crystals of **9** were obtained by slow concentration of an Me_2CO solution of **8**. About NMR data, see Results and Discussion.

Synthesis of $[Pd_2\{CH_2C(O)Me\}_2(\mu\text{-}Cl)_2(tht)_2]$ (10). To a suspension of **1** (80 mg, 0.4 mmol) in Me_2CO (15 mL) was added tetrahydrothiophene (tht, 90 μL, 1.01 mmol). The reaction mixture was stirred until **1** disolved and then filtered through Celite. The resulting yellow solution was concentrated (ca. 2 mL), and *n*-hexane (15 mL) was added to give a suspension, which was filtered; the solid was washed with Et_2O (5 mL) and air-dried to give complex **10** as a yellow solid. Yield: 91 mg, 80%. Mp: 96−98 °C. IR (cm^{-1}): ν(C=O), 1650 (s), ν(PdCl) 278 (m), 250 (m). ^{1}H NMR (CDCl$_3$ 50 °C): δ 2.07 (bs, 4 H, tht), 2.26 (bs, 3 H, *Me*CO), 2.72 (bs, 2 H, Pd*CH$_2$*), 3.11 (bs, 4 H, tht). Anal. Calcd for $C_7H_{13}ClOPdS$: C, 29.29; H, 4.56; S, 11.17. Found: C, 29.04; H, 4.42; S, 11.17. Single crystals of **10** were obtained by slow concentration of an Me_2CO solution of **10**.

X-ray Structure Determinations. The crystals were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. The structures were solved by the heavy atom method and refined anisotropically on F^2

Scheme 2



(program SHELX-93, G. M. Sheldrick, University of Göttingen).

For compound **9** unit cell parameters were determined from a least-squares fit of 86 accurately centered reflections (14.56° $< 2\theta <$ 24.76°) . Maximun $\Delta/\sigma = 0.001$, maximun $\Delta\rho = 1.52$ e Å^{-3}. The largest residual peak of 1.52 electrons was 0.98 Å from Pd1. Hydrogen atoms were included using a riding method.

For compound **10** unit cell parameters were determined from a least-squares fit of 67 accurately centered reflections (14.59°$< 2\theta <$ 26.00°). Maximun $\Delta\rho = 1.02$ e Å^{-3}. Hydrogen atoms were included using a riding method; methyls using a rigid method.

For compound $[Hg\{CH_2C(O)Me\}_2]$ unit cell parameters were determined from a least-squares fit of 80 accurately centered reflections (10.6° $< 2\theta <$ 23.8°). Maximun $\Delta/\sigma = 0.001$, maximun $\Delta\rho = 1.40$ e Å^{-3}. The largest residual peak of 1.40 electrons was 1.05 Å from Hg1. Hydrogen atoms were included using a riding method.

Results and Discussion

By reacting $[Hg\{CH_2C(O)Me\}_2]$ with the palladium complex $[PdCl_2(MeCN)_2]$ (1:1) in Me_2CO or $(Me_4N)_2[Pd_2Cl_6]$ (2:1) in water, complex $[Pd\{CH_2C(O)Me\}Cl]_n$ (**1**) precipitated immediately in almost quantitative yield (Scheme 2). We have previously shown the great synthetic interest of organomercury compounds as transmetallating agents.[28] An attempt to prepare **1** by reacting $ClCH_2C(O)Me$ with $[Pd(dibenzylideneacetone)_2]$ in refluxing toluene led to Pd metal.

Species like **1** have been postulated as intermediates in the synthesis of 2-cyclopentenones.[2,29] The isolation of some related compounds formulated as enolates $[Pd(OR)Cl]_n$ (R = ClCH=CR′, R′ = Ph, Me,[10] α-pinenyl, $^tBuC{=}CH_2$[30]) or as a dimer $[Pd\{CH_2C(O)(CH_2)_2C(Ph){=}CH_2\}(\mu\text{-}Cl)]_2$[29] were long ago preliminarily reported, but we are not aware that they had been later fully described.

Complex **1** can be used as the starting material for the synthesis of some new ketonyl complexes as well as the previously reported $[Pd\{CH_2C(O)Me\}Cl(tmeda)]$ (**2**)[9] and $[Pd\{CH_2C(O)Me\}Cl(PPh_3)_2]$ (**3**)[4,8,12] by reacting it with the appropriate ligands.

Complex **1** is insoluble in weak donor solvents, probably because it is a polymer (see below). It is soluble in MeCN or dmso, certainly because it reacts to give monomeric or oligomeric species (see below). An MeCN solution can be used to prepare, for example, the homologous polymeric complex $[Pd\{CH_2C(O)Me\}I]_n$ (**4**) by reacting it with NaI. The resulting solution after removing NaCl could also contain some MeCN adduct of **4**, but addition of Et_2O or water precipitated the polymer. The same occurred when we attempted to isolate some MeCN adduct of **1**. Similarly, phen·H_2O reacted with **1** in MeCN to give $[Pd\{CH_2C(O)Me\}Cl(phen)]$ (**5**). In addition, other ligands reacted with Me_2CO or THF suspensions of **1** to give acetonyl complexes (e.g., **2** or **3**, respectively). Cl_2CH_2 suspensions of **1** reacted with equimolar amounts of 2,2′-bipyridine (bpy) or 4,4′-$(^tBu)_2$-2,2′-bipyridine (dbbpy) to give $[Pd\{CH_2C(O)Me\}ClL_2]$ [L_2 = bpy (**6**), dbbpy (**7**)].

To study the potentiality of complex **1** for the synthesis of new classes of acetonyl complexes, its reactivity with dmso and tetrahydrothiophene (tht) was explored. When an excess of dmso was added to a suspension of **1** in Me_2CO (5:1 molar ratio), a yellow solution was obtained, from which, by addition of Et_2O, $[Pd\{CH_2C(O)Me\}Cl(dmso)_2]$ (**8**) could be isolated as a solid stable at room temperature. Slow evaporation of an Me_2CO solution of **8** afforded single crystals of the dinuclear complex $[Pd_2\{CH_2C(O)Me\}\{\mu\text{-}\kappa^2\text{-}C,O{-}CH_2C(O)Me\}(\mu\text{-}Cl)Cl(dmso)_2]$ (**9**), which can also be obtained by reacting **1** with dmso (1:3) or by recrystallizing **8** from Me_2CO/Et_2O.

Addition of tht to a suspension of **1** in Me_2CO in a molar ratio of 1:1, 2.5:1, 3:1, or 5:1 led to the isolation of the dinuclear complex $[Pd_2\{CH_2C(O)Me\}_2(\mu\text{-}Cl)_2(tht)_2]$ (**10**). Although probably **10** is in equilibrium with $[Pd\{CH_2C(O)Me\}Cl(tht)_2]$, the homologue of **8**, particularly when a strong excess of tht is used, its scarce solubility allowed its isolation.

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[28] See for example: Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269. Vicente, J.; Arcas, A.; Blasco, M. A.; Lozano, J.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 5374. Vicente, J.; Chicote, M. T.; González-Herrero, P.; Grünwald, C.; Jones, P. G. *Organometallics* **1997**, *16*, 3381. Vicente, J.; Bermúdez, M. D.; Carrión, F. J.; Jones, P. G. *Chem. Ber.* **1996**, *129*, 1395, and references therein.

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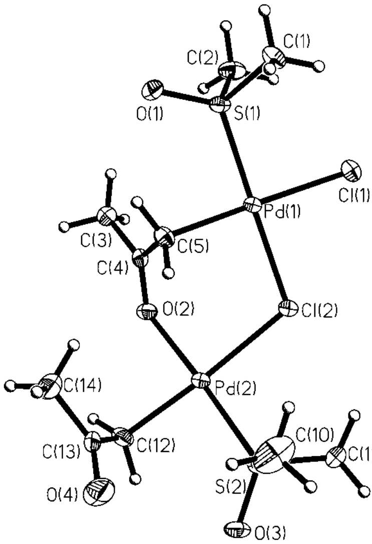

Figure 1. Crystal structure of complex **9**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(5) 2.082(3), Pd(1)−S(1) 2.2377(9), Pd(1)−Cl(2) 2.3475(8), Pd(1)−Cl(1) 2.3640(9), Pd(2)−C(12) 2.050, Pd(2)−O(2) 2.062(2), Pd(2)−S(2) 2.2320(9), Pd(2)−Cl(2) 2.4247(8), O(1)−S(1) 1.471(2), O(3)−S(2) 1.466(2), O(2)−C(4) 1.263(4), O(4)−C(13) 1.229(4), C(4)−C(5) 1.443(5), C(13)−C(14) 1.495(5), Cl(2)−Pd(1)−S(1) 178.49(3), C(5)−Pd(1)−Cl(1) 177.53(9), O(2)−Pd(2)−S(2) 176.64(7), C(12)−Pd(2)−Cl(2) 176.44(10).

The reactions of [Pd{$CH_2C(O)CR_3$}Cl(PPh_3)$_2$] [R = H (**3**), Me][12] with O_2 or [$PdCl_2(PhCN)_2$] have been reported to give species [Pd{$CH_2C(O)CR_3$}Cl(PPh_3)]$_2$, which, on the basis of their IR spectra, are supposed to contain acetonyl (R = H) or chloro (R = Me) bridging ligands (see below). The last one would be isostructural with **10**.

Structure of Complexes. The crystal structure of **9** was determined by X-ray crystallography (Figure 1). The structure consists of [PdCl(dmso)]$^+$ and [Pd{$CH_2C(O)Me$}(dmso)]$^+$ units bridged through chloro and C,O-acetonyl ligands. The dmso ligands are located trans to O and Cl ligands and both are S-bonded. The Pd−S(1) bond distance trans to chloro [2.2377(9) Å] is longer than the Pd−S(2) [2.2320(9) Å] one trans to the oxygen donor. The S−O bond lengths are not significantly different [O(1)−S(1) 1.471(2) Å, O(2)−S(2) 1.466(2) Å]. The three very different Pd−Cl distances show, in order of importance, the greater trans influence of C- than S-donor ligands and the lengthening of bond distances when a ligand is bridging. The Pd(1)−Cl(2) [2.3475(8) Å] bond distance is shorter than the Pd(1)−Cl(1) [2.3640(9) Å] one despite Cl(2) being a bridging ligand and Cl(1) a terminal one. The much greater trans influence of the acetonyl ligand with respect to S-dmso is responsible for such values. The Pd(2)−Cl(2) [2.4247(8) Å] bond length is, as expected, the longer Pd−Cl bond because Cl(2) is both bridging and trans to the acetonyl ligand. The C,O bridging coordination of the acetonyl ligand causes the lengthening of the C−O [O(2)−C(4) 1.263(4) Å] and Pd−C [Pd(1)−C(5) 2.082(3) Å] bond distances with respect to those in the terminal acetonyl ligand [O(4)−C(13) 1.229(4) Å, Pd(2)−C(12) 2.050(3) Å]. However, the C−C(O) bond distances of these ligands are not significantly different [C(4)−C(5) 1.443(5) Å, C(12)−C(13) 1.463(5) Å]. In the enolato complex [K(18-C-6)-{OC(=CHMe)Ph}],[31] the C−C bond distance is significantly shorter, 1.340(5) Å, and the C−O bond length longer, 1.298(5) Å, than those in **9**. The two reported crystal structures of ketonyl palladium(II) complexes—derived from acetophenone—*trans*-[Pd{$CH_2C(O)Ph$}Cl(PPh_3)$_2$] [C−O 1.211(6) Å, C−Pd 2.093(5) Å, C−C(O) 1.501(6) Å] and [Pd_2{μ-κ^2-C,O−$CH_2C(O)Ph$}$_2$(PPh_3)$_4$]$^{2+}$ [mean values C−O 1.258(11) Å, Pd−C 2.149(10) Å, C−C(O) 1.443(12) Å] show C−O and Pd−C bond distances longer and C−C(O) ones shorter for the bridging than for the terminal ketonyl.[7] In the crystal structure of the complex [Pd{$(CH_2)_2C{=}O$}(PPh_3)$_2$] the C−O, Pd−C, and C−C(O) bond lengths are similar to those found in terminal ketonyl ligands.[13] In accordance with NMR data at 223 K, it has been proposed that the complex [Pd{$CH_2C(O)Me$}Cl(PPh_3)]$_2$ is in solution a mixture of three species, one of which has the same structure as **9**.[12]

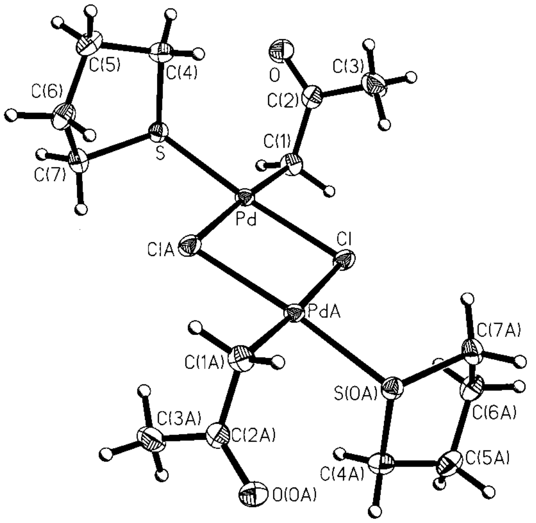

Figure 2. Crystal structure of complex **10**. Selected bond lengths (Å) and angles (deg): Pd−C(1) 2.053(3), Pd−S 2.2862(7), Pd−Cl 2.3650(7), Pd−Cl#1 2.4660(7), O−C(2) 1.226(4), C(1)−C(2) 1.484(4), C(2)−C(3) 1.508(4), C(1)−Pd−S 85.44(9), C(1)−Pd−Cl 90.61(9), S−Pd−Cl#1 98.23(2), Cl−Pd−Cl#1 85.72(2), Pd−Cl−Pd#1 94.28(2), C(2)−C(1)−Pd 105.1(2).

The crystal structure of **10** (Figure 2) consists of dimers formed through chloro bridges. The terminal ligands adopt a trans geometry. As usual in this class of complexes, both palladium and the six donor atoms are coplanar.[32] The C−O [1.226(4) Å] and Pd−C [2.053(3) Å] bond distances are very similar to those in the terminal acetonyl ligand in **9** [1.229(4) and 2.050(3) Å, respectively]. The Pd−Cl bond length trans to tht [2.3650(7) Å] and that trans to the acetonyl ligand [2.4660(7) Å] are longer in **10** than those trans to the dmso and to the acetonyl ligands in **9** [2.3475(8) and 2.4247(8) Å, respectively]. The Pd−S bond distances in **10** [2.2862(7) Å] are notably longer than those in **9** [2.2377(9), 2.2320(9) Å] probably because of the π acceptor character of dmso. Solutions of complexes [Pd{$CH_2C(O)CR_3$}Cl(PPh_3)]$_2$ (R = H, Me) are shown to contain different species, one of which is isostructural with **10**.[12]

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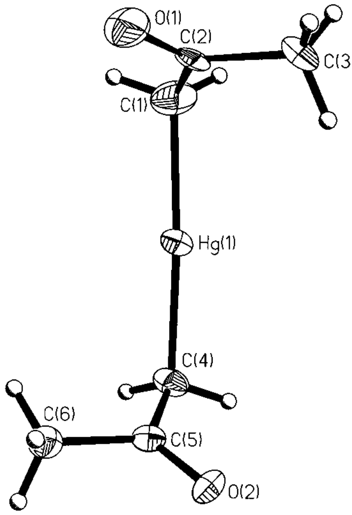

Figure 3. Crystal structure of [Hg{$CH_2C(O)Me$}$_2$]. Selected bond lengths (Å) and angles (deg): Hg(1)−C(1) 2.130(8), Hg(1)−C(4) 2.130(7), O(1)−C(2) 1.224(9), O(2)−C(5) 1.227(8), C(1)−C(2) 1.451(11), C(2)−C(3) 1.522(12), C(4)−C(5) 1.462(10), C(5)−C(6) 1.499(10), C(1)−Hg(1)−C(4) 174.2(3), C(2)−C(1)−Hg(1) 110.3(5), O(1)−C(2)−C(1) 123.0(8), O(1)−C(2)−C(3) 120.1(8), C(1)−C(2)−C(3) 117.0(8), C(5)−C(4)−Hg(1) 110.6(5), O(2)−C(5)−C(4) 123.5(7), O(2)−C(5)−C(6) 119.9(6), C(4)−C(5)−C(6) 116.5(6).

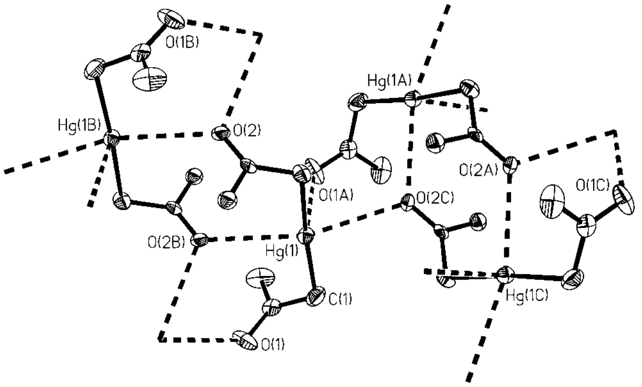

Figure 4. Packing diagram showing Hg···O interactions. Hg(1)−O(1A) 2.908(6), Hg(1)−O(2B) 2.900(5), Hg(1)−O(2C) 2.937(5).

Comparing the structures of **9** and **10** we conclude that (i) dmso favors the bridging mode of the acetonyl ligand and (ii) the transphobia[23] of the pair of ligands $MeC(O)CH_2$/S-donor ligand is greater than that of the pair $MeC(O)CH_2/Cl$. In fact, the only reported X-ray crystal structure of an organopalladium(II) complex containing an S-bonded dmso ligand has the S and C atoms in cis position, as in **9**.[27] In addition, the four structurally characterized organopalladium(II) complexes containing the dmso ligand trans to the carbon atom have the O-dmso ligand.[33]

The crystal structure of [Hg{$CH_2C(O)Me$}$_2$] shows an almost linear coordination with a C−Hg−C angle of 174.2(3)° (Figure 3). In addition, each Hg atom is connected to three oxygen atoms of three different molecules through weak Hg···O intermolecular interactions at 2.908(6), 2.900(5), and 2.937(5) Å, leading to a polymeric structure (Figure 4). These distances are shorter than the sum of the van der Waals radii of oxygen (1.40 Å)[34] and mercury (1.73 Å).[35] This type of weak Hg···O intermolecular interaction is frequent in similar complexes, e.g., [$(HgCl)_2${μ-C{C(O)Me}$_2$}] [3.01, 3.02 Å,[36] 2.88(1), 2.844(9) Å[37]], [HgCl(CH_2CHO)] [2.84(2), 2.87(1) Å],[38] [HgBr{$CH_2C(O)Me$}] [2.81(2), 2.82(2) Å],[39] [HgCl{CH{C(O)Me}$_2$}] [2.57(1), 2.69(1) Å],[40] and [$(HgCl)_2${μ-{C{C(O)Me}(CO_2Me)}}] [range 2.80(1)−2.91(1) Å].[41] However, the bridging role of one of the carbonyl groups [C−O(2)] has only one precedent in this family of complexes, [HgCl(CH_2CHO)].[38]

Complexes **1**, **4**, and **6** are insoluble in noncoordinating solvents, and **9** slowly decomposes in solution to give an insoluble product, probably some polymer related to **1** such as [Pd{$CH_2C(O)Me$}Cl]$_n$·2dmso. Complexes **5** and **7** show two singlets at around 2.4 (Me) and 3 (CH_2) ppm corresponding to the acetonyl ligand. The ^{1}H NMR spectrum of **8** in $CDCl_3$ shows a complex fluxional behavior in the range +55 to −60 °C, probably involving, among others processes, decoordination of dmso to give **9** and recoordination, such as observed in the case of **3**.[12] In dmso-d_6 at room temperature, one singlet for the Me and another one for the CH_2 group is observed. The ^{1}H NMR spectrum of **10** in $CDCl_3$ shows a complex fluxional behavior in the range +30 to −60 °C. However, at 50 °C singlets at 2.26 (Me) and 2.72 (CH_2) ppm are observed.

One absorption asignable to ν(CO) is observed in the IR spectra of complexes **1** and **4**, at 1565 and 1554 cm^{-1}, respectively, and in the range 1685−1628 cm^{-1} in those of complexes **2**, **3**, **5**−**8**, and **10**, whereas **9** shows two bands at 1650 and 1534 cm^{-1}. In the mercurials [Hg{$CH_2C(O)Me$}$_2$] and [Hg{$CH_2C(O)Me$}Cl], ν(CO) appears at 1650 cm^{-1}. Therefore, the band at 1685−1628 cm^{-1} should be assigned to the terminal acetonyl ligand, ν_t(CO), and that at 1565−1534 cm^{-1} to the bridging acetonyl ligand, ν_b(CO), in accordance with the longer C−O bond distance in the bridging than in the terminal acetonyl ligand observed in **9**. All these IR data suggest that, in the solid state, **1** and **4** are polymers with bridging acetonyl ligands and that all the other complexes have the structures shown in Scheme 2. That of complex **8** could be one of the five structures shown in Scheme 3, if two isomers with trans acetonyl and S-dmso ligands are discarded because of their mutual transphobia (see above). There are examples of palladium(II) complexes with two dmso ligands coordinated with respect to each other as they are in **A**,[42] **B**,[43] **D**,[44] and **E**[44] (Scheme 3). On the basis of ν(PdCl) and ν(SO)

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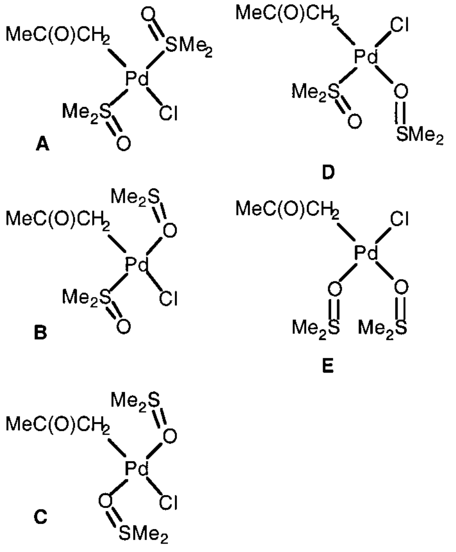
Scheme 3



we propose for complex **8** structure **D**. The IR spectrum of the only X-ray-characterized complex containing a bridging ketonyl ligand, $[Pd_2\{\mu\text{-}\kappa^2\text{-}C,O\text{-}CH_2C(O)Me\}_2(PPh_3)_4]^{2+}$, does not show any carbonyl band in the solid state (Nujol) or in Cl_2CH_2.[7] Therefore, on the basis of the crystal structure of **9**, we show, for the first time, the different values of $\nu_b(CO)$ and $\nu_t(CO)$ in ketonyl complexes. Consequently, some reported solid-state structures of ketonyl complexes, based on IR data, should be revised. Thus, the complex $[Pd\{CH_2C(O)Me\}Cl(PPh_3)]_2$ was reported to contain acetonyl bridges in the solid state considering the lowering of the $\nu(CO)$ band to 1654 cm^{-1}, compared to that at 1685 cm^{-1} in the mononuclear complex $[Pd\{CH_2C(O)Me\}Cl(PPh_3)_2]$.[12] However, the absence of a band in the region of 1565−1530 cm^{-1} in the dinuclear complex[45] suggests that its structure in the solid state is a dimer with chloro bridges. In complexes formulated as O-enolates, $[Pd_3(\mu\text{-}Cl)_4\{OC(^tBu){=}CH^tBu\}_2(NCPh)_2]$ and [Pd(camphor-H)Cl]$_4$, the $\nu(CO)$ band was observed at 1650 and 1657 cm^{-1}, respectively.[30] However, considering our IR assignments and that authentic enolatopalladium(II) complexes show the $\nu(CO)$ band around 1500 cm^{-1},[19,20] these compounds should be formulated with terminal ketonyl ligands and not as enolato complexes.

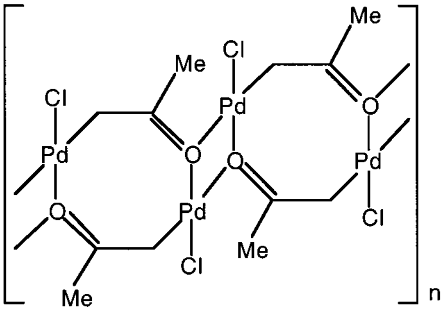
In agreement with the crystal structures of complexes **9** and **10** their IR spectra should show three and two $\nu(PdCl)$ bands, respectively. In the case of **9**, several bands in the 360−200 cm^{-1} region make difficult their assignments. However, complex **10** shows the expected two bands at 278 (m) and 250 (m) cm^{-1} assignable to $\nu_b(PdCl)$ trans to tht and $\nu_b(PdCl)$ trans to C, respectively (see Table 2). In the complex $[Pd\{CH_2C(O)Me\}Cl(PPh_3)]_2$ the corresponding bands appear at 279 and 262 cm^{-1}.[45] In complexes **2** and **5**−**7** one medium band in the 318−340 cm^{-1} region should be assigned to $\nu_t(PdCl)$ trans to N, whereas the band at 262 cm^{-1} in **3** has been assigned to $\nu_t(PdCl)$ trans to C.[12] The IR spectrum of **1** shows a band at 354 (m) cm^{-1} assignable to $\nu(PdCl)$ since it is not present in the iodo complex **4**. However, it is rather high with respect to the bands above assigned to $\nu_b(PdCl)$ or $\nu_t(PdCl)$ trans to C. Therefore, it should be assigned to $\nu_t(PdCl)$ trans to O. In fact, a band at 353 or 352 cm^{-1} has been assigned to $\nu_t(PdCl)$ trans to O in two different complexes.[46] In accord with this assignment, the structure of complex **1** has a terminal chloro ligand trans to O, and, consequently, each acetonyl ligand should occupy three coordination sites. In Scheme 4 we show a possible structure of **1** assuming that each oxygen atom is bridging two palladium atoms, similar to that observed in the crystal structure of $[Hg\{CH_2C(O)Me\}_2]$. The slightly low value of %C found in **1** (17.60%, required 18.11%) can be explained assuming that some metallic palladium or mercury is adsorbed by the polymer. However, this contamination does not affect the synthetic utility of **1**. Not unexpectedly, recrystallization from $MeCN/Et_2O$ led to **1** containing variable amounts of N, reasonably corresponding to two MeCN molecules required to complete the tetracoordination of the two palladium atoms at the extremes of the polymer. The maximum value of %N found in these recrystallized products was 0.54%, which corresponds to an average value of $n = 26$ in the formula $[Pd\{CH_2C(O)Me\}Cl]_n\cdot(MeCN)_2$.

Table 2. Assignments of $\nu(PdCl)$[a]

	1	2	3	5	6	7	8	9	10
$\nu_t(PdCl)_C$			262					b	
$\nu_t(PdCl)_{S\text{-}dmso}$							312		
$\nu_t(PdCl)_N$		318		328	334	340			
$\nu_t(PdCl)_O$	354								
$\nu_b(PdCl)_C$								b	250
$\nu_b(PdCl)_{S\text{-}dmso}$								b	
$\nu_b(PdCl)_{tht}$									278

[a] $\nu_b(PdCl)$ = Pd−Cl bridging stretching mode; $\nu_t(PdCl)$ = Pd−Cl terminal stretching mode; $\nu(PdCl)_E$ = Pd−Cl trans to E stretching mode. [b] See Results and Discussion.

Scheme 4



In agreement with the above IR assignments, the medium band at 312 cm^{-1} in the IR spectrum of **8** could neither be $\nu_t(PdCl)$ trans to C (∼262 cm^{-1})—hence excluding structures **A**−**C** in Scheme 3—nor $\nu_t(PdCl)$ trans to O-dmso (∼350 cm^{-1})—excluding structure **E**. Therefore, we tentatively propose structure **D** for complex **8** and assign the band at 312 cm^{-1} to $\nu_t(PdCl)$ trans to S-dmso (Table 2).

The two bands at 1142 and 1132 cm^{-1} observed in the IR spectrum of **9** can be assigned to $\nu(SO)$ of the

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two different dmso ligands. The IR spectrum of **8** shows a band at 1126 cm^{-1} assignable to the S-bonded dmso ligand (see **D** in Scheme 3). However, it is difficult to assign ν(SO) of the O-dmso ligand because of several bands appearing in the 1000−950 cm^{-1} region of the IR spectrum of **8**.

Conclusions

We report the synthesis of the simplest monoacetonylpalladium(II) complex, $[Pd\{CH_2C(O)Me\}Cl]_n$, obtained by transmetalation reactions using $[Hg\{CH_2C(O)Me\}_2]$ and $[PdCl_2(MeCN)_2]$ or $(Me_4N)_2[Pd_2Cl_6]$. We have shown that it can be used to prepare some of the already reported complexes as well as complexes with different bidentate chelating ligands and with dmso or tht. The use of these monodentate ligands affords new classes of acetonyl complexes, some of which have been postulated in solution but not isolated. The assignment of the band corresponding to the ν(CO) mode in a bridging ketonyl ligand is reported for the first time. We report the first crystal structures of acetonyl palladium(II) complexes.

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Note Added in Proof. During the correction of the galley proof of this article, a report appeared describing the synthesis of some acetonyl palladium(II) complexes (Ruiz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P.; Hitchcock, P. B. *Organometallics* **2001**, *20*, 1973). The IR data of these complexes support our proposal to distinguish terminal and bridging acetonyl ligands using the position of the band assigned to the ν(CO) mode. Some of our results were preliminarily communicated in a meeting on organometallic chemistry [XIX Reunión del Grupo Especializado de Química Organometálica, poster PB01; Valladolid (Spain), July 19−21, 2000].

Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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