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Synthesis and crystal structures of 3-alkyl-2,4-pentanedionates and 3-phenyl-2,4-pentanedionate of palladium

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ABSTRACT

A series of 3-substituted pentane-2,4-dionate complexes of palladium have been synthesized and characterized. These complexes are stable at room temperature in air; however, they slowly decompose in solution. The crystal structures of these complexes show that the palladium is square planar with respect to the two pentane-2,4-dionate ligands.

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POLYHEDRON

1. Introduction

The syntheses of metal derivatives of 1,3-diketones have been well studied [1]. These metal n, n + 2-dionate complexes can be synthesized using a variety of methods. Many different metals have been used and various β -dicarbonyl compounds have been employed to often give very brightly colored metal complexes. These metal dionate complexes exhibit a wide degree of physical and chemical properties, often with a lower degree of metal reactivity.

While the literature is rife with the use of β-dicarbonyl compounds with various groups attached to the terminal ends of the alkanedione chains, very few examples of 3-alkyl or 3-aryl substituted pentane-2,4-diones (acetylacetones or "acacs") are found [2,3]. One reason for the lack of literature on these types of complexes is due to hydrodeacylation of the 3-substituted β-diketone during formation of the complexes [2]. Hydrodeacylation is not observed with the unsubstituted pentane-2,4-dione. Puchberger investigated the synthesis of 3-ethylpentane-2,4-dione complexes with Al, Ti and Zr alkoxides. At low ligand to metal ratios (1 or 2 equivalents of 3-ethylpentane-2,4-dione to metal), a complex mixture of diacac complexes and hydrodeacylation products was formed. More hydrodeacylation products were obtained when Al(O–iPr)₄ was used compared to Ti and Zr alkoxides. At very high ratios of 3-ethylpentane-2,4-dione (5:1), hydrodeacylation was completely suppressed.

Our interest is in 3-substituted β -diketone complexes of palladium. There is only one example in the Cambridge Crystallographic Database of a 3-substututed pentane-2,4-dionate complex and this is of the 3-acetyl derivative (CCDC ID: 657358). (In this paper, only pentane-2,4-dionate or acac complexes are discussed. A future paper will deal with longer chain *n*, *n* + 2 dionates.) These complexes may be of value as homogeneous catalysts in non-polar organic solvents. Herein, we report the synthesis and structural characterization of a variety of palladium complexes with 3-substituted pentane-2,4-dionate ligands.

2. Experimental

2.1. General considerations

All chemicals were reagent grade and used without further purification. The proton and carbon NMR spectra were obtained on a Bruker INNOVA 400 MHz instrument. All elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

2.2. General procedure for the synthesis of palladium 3-alkyl-3acetylacetonate

Palladium(II) acetate, $[Pd(OAC)_2]_3$ (0.28 g, 1.25 mmol) was dissolved in a 5:1 mixture of acetone and water (30 mL). The 3-alkylacetylacetone (6.25 mmol) was dissolved in the acetone water mixture (10 mL) and slowly added to the orange palladium solution. The solution was stirred overnight to give a suspension of the product. The precipitate was filtered, washed with 5:1 acetone



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Table 1			
Crystallographic	data for	compounds	1-5.

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Compound	1	2	3	4	5
Formula	C ₁₂ H ₁₈ O ₄ Pd	C14H22O4Pd	C ₁₈ H ₃₀ O ₄ Pd	C ₂₂ H ₃₈ O ₄ Pd	C ₂₂ H ₂₂ O ₄ Pd
Formula weight	332.66	360.72	416.82	472.96	456.80
Crystal system	triclinic	orthorhombic	triclinic	triclinic	triclinic
Space group	ΡĪ	Pbca	ΡĪ	ΡĪ	ΡĪ
a (Å)	7.0243(5)	7.993(3)	4.9291(9)	4.9248(3)	7.3317(8)
b (Å)	7.528(3)	13.555(2)	7.9529(9)	7.9984(6)	7.7944(6)
c (Å)	7.7356(9)	13.274(3)	12.381(6)	14.6764(15)	17.044(8)
α (°)	61.08(3)	90	87.318(19)	92.683(7)	98.044(16)
β (°)	64.007(11)	90	85.29(2)	92.621(7)	90.789(18)
γ (°)	67.94(2)	90	73.943(13)	106.892(6)	96.224(8)
$V(\dot{A}^3)$	314.76(14)	1438.2(7)	464.7(2)	551.5(8)	958.3(4)
Ζ	1	4	1	1	2
ho (g cm ⁻³)	1.755	1.671	1.488	1.424	1.583
μ (Μο Κα)	1.474	1.297	1.014	0.864	0.993
F(000)	168	736	216	248	464
T (K)	100	100	100	100	100
Reflections (total)	3091	12087	3875	5773	10006
Reflections (unique), R _{int}	1811, 0.017	1794, 0.059	2601, 0.052	3197, 0.037	5531, 0.040
Index ranges	$-6\leqslant h\leqslant 9$	$-14 \leqslant h \leqslant 17$	$-6 \leqslant h \leqslant 5$	$-5\leqslant h\leqslant 6$	$-9 \leqslant h \leqslant 10$
	$-10 \leqslant k \leqslant 10$	$-10 \leqslant k \leqslant 10$	$-11 \leqslant k \leqslant 11$	$-11 \leqslant k \leqslant 11$	$-10 \leqslant k \leqslant 10$
	$-10 \leqslant l \leqslant 10$	$-17 \leqslant l \leqslant 18$	$-17 \leqslant l \leqslant 16$	$-20 \leqslant l \leqslant 20$	$-24 \leqslant l \leqslant 23$
Completeness to $2\theta = 60^{\circ}$ (%)	98.4	99.8	95.4	98.5	98.8
Goodness-of-fit (GOF)on F ²	1.059	1.004	1.017	1.012	0.940
$R_1, wR_2 [I > 2\sigma(I)]$	0.0190, 0.0478	0.0243, 0.0419	0.0530, 0.1252	0.089, 0.0740	0.0389, 0.0889
R_1, wR_2 (all data)	0.0193, 0.0479	0.068, 0.0433	0.0619, 0.1368	0.0422, 0.0726	0.0832, 0.0928

Table 2

Selected bond lengths (Å) and angles (°).

	1 (R = Me)	2 (R = Et)	3 (R = Bu)	4 (R = Hex)	5 (R = Ph) molecule a	5 (R = Ph) molecule b
$Pd-O_1$	1.9723(12)	1.9635(18)	1.973(2)	1.984(2)	1.981(2)	1.972(2)
$Pd-O_2$	1.9698(12)	1.9611(18)	1.9755(17)	1.9761(16)	1.966(2)	1.964(2)
O_1-Pd-O_2	87.04(5)	92.77(8)	93.60(8)	93.25(8)	92.69(10)	93.32(10)
$C_2-C_3-C_4$	123.07(14)	123.2(3)	123.1(2)	123.92(16)	123.4(3)	124.7(3)
$C_2-C_3-C_6$	118.66(15)	118.7(3)	118.9(2)	118.20(16)	120.1(3)	119.2(3)
$Pd-O_1-C_2-C_3$ $Pd-O_2-C_4-C_3$ $C_2-C_3-C_6-C_7$	-0.9(2) -1.1(2)	0.9(4) -3.0(4) 87.7(3)	-1.9(4) 1.0(3) 89.1(3)	2.1(2) -0.4(2) -89.7(2)	-2.5(5) 5.1(5) -87.2(4)	0.1(5) -0.2(5) 91.9(4)

water followed by water. The solid was dried to give a yellow or greenish yellow powder. All of the compounds appear to be quite stable in air at room temperature in the solid state. In protic solvents, the acac compounds all decompose rapidly (minutes to hours). In non-protic solvents, they slowly decompose over a period of days to weeks.

2.2.1. Synthesis of palladium 3-methyl-3-acetylacetonate (1)

Yield: (31%). Recrystallized from acetone. ¹H NMR (CDCl₃): δ 1.87 (s, 6H), 2.14 (s, 12H); ¹³C NMR (CDCl₃): δ 16.28, 26.15, 1003.97, 185.52.

2.2.2. Synthesis of palladium 3-ethyl-3-acetylacetonate (2)

Yield: (54%). Recrystallized from acetone. ¹H NMR (CDCl₃): δ 1.01 (t, *J* = 7.2 Hz, 6H), 2.16 (s, 12H), 2.30 (q, *J* = 7.2 Hz, 4H); ¹³C NMR (CDCl₃): δ 14.71, 23.57, 25.00, 111.27, 185.71.

2.2.3. Synthesis of palladium 3-butyl-3-acetylacetonate (3)

Yield: (41%). Recrystallized from acetone. ¹H NMR (CDCl₃): δ 0.93 (t, *J* = 6.8 Hz, 6H), 1.34 (m, 8H), 2.16 (s, 12H), 2.22 (t, *J* = 8 Hz, 4H); ¹³C NMR (CDCl₃): δ 13.83, 22.74, 25.21, 30.34, 32.81, 110.12, 185.83. ESI-MS: *m*/*z* 857.2287 [2M+Na]⁺. *Anal.* Calc. for C₁₈H₃₀O₄Pd: C, 51.86; H, 7.70. Found: C, 51.64; H, 7.09%.

2.2.4. Synthesis of palladium 3-hexyl-3-acetylacetonate (4)

Yield: (100%). Recrystallized from butanone. ¹H NMR (CDCl₃): δ 0.89 (t, *J* = 6.4 Hz, 6H), 1.30 (br m, 16H), 2.16 (s, 12H), 2.22 (m, 4H); ¹³C NMR (CDCl₃): δ 14.07, 22.70, 25.27, 29,41, 30.68, 31.63, 110.19, 185.87. ESI-MS: *m*/*z* 969.3615 [2M+Na+H]⁺.

2.2.5. Synthesis of palladium 3-phenyl-3-acetylacetonate (5)

Yield: (quantitative). Recrystallized from toluene. ¹H NMR (CDCl₃): δ 1.83 (s, 12H), 7.14 (d, *J* = 8 Hz, 4H), 7.36 (m, 6H); ¹³C NMR (CDCl₃): δ 26.92, 115.53, 127.25, 129.01, 131.60, 140.33, 186.19. ESI-MS: *m*/*z* 937.1089 [2M+Na]⁺. *Anal.* Calc. for C₂₂H₂₂O₄Pd: C, 57.84; H, 4.85. Found: C, 58.22; H, 4.87%.

2.3. X-ray structural determination

X-ray crystal structures were obtained using Mo K α ($\lambda = 0.710713$ Å) radiation at 100 K. The chosen crystal was mounted on a nylon CryoLoopTM (Hampton Research) with Krytox[®] Oil (DuPont) and centered on the goniometer of an Oxford Diffraction XcaliburTM diffractometer equipped with a Sapphire 3TM CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro [4]. Structure solution and refinement were performed with the graphical user interface WinGX [5]. The structure was solved by either by SIR92 [6] or SHELXS and refined using SHELX97 [7]. The final refinement model involved anisotropic displacement parameters for

non-hydrogen atoms and a riding model for all hydrogen atoms. The program package ORTEP-3 was used for molecular graphics generation [8]. Calculations of least square planes and angles between planes were accomplished using Mercury CSD 2.0 [9].

3. Results and discussion

3.1. Synthesis and characterization of compounds

A variety of methods for the synthesis of the 3-substituted pentanedionate (3-substituted acac) complexes of palladium was investigated. Direct reaction of PdCl₂ with 3-R-acac and base in a variety of aqueous and alcoholic solutions were unsuccessful due to the lack of solubility of the PdCl₂, and generally resulted in a black precipitate, that presumably was palladium or palladium oxide.



Fig. 1. Thermal ellipsoid plot for the 3-methyl derivative, 1.



Fig. 2. Thermal ellipsoid plot for the 3-ethyl derivative, 2.





The use of acetone soluble palladium acetate allowed for a reaction to take place with the 3-substituted acetylacetones while also providing an equivalent of base for the reaction. Furthermore, by using a 5:1 mixture of acetone to water, the reactions resulted in precipitates that could be filtered, washed and dried to give the essentially pure compounds **1–5**.

Each of the compounds was recrystallized from various aprotic solvents, such as acetone, hexane or toluene. However, upon sitting in these solvents for extended periods of time, a fine black precipitate was observed. All attempts to recrystallize complexes 1-5 from protic solvents, such as ethanol or methanol resulted in the deposition of palladium mirrors on the recrystallization vessel within 24 h. Chloroform-d solutions used to obtain NMR spectra resulted in palladium mirrors within 12 h of preparation. This suggests that the complexes are acid sensitive. Acid sensitivity may be explained by the increase in basicity of the 3-carbon atom in these 3-substituted β-diketones and therefore the greater propensity for the 3 carbon in the complex to be protonated and dissociate from the metal. Alkyl substitution on the α -position of β -diketones has been shown to increase the pK_a of the α -proton by at least 2 units, a phenomenon showed both experimentally and calculationally [10-12].

3.2. Crystal and molecular structures

The compounds **1–5** were analyzed by X-ray diffraction (Table 1) and selected bond lengths and angles for those compounds are reported in Table 2. Thermal ellipsoid plots showing the molecular structures of **1–**5 can be found in Figs. 1–5. In all cases but one, the 6-membered chelate rings in the Pd 3-substituted acetylacetonate complexes deviate only slightly from ideal planarity. The largest deviation from planarity in the alkyl complexes is found for R = ethyl and in that case C3 is 0.071 Å out of the plane defined by the palladium and the four coordinating oxygen atoms. This is consistent with that of the unsubstituted Pd(acac)₂ which crystallizes in the $P2_1/n$ space group [13]. Pd(acac)₂ was also found to have a O_1 -Pd- O_2 bond angle of 95.19(4)°. All of the 3-substituted



Fig. 3. Thermal ellipsoid plot of the 3-butyl derivative, 3.



Fig. 4. Thermal ellipsoid plot of the 3-hexyl derivative, 4.



Fig. 5. Thermal ellipsoid plot for the 3-phenyl derivative, 5, showing the two independent molecules in the unit cell. Hydrogen atoms omitted for clarity.



Fig. 6. Space filling model of the two independent molecules of bis-(acetylacetonate)palladium showing the angle and steric interaction between molecules.



Fig. 7. Space filling models showing a portion of the molecular packing for bis-(3-methylacetylacetonate)palladium, **2**.

compounds reported here have an O_1 -Pd- O_2 bond angle less than 94°, most likely due to steric strain of the substituent on C_3 .

Closer examination of compounds 1–5 shows that there is a profound effect of the R group on the crystal packing (and the space group) that in turn can have a subtle effect on some of the bond lengths and angles for the complexes. The parent unsubstituted acetylacetone complex of palladium (CCDC ID: 289749), crystallizes in $P2_1/n$ as mentioned above and there are two unique molecules in the unit cell. Each of the unique molecules pack in stacks as described in the literature reference but that paper ignores any steric effects imposed by the second stack of molecules that places two ends of the independent molecules very close to each other with an angle of approximately 74°. This potential negative steric interaction is not discussed by Mazhar and co-workers [13] but is very well illustrated in Fig. 6. Placement of a methyl group at the 3-position will put a significant "spacer" in this same type of packing motif and result in significant crystal void space were it to be followed. Instead, the 3-methyl derivative crystallizes in space group $P\bar{1}$ and the molecules stack in such a manner that each palladium atom sits atop the space between two molecules beneath it, above the two methyl groups, Fig. 7. The ethyl derivative is very interesting in terms of packing, but since it crystallizes in the much higher symmetry space group, Pbca, it is probably best not to include it in this particular comparison. Now, with the longer alkyl chains butyl and hexyl, the compounds both crystallize in P-1 but now the packing is characterized by what we dub "molecular spooning" dominated by alkyl side chain van der Waals interactions (Figs. 8 and 9). Another phenomenon that is most likely attributable to packing forces is that the C₃ alkyl chain is not perfectly orthogonal to the rest of the molecule, but is slightly bent from an imaginary Pd-C₃ axis by 16° for R = butyl and 12° for



Fig. 8. Space filling model showing a portion of the packing for bis(3-butylacetyl-acetonate)palladium, **3**.



Fig. 9. Space filling model of a portion of the molecular packing for bis-(3-hexylacetylacetonate)palladium, 4.



Fig. 10. Space filling model of a portion of the molecular packing for bis-(3-phenylacetylacetonate)palladium, **5**, showing the intermolecular interaction between unique molecules.

R = hexyl. Each of the compounds **1–4** has a $C_2-C_3-C_6$ bond angle less than the expected 120° if C_3 is sp² hybridized. So, examination of the crystal packing of the butyl and hexyl derivatives **3** and **4** shows that the alkyl chains of neighboring molecules pack together well. The flexibility of these chains allows for tighter packing and is probably responsible for the deviation from the Pd–C₃ axis.

The biggest anomaly in this regard is found for compound **5** where $R = C_6H_5$. In this case, there are two unique molecules per unit cell as is the case for the parent compound. For one of the

molecules, the adherence to planarity of the chelate ring is followed with the largest deviation involving C3 being 0.004 Å out of the plane. However, the second molecule in the unit cell is quite distorted with C2 and C4 being 0.188 and 0.179 Å out of the PdO₄ plane and C3 being 0.356 Å out of that plane. Examination of the crystal lattice of compound **5** suggests that this deviation comes from intermolecular interactions such as shown in Fig. 10 where the phenyl of one of the independent molecules impinges upon the end of the other molecule causing the observed out of plane distortion.

4. Conclusions

A series of 3-substituted acetylacetonate complexes of palladium have been synthesized and fully characterized including by X-ray crystallography. The crystallography of these compounds, especially in their different packing motifs, show a profound effect of the side chains on the intermolecular interactions which in turn have subtle effects on some bond lengths and angles. The important message is that these *intermolecular* interactions must be examined and analyzed before making any conclusions about bonding in the molecules themselves. These complexes are quite stable in the solid state as well as in non-protic organic solvents so long as they are protected from light. Their sensitivity to protic solvents may diminish their utility as catalysts, but they may be excellent catalyst precursors given the easy displacement of the substituted acac ligands.

Acknowledgments

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Appendix A. Supplementary data

CCDC 855244, 855242, 855241, 855245 and 855243 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/con-ts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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