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Formation of β-carbonylmethylpalladium(II) complexes and alkenones directly from ketones via C–H bond activation by the palladium(II) acetate–dialkyl sulfide system

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Abstract

Aliphatic C–H bond activation of some ketones by the $Pd(O_2CMe)_2$–SBu^i_2 system has been studied. Heating the system in acetone or t-butyl methyl ketone at 70 °C, and the following treatment of the resulting mixture with Me_2bipy (4,4′-dimethyl-2,2′-bipyridyl) and NaCl affords the β-carbonylmethylpalladium(II) complex $[PdCl(CH_2COR)(Me_2bipy)]$ (R = Me, Bu^t). In the case of the reaction in ethyl methyl ketone, the 2-butanonyl complex $[PdCl(CH_2COCH_2CH_3)(Me_2bipy)]$ is isolated, together with the formation of methyl vinyl ketone. On the contrary, for reactions in cyclopentanone and cyclohexanone, only the corresponding 2-cycloalken-1-ones are yielded. The relationship between the formation of β-carbonylmethyl complexes and alkenones has been discussed.

Introduction

Carbon–hydrogen bond activation of hydrocarbons is a subject undergoing current research in organometallic chemistry [1]. We have been investigating aromatic C–H bond activation by the palladium(II) acetate–dialkyl sulfide system and have found the system to be very active. The diaryltripalladium(II) complexes $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SR_2)_2]$ [2] and the cyclic tetranuclear palladium(II) complexes $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$ [3] have been obtained directly from aromatic hydrocarbons.

It was also of interest to examine the ability of the palladium(II) acetate–dialkyl sulfide system to activate aliphatic C–H bonds. At the beginning of this project, we chose dialkyl ketones as the aliphatic compounds, though they are not pure aliphatic hydrocarbons, the C–H bonds were slightly activated by the carbonyl group. This paper deals with the reactions of the above system with alkyl ketones, resulting in the formation of β-carbonylmethylpalladium(II) complexes and alkenones.

Experimental

All experiments were carried out under nitrogen unless noted otherwise. Solvents were dried by the usual methods and distilled. Other reagents were used without purification. The ^1H NMR spectra were measured on a JEOL JNM GX-270 instrument with $CDCl_3$ as solvent and are reported in δ (ppm) relative to tetramethylsilane. Yields of the acetoacetic acid esters and 2-cycloalken-1-ones were analyzed with a Shimadzu GC-14A gas chromatograph with a flame ionization detector on a BP-1 (50 m × 0.25 mm) capillary column. Melting points were determined on a Yanaco melting point apparatus MP-500D.

Preparation of β-carbonylmethylpalladium(II) complexes $[PdCl(CH_2COR)(Me_2bipy)]$ (1, R = Me; 2, R = Bu^t; 3, R = Et)

Complexes **1**–**3** were synthesized similarly. A typical example is as follows. A suspension of palladium(II) acetate (0.100 g, 0.445 mmol) and SBu^i_2 (0.043 g, 0.297 mmol) was heated in acetone (10 cm^3) at 70 °C for 1.5 h. Upon cooling to ambient temperature, solid Me_2bipy (0.082 g, 0.445 mmol) was added and the mixture was stirred for 5 h at room temperature. Then, sodium chloride (0.130 g, 2.23 mmol) in water (4 cm^3) was added and the mixture was stirred for 12 h at room temperature. The resulting mixture was evaporated to dryness and the residue was extracted with $CHCl_3$ (40 cm^3) to remove most of the by-product $[PdCl_2(Me_2bipy)]$. The extract was chromatographed on a silica gel column (200 mesh, 1.2 × 20 cm). The second yellow fraction eluted by $CHCl_3$ was collected and was recrystallized from CH_2Cl_2–hexane to give yellow crystals of **1**: yield 0.110 g, 47% based on

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$Pd(O_2CMe)_2$; m.p. 232 °C (decomp.). *Anal.* Found: C, 46.6; H, 4.5; N, 7.2. Calc. for $C_{15}H_{17}ClN_2OPd$: C, 47.0; H, 4.5; N, 7.3%. **2**: obtained as 1/4 benzene adduct; yield 14%; m.p. 233 °C (decomp.). *Anal.* Found: C, 52.5; H, 5.4; N, 6.1. Calc. for $C_{18.5}H_{24.5}ClN_2OPd$: C, 52.7; H, 5.6; N, 6.3%. **3**: obtained as 1/2 benzene adduct; yield 7%; m.p. 238 °C (decomp.). *Anal.* Found: C, 51.9; H, 5.0; N, 6.4. Calc. for $C_{19}H_{22}ClN_2OPd$: C, 52.3; H, 5.1; N, 6.4%.

Formation of methyl vinyl ketone in the reaction mixture obtained by the reaction between the system and ethyl methyl ketone was confirmed by measuring the ^1H NMR spectrum ($CDCl_3$) of the supernatant solution. In this spectrum, vinyl protons were observed as 12 lines at δ 5.90, 5.91, 5.939, 5.944, 6.16, 6.17, 6.23, 6.24, 6.28, 6.32, 6.35 and 6.39, and methyl protons resonated at δ 2.29, which were quite similar to the authentic sample.

Reactions of the acetonylpalladium(II) complex with carbon monoxide in alcohol

An acetone (10 cm^3) suspension containing palladium(II) acetate (0.100 g, 0.445 mmol) and SBu^i_2 (0.043 g, 0.297 mmol) was heated at 70 °C for 1.5 h and then the resulting mixture was cooled to room temperature. Ethanol (5 cm^3) was introduced and then carbon monoxide was bubbled through the mixture for 1 h. Yield of ethyl acetoacetate determined by GLC was 30% based on the starting palladium(II) acetate. Similarly, by the reaction of carbon monoxide in methanol, methyl acetoacetate was obtained in 23% yield.

Reactions of palladium(II) acetate–diisobutyl sulfide system with cyclic ketones

Reactions were performed under nitrogen or oxygen atmosphere. A typical example is as follows. A suspension of palladium(II) acetate (0.050 g, 0.223 mmol) and SBu^i_2 (0.022 g, 0.148 mmol) was heated in cyclopentanone (5 cm^3) at 70–75 °C for 1.5 h. The yield of 2-cyclopenten-1-one determined by GLC was 74% based on palladium(II) acetate. The ^1H NMR spectrum ($CDCl_3$) of the reaction mixture exhibited olefinic resonances near δ 6.2 and 7.8 as multiplets which were identical with those of the authentic sample, but showed no signals near δ 6.1 (measured in neat) [4] due to the olefinic protons of 3-cyclopenten-1-one. Similarly, the ^1H NMR spectrum of the reaction mixture obtained by the reaction with cyclohexanone showed signals due to 2-cyclohexen-1-one (near δ 6.0 and 7.0, identical with the authentic sample), but the resonance due to 3-cyclohexen-1-one (near δ 5.8 in CCl_4 [5]) was not observed.

Results and discussion

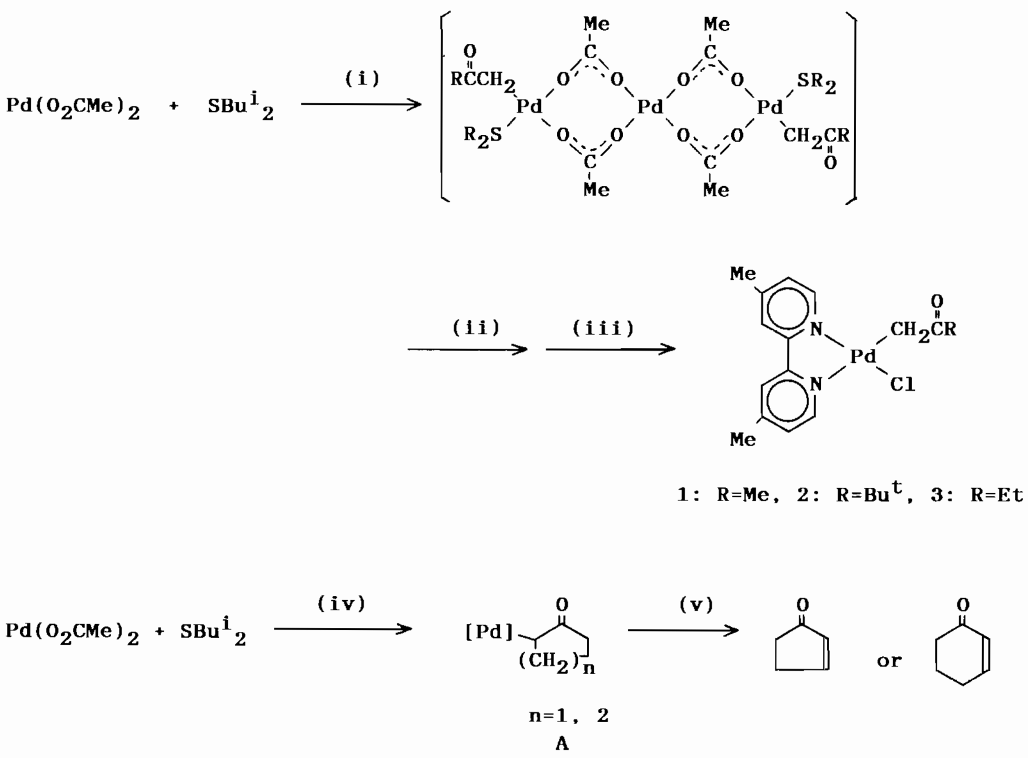
Reaction of the $Pd(O_2CMe)_2$–SBu^i_2 system with linear ketones, acetone, t-butyl methyl ketone and ethyl methyl ketone

A mixture containing palladium(II) acetate and diisobutyl sulfide in a molar ratio of 1:2/3 was heated in acetone at 70 °C to give 'a pale brown solution', from which only intractable 'oil' was obtained after reprecipitation with hexane. However, a bridge splitting reaction of 'the oil' or 'the pale brown solution' with Me_2bipy (4,4′-dimethyl-2,2′-bipyridyl) and subsequent ligand exchange reaction of the acetato ligand with Cl^- performed by NaCl afforded yellow crystals of **1** (47% yield) (Scheme 1). The ^1H NMR spectrum of **1** exhibited signals at δ 2.91 and 2.38 assignable to methylene and methyl protons, respectively, together with characteristic resonances due to the Me_2bipy ligand (Table 1). In the $^{13}C\{^1H\}$ NMR spectrum (Table 2), resonances due to the Me_2bipy ligand appeared as 12 signals, in addition to methyl (δ 30.65), methylene (δ 25.04) and carbonyl carbon (δ 213.73). On the basis of these results and the elemental analysis, **1** was assigned as the acetonylpalladium(II) complex $[PdCl(CH_2COCH_3)(Me_2bipy)]$. It is noteworthy that **1** was obtained only in low yield when SPr^i_2 (trace) and SEt_2 were used instead of SBu^i_2.

Moreover, formation of ethyl acetoacetate (30% yield) or methyl acetoacetate (23% yield) was confirmed (GLC analysis) in the reaction mixture, obtained by the reaction of the initial 'yellow brown solution' with ethanol (or methanol) and carbon monoxide. This fact and the isolation of **1** clearly indicate that in the initial 'pale brown solution' acetonylpalladium species are formed.

On the contrary, in the absence of diisobutyl sulfide, the yield of **1** was very low (2%). These results indicate that the $Pd(O_2CMe)_2$–SBu^i_2 system activates the aliphatic C–H bond of acetone much more easily than palladium(II) acetate alone; in other words the additive diisobutyl sulfide enhanced the ability of palladium(II) acetate to activate the C–H bond. The aliphatic C–H bond activation of ketones has already been achieved by Pt(0) [6], Pt(II) [7], Fe(0) [8], Ru(0) [8] and Ir(I) [9] species. These reactions proceed by oxidative addition (nucleophilic process) of the C–H bond in ketones to coordinatively unsaturated metal complexes, which are photochemically or thermally generated. However, in the case of the $Pd(O_2CMe)_2$–SBu^i_2 system reaction is supposed to proceed by an electrophilic process [10].

The structure of the acetonylpalladium(II) species was difficult to judge only from the ^1H NMR spectrum of 'the oil'. The yield of **1** was highest (47%) when the molar ratio of $Pd(O_2CMe)_2$:SBu^i_2 was 1:2/3, while lower yields were obtained at the molar ratios of 1:2 (20%) and 1:1 (21%). On the basis of these results



Scheme 1. Reactions of the Pd($O_2CMe)_2$-SBu$^i_2$ system with ketones: (i) linear ketones, 70 °C, 1.5 h; (ii) Me$_2$bipy, r.t.; (iii) NaCl, r.t.; (iv) cyclic ketones, 70–75 °C, 1.5 h; (v) β-elimination.

TABLE 1. ^{1}H NMR and IR spectra of **1**–**3**

Complex	^{1}H NMR[a]							IR (cm^{-1})[b]	
	β-carbonylmethyl group			Me$_2$bipy				ν(C=O)[c]	ν(C=N)[d]
	PdCH$_2$	CH$_2$	CH$_3$	CH$_3$	3 or 3′	5 or 5′	6 or 6′		
1	2.91s		2.38s	2.53s 2.54s	7.83br[e]	7.31dd[f] 7.35dd[g]	9.02d[h] 9.20d[i]	1635	1610
2[j]	2.97s		1.35s	2.52s[e]	7.83br[e]	7.29dd[f] 7.36dd[g]	9.09d[h] 9.32d[i]	1625	1615
3[j]	2.91s	2.78q[k]	1.10t[k]	2.53s[e]	7.81br[e]	7.30dd[f] 7.35dd[g]	9.00d[h] 9.27d[i]	1620	1615

[a] Recorded at 270 MHz in CDCl$_3$ at 25 °C. δ value from TMS: s = singlet, d = doublet, dd = double doublets, t = triplet, q = quartet, br = broad. [b] In KBr. [c] In β-carbonylmethyl moiety. [d] In Me$_2$bipy ligand. [e] Overlapping signal. [f] $J = 5.4$, 1.0 Hz. [g] $J = 5.9$, 1.0 Hz. [h] $J = 5.9$ Hz. [i] $J = 5.4$ Hz. [j] Benzene was detected at δ 7.36 s. [k] $J = 7.3$ Hz.

and the isolation of trinuclear complexes [(R_2S)ArPd(μ-$O_2CMe)_2$Pd(μ-$O_2CMe)_2$PdAr(SR_2)] in the case of the aromatic C–H bond activation by the Pd($O_2CMe)_2$–SR_2 system [2], it is most plausible that the acetonylpalladium(II) complex present in the 'pale brown solution' has a trinuclear structure, [(Bu$^i_2$S)(CH_3COCH_2)Pd(μ-$O_2CMe)_2$Pd(μ-$O_2CMe)_2$Pd(CH_2COCH_3)(SBu$^i_2$)].

t-Butyl methyl ketone also afforded yellow crystals of [PdCl(CH_2COBu^t)(Me$_2$bipy)] (**2**), by reaction with the Pd($O_2CMe)_2$–SBu$^i_2$ system, followed by treatment with Me$_2$bipy and NaCl. On the contrary, when the reaction of the system with ethyl methyl ketone was performed, the reaction mixture turned almost black with accompanying precipitation of considerable amounts of palladium black. The ^{1}H NMR spectrum of the supernatant solution of the reaction mixture showed the presence of methyl vinyl ketone. It is reasonable to assume that this compound was formed by the subsequent β-hydrogen elimination of the initial reaction product, '$PdCH_2CH_2COMe$' and/or 'Pd-CHMeCOMe'. However, the yield of methyl vinyl ketone could not be measured even by GLC analysis, owing to the similarity of the boiling points of methyl vinyl ketone (b.p. 81.4 °C) [11] and ethyl methyl ketone (b.p.

TABLE 2. $^{13}C\{^1H\}$ NMR spectra[a] of **1**–**3**

Complex	β-carbonylmethyl group					Me_2bipy					
	$PdCH_2$	C=O	CH_2	CH_3	C	CH_3	2 or 2′	3 or 3′	4 or 4′	5 or 5′	6 or 6′
1	25.04	213.73	^{c}	30.65	^{c}	21.54	153.52	127.04	150.91	122.08	148.98
						21.68	156.11	127.61	151.18	122.72	151.57
2^{b}	15.75	^{c}	^{c}	28.77	43.81	21.51	153.63	126.91	150.74	122.08	149.07
						21.64	156.06	127.57	150.98	122.72	152.15
3^{b}	24.00	216.88	35.72	9.62	^{c}	21.54	153.49	126.99	150.90	122.17	149.07
						24.68	156.06	127.56	151.17	122.80	152.15

[a] Recorded at 67.5 MHz at 30 °C in $CDCl_3$. δ value from TMS. [b] Solvated benzene was observed at δ 128.33. [c] Not detected.

TABLE 3. Yields of 2-cycloalken-1-one[a]

Product	Run no.	Yield (%)[b]	Atmosphere
2-Cyclopenten-1-one	1^{c}	20	N_2
	2	74	N_2
	3	413	O_2
2-Cyclohexen-1-one	4^{c}	trace	N_2
	5	32	N_2
	6	371	O_2

[a] Reaction conditions: $Pd(O_2CMe)_2$, 50 mg (0.223 mmol); SBu^i_2, 2/3 molar equivalent to $Pd(O_2CMe)_2$; cycloalkanone 5.0 cm^3; 70 °C for 1.5 h. [b] Determined by GLC and calculated based on $Pd(O_2CMe)_2$. [c] Absence of SBu^i_2.

79.6 °C) [11]. At the same time, from the resulting mixture, a small amount (yield 7%) of $[PdCl(CH_2COEt)(Me_2bipy)]$ (**3**) was isolated after the following reactions with Me_2bipy and NaCl. The presence of the isomer $[PdCl(CH_2CMe_2COMe)(Me_2bipy)]$ was excluded on the basis of both ^1H and $^{13}C\{^1H\}$ NMR measurements.

The carbonyl stretching frequencies for the β-carbonylmethyl complexes **1**–**3** (Table 1) fall in the range 1635–1620 cm^{-1}. These values were lower than the value (1680 cm^{-1}) in the anionic complex $[PtCl_4(CH_2COCH_3)(NH_3)]NH_4$ [7], but were similar to the value (1620 cm^{-1}) in $[Pt(CH_2COCH_3)(cyclohexenyl)(Ph_2PCH_2CH_2PPh_2)_2]$ [6]. Bennett *et al.* analyzed the structure of the latter complex by X-ray crystallography, and concluded the absence of interaction between the carbonyl group and platinum atom. Furthermore, in the *ortho*-ruthenated complexes of di(*p*-tolyl)ketone, $[RuCH_3C_6H_3COC_6H_4CH_3)Cl(CO)L_2]$ (L = PMe_2Ph and $AsMe_2Ph$), where the carbonyl group is bonded to the ruthenium atom, ν(CO) frequencies were observed at a much lower wavenumber, around 1580 cm^{-1} [12]. Taking these facts into consideration, it seems probable there is no interaction between the carbonyl group and palladium atom in **1**–**3**.

Reactions of the $Pd(O_2CMe)_2$–SBu^i_2 system with cyclic ketones, cyclopentanone and cyclohexanone

The reactions of the system with the cyclic ketones at 70–75 °C proceeded very rapidly accompanied by precipitation of metallic palladium. From the resulting mixture no reasonable amount of the complexes could be isolated, but the formation of cycloalkenones was detected by GLC analyses (Table 3). The ^1H NMR spectra revealed that the reaction mixtures contained only 2-cycloalken-1-ones and excluded the presence of the isomer 3-cycloalken-1-ones. Palladium(II) acetate alone reacted with cyclopentanone to produce 2-cyclopenten-1-one in 20% yield under nitrogen atmosphere, while with cyclohexanone it afforded only a trace amount of 2-cyclohexen-1-one (Table 3, run nos. 1 and 4). On the contrary, when the same reactions were performed in the presence of SBu^i_2, the yields of 2-cyclopenten-1-one and 2-cyclohexen-1-one increased up to 74 and 32%, respectively (Table 3, run nos. 2 and 5). Moreover, under oxygen atmosphere the yields were over 100% (Table 3, run nos. 3 and 6), implying that the system acts as a catalyst. Such an effect of oxygen was also observed for the synthesis of biphenyl by the system with benzene [13].

The formation of 2-cycloalken-1-ones is supposed to be achieved by β-hydrogen elimination of the 2-cycloalkanonyl complex **A** (Scheme 1) which was formed by the system via activation of the C–H bond at the most activated α position of the carbonyl group.

Conclusions

With the aid of diisobutyl sulfide, palladium(II) acetate activates the aliphatic C–H bond of ketones easily to afford alkanonylpalladium(II) complexes. When the alkanonyl species have no β-hydrogen, stable β-carbonylmethylpalladium(II) complexes **1**–**3** have been isolated. In the cases when the alkanonyl complexes have a β-hydrogen, such as the products of the reactions of cyclopentanone and cyclohexanone, the β-hydrogen elimination reaction easily occurs and the corresponding 2-cycloalken-1-ones are formed. This dehydrogenation reaction proceeds catalytically under oxygen atmosphere. However, the role of the added diisobutyl sulfide in the C–H bond activation of the alkyl group in ketones is not clear at this stage, and must be further investigated.

In conclusion, this study revealed that the $Pd(O_2CMe)_2$–SBu^i_2 system can activate the C–H bond of aliphatic compounds as well as aromatic compounds.

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