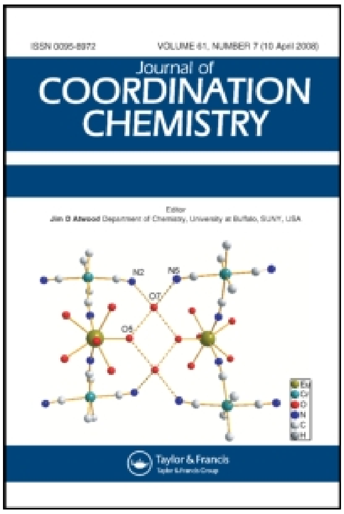

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Synthesis and characterization of η^3-allyl palladium(II) complexes, $[(\eta^3\text{-allyl})Pd(S_2X)]$ ($X = CNMe_2$, $CNEt_2$, COEt, PPh_2)

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The complexes $[(\eta^3\text{-}C_6H_9)Pd(\eta^2\text{-}S_2CNR_2)]$ ($R = Me$, **1**; Et, **2**), $[(\eta^3\text{-}Me_2CCMeCH_2)Pd(\eta^2\text{-}S_2COEt)]$ **3** and $[(\eta^3\text{-}Me_2CCMeCH_2)Pd(\eta^2\text{-}S_2PPh_2)]$ **4** have been synthesized by reaction of $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ with NaS_2CNR_2 ($R = Me$, Et), KS_2COEt and NaS_2PPh_2. They have been characterized by elemental analysis, FTIR, ^1H NMR and FAB mass spectrometry. Spectroscopic studies suggest that sulfur donor ligands are bidentate, forming Pd–S–C–S and Pd–S–P–S palladacycles, an η^3-allyl group completing the coordination sphere.

Keywords: Allyl; Palladium; Dithiocarbamate; Dithiophosphinate; Xanthate

1. Introduction

η^3-Allyl complexes of palladium(II) and nickel(II) with bidentate chelating ligands have been widely reported in the literature [1]. Reaction of bridged $[(\eta^3\text{-allyl})Pd(\mu\text{-}X)]_2$ complexes with the anion of a bidentate chelating agent may result in monomeric products as in the case of dithiocarbamate [2,3] and xanthate [4] complexes. Halide exchange reactions also result in the formation of the monomeric ketoamine η^3-allyl palladium complexes [5], and amino acid complexes $[Pd(\eta^3\text{-}C_3H_5)(AA)]$ (AA = glycinato) [6] have also been reported. As studies of the reactions of η^3-allylic palladium(II) complexes containing anionic chelate ligands with unsaturated hydrocarbons suggest that such complexes may be useful for a variety of organic syntheses and as model systems for catalytic reactions, we considered it worthwhile to synthesize some η^3-allyl complexes of palladium(II) with dithiocarbamate, xanthate and dithiophosphinate as potentially bidentate chelating agents [7–9]. In this paper, the

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preparation of a series of palladium complexes, $[(\eta^3\text{-}C_6H_9)Pd(\eta^2\text{-}S_2CNR_2)]$ (R = Me, **1**; Et, **2**), $[(\eta^3\text{-}Me_2CCMeCH_2)Pd(\eta^2\text{-}S_2COEt)]$ **3** and $[(\eta^3\text{-}Me_2CCMeCH_2)Pd(\eta^2\text{-}S_2PPh_2)]$ **4**, is reported. They have been characterized by elemental analysis, FTIR, ^{1}H NMR and FAB mass spectrometry. Spectroscopic studies suggest that sulfur donor ligands are bidentate, forming Pd–S–C–S and Pd–S–P–S palladacycles, an η^3-allyl group completing the coordination sphere.

2. Experimental

2.1. *Materials*

Allyl complexes $[(\eta^3\text{-}C_6H_9)Pd(\mu\text{-}Cl)]_2$ and $[(\eta^3\text{-}Me_2CCMeCH_2)Pd(\mu\text{-}Cl)]_2$ were prepared according to published methods [10]. All sulfur donor ligands were supplied by Sigma-Aldrich or Merck.

2.2. *Apparatus*

All solvents were dried and degassed using standard techniques [11]. Elemental analyses were performed on a Carlo Erba 1106 instrument. IR spectra were measured using KBr disks on a Perkin Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra ($CDCl_3$ solutions) were recorded using a Bruker FX400 FT spectrometer and chemical shifts are reported relative to TMS as internal reference. All chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. Positive-ion FAB mass spectra were recorded on a JEOL SX102 spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using 3 keV xenon atoms.

2.3. *Preparation of complexes*

η^3-Allylic palladium complexes **1–4** were isolated in moderate yields by reaction of the corresponding allylpalladium chloride complex with the appropriate sodium dialkyldithiocarbamate, potassium ethylxanthate and sodium diphenyldithiophosphinate salt. The following procedure is typical. A methanol solution (10 cm^3) of $NaS_2CNMe_2 \cdot 3H_2O$ (0.14 g, 0.83 mmol) was added dropwise to diethylether solution (10 cm^3) of $[Pd(\eta^3\text{-}C_6H_9)(\mu\text{-}Cl)]_2$ (0.22 g, 0.50 mmol) and the mixture stirred at room temperature for 3 h. After this time, volatiles were removed under reduced pressure to yield a sticky solid, which was dissolved in Et_2O and washed with water (3×10 cm^3) and dried over $MgSO_4$. The solution was filtered off and evaporated to give $[(\eta^3\text{-}C_6H_9)Pd(\eta^2\text{-}S_2CNMe_2)]$, **1**, as a yellow oil (0.27 g, 78%). Yields and appearance of other complexes are given in table 1.

3. Results and discussion

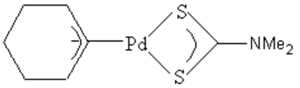
Treatment of $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ with two equivalents of sodium or potassium salts of dithiolate ligands at room temperature gave mononuclear complexes of the type $[(\eta^3\text{-allyl})Pd(\eta^2\text{-dithiolate})]$ **1–4**. Syntheses were straightforward and all complexes were prepared in good yield. Dithiocarbamate complexes were obtained as brown

Table 1. Yields and elemental analyses for **1**–**4**.

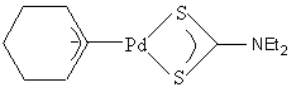
Complex	Yield (%)	Found (calcd.) (%)		
		C	H	S
1[a]	78			
2[a]	64			
3[b]	72	34.48 (34.79)	5.10 (5.15)	20.60 (20.62)
4[b]	74	49.22 (49.27)	4.70 (4.79)	14.40 (14.60)

[a] Light brown liquid. [b] Yellow solid.

oils and satisfactory elemental analysis data could not be obtained. The xanthate and dithiophosphinate complexes were yellow solids. There is no simple correlation between reaction yields and the nature of the substituents on the allyl ligands. The least stable complexes are the cyclohexenyl derivatives **1** and **2**, which decompose in solution over a period of about 1 week. By contrast, the others can be stored for long periods at room temperature. All have been characterized by IR, ^{1}H NMR spectroscopy and mass spectrometry (tables 2–4).



1



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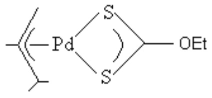

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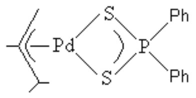


4

Assignments of IR spectra (table 2) were made by reference to literature data on related complexes. As the allyl group is η^3-bonded to the metal, no C=C stretching band is observed in the 1580 to 1600 cm^{-1} region [12,13]. Instead, three bands of medium or strong intensity are observed at 1510 to 1375 cm^{-1}. In the low-frequency region, metal–olefin vibrations appear in the range 570 to 320 cm^{-1}. Allyl group stretching frequencies for **1**–**4** are in good agreement with literature data [14]. The difference between the asymmetric and symmetric stretching vibrations of ν(CS) and ν(PS) may be indicative of the coordination mode of the ligand. Bidentate coordination gives a single band for ν(CS) and ν(PS), whereas the unidentate mode shows a doublet in the same region [12–14]. The single absorption band, which is attributed to ν(CS) at 966 and 988 cm^{-1}, indicates bidentate behavior of the dithiocarbamates in **1** and **2**, respectively. IR spectra of **1** and **2** also contain characteristic bands in the regions 1500–1525 and 965–990 cm^{-1}, which are assigned to (C=N) and (C–S) stretching modes, respectively. Interesting trends in ν(C=N) stretching frequencies as a function of the alkyl group of the dithiocarbamate ligands are evident for **1** and **2**; ν(C=N) decreases as Me$_2$ > Et$_2$. IR spectra of **3** exhibit bands characteristic of a bidentate xanthate ligand at 1111 and 1229 cm^{-1}, these being attributed to C–O stretching,

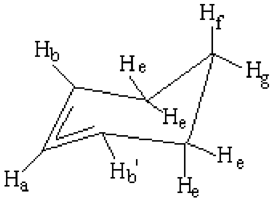
Table 2. Selected IR data (cm^{-1}) for **1**–**4**.

Complex	ν(η-allyl)	ν(CN)	ν(CS)	ν(CO)	ν(PS)
1	1450 m, 1375 s, 1350 m	1530vs	966 s		
2	1460 m, 1382 s, 1346 m	1525vs	988 s		
3	1455 m, 1376 s, 1345 m		1024 s	1111 s, 1229 s	
4	1467 m, 1380 s, 1350 m				586 s

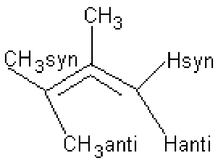
m, medium; s, sharp; vs, very sharp.

Table 3. ^1H NMR data for compounds **1**–**4** in $CDCl_3$ (ppm).

a



b



a: (η^3-$CH_bCH_aCH_{b'}CH_eH_eCH_fH_gCH_eH_e$)

	H_g	$H_e + H_f$	$H_b +\ H_{b'}$	H_a	CH_3	CH_2CH_3 (italic CH_3)	CH_2CH_3 (italic CH_2)
1	1.09 m	1.78–1.86 m	5.17 m	5.50 m	3.35 s		
2	1.08 m	1.76–1.85 m	5.17 m	5.50 m		1.25 t ($J^3_{HH} = 7.2$)	3.77 q ($J^3_{HH} = 7.2$)

b: (η^3-$Me_2CCMeCH_2$)

	Me_{ant}	Me_{syn}	$Me_{central}$	H_{anti}	H_{syn}	OCH_2CH_3	OCH_2CH_3	$S_2P(C_6H_5)_2$
3	1.35 s	1.72 s	1.93 s	3.00 s	3.79 s	1.40 t ($J^3_{HH} = 7.1$)	4.57 q ($J^3_{HH} = 7.1$)	
4	1.24 s	1.59 s	1.92 s	3.03 s	3.69 s			7.38–7.87 m

m, multiplet; s, singlet; t, triplet; q, quartet.

Table 4. Mass spectroscopic data for **1**–**4**.

Complex	MW	Relative intensities of the ions, m/e, and assignment[a]
1	307	307(6), [M^+], [Pd(S_2CNMe_2)(allyl)]; 289(6), 165(4), 154(100), 136(65), 120(10), 107(17)
2	335	591(7), [$Pd_2(S_2CNEt_2)_2$(allyl)]; 402(12), [$Pd(S_2CNEt_2)_2$]; 335(3), [M^+], [Pd(S_2CNEt_2)(allyl)]; 254(12), [Pd(S_2CNEt_2)]; 187(3), [Pd(allyl)]; 116(95), 86(100), (allyl); 57(25), (CNEt)
3	310	310(8), [M^+], [Pd(S_2COEt)(allyl)]; 292(90); 266(35); 177(100)
4	437	437(3), [M^+], [Pd(S_2PPh_2)(allyl)]; 355(15), [Pd(S_2PPh_2)]; 301(100); 266(60); 189(18), [Pd(allyl)]; 153(20)

[a] Relative intensities are given in parentheses; probable assignments are shown in square brackets. For all assignments, the most abundant isotope of Pd has been selected (^{106}Pd, 27.5% abundance).

while the strong band at $1024\,\mathrm{cm}^{-1}$ results from the ν(C–S) vibration. Absorption at $586\,\mathrm{cm}^{-1}$ in **4** is most likely due to P–S stretching and is consistent with bidentate coordination of S_2PPh_2. The ν(Pd–S) and ν(Pd–allyl) stretching vibrations overlap in the 300 to $500\,\mathrm{cm}^{-1}$ region, making unambiguous assignment impossible.

^{1}H NMR spectroscopy is an extremely powerful method for the elucidation of the structure and dynamic behavior of allyl palladium species in solution. All compounds gave good ^{1}H NMR spectra (table 3). ^{1}H NMR assignments were made in accordance with previous publications [12–14]. NMR spectra of **1** and **2** exhibit the expected resonances considering the symmetry of the allyl and dialkyldithiocarbamate groups. In both, there are four resonances with intensity ratio of 1 : 5 : 2 : 1 assigned to $H_g : H_e + H_f : H_b + H_{b'} : H_a$ of the cyclohexenyl group; chemical shifts are essentially invariant with different dithiocarbamate substituents. Methyl and methylene proton signals of the dithiocarbamate ligands are consistent with bidentate coordination of the ligand. In ^{1}H NMR spectra of **3** and **4**, there are five resonances with intensity ratio 3 : 3 : 3 : 1 : 1, assigned to Me_{anti}, Me_{syn}, $\mathrm{Me}_{central}$ and H_{anti}, H_{syn} protons of the 1,1,2-trimethylallyl ligand. All are singlets, appearing slightly upfield of the corresponding allyl protons of $[(\eta^3\text{-Me}_2\text{CCMeCH}_2)\text{Pd}(\mu\text{-Cl})]_2$ [10]. The Me_{anti} and H_{anti} resonances are at higher field than the *syn* analogues, because Me_{anti} and H_{anti} are nearer the metal and consequently more shielded.

Mass spectroscopy data for **1**–**4** are given in table 4. All complexes show molecular ion peaks. Mass spectra of **1** and **2** also show peaks assigned to the binuclear species $[\text{Pd}_2(\text{allyl})_2(\text{S}_2\text{CNR}_2)]$ and $[\text{Pd}_2(\text{allyl})(\text{S}_2\text{CNR}_2)_2]$ (R = Me, Et), showing the bridging ability of the dithiocarbamate ligand as mentioned previously [15]. All complexes show quite distinctive fragmentation patterns.

4. Conclusion

In summary, sulfur donor ligands, methyl- and ethyldithiocarbamato in **1** and **2**, ethylxanthato in **3** and diphenyldithiophosphinato in **4**, are bidentate, forming Pd–S–C–S and Pd–S–P–S palladacycles; an η^3-allyl group, cyclohexenyl and 1,1,2-trimethylallyl groups complete the coordination sphere.

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