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Note

Palladium(II) phosphine thiocarboxylates. Structures of *cis*-Pd(κ*S*-SOCMe)$_2$(dppf) [dppf = 1,1′-bis(diphenylphosphino)ferrocene] and *trans*-Pd(κ*S*-SOCMe)$_2$(PPh$_3$)$_2$

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Abstract

Although palladium phosphine acetates are generally unstable and served as catalytic precursors, their monothioacetate analogues can be isolated and structurally characterized. Spectroscopic and X-ray single-crystal crystallographic analyses suggested that Pd(κ*S*-S{O}CMe)$_2$(P$_2$) [P$_2$ = dppf, **I**; P = PPh$_3$, **II**] are mononuclear with thioacetate coordinates in a unidentate manner through sulfur. Dppf imposes a *cis* configuration on **I** whereas PPh$_3$ promotes a *trans*-structure for **II**. The compounds are obtained in isomerically pure form—there is no evidence for chelating or bridging thioacetate or bridging diphosphine. The Me group of thioacetate is significantly more shielded in **II** than **I** by the Ph rings of the neighboring phosphine.

Keywords: Palladium; Ferrocenylene phosphine; Thioacetate; Diphosphine

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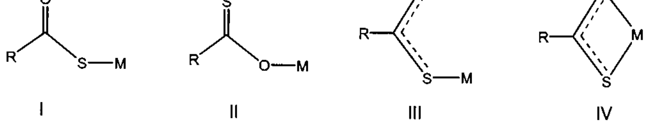
1. Introduction

Monothiocarboxylate, RC{O}S$^-$, is a interesting class of ligands. With both soft (S) and hard (O) binding sites, it shows diverse bonding modes [1,2] and the ability to stabilize a range of homonuclear [3,4] and heterometallic [5] systems of both early and late metals. Among the monothiocarboxylates, thioacetate [1,4,6–8] and thiobenzoate [1–5,8–10] have received most attention. Their coordination commonly takes the following forms shown in Scheme 1.



Scheme 1.

It is therefore surprising that metal thiocarboxylates have been relatively unexplored compared to that of their thiolate, thiocarbamate and dithiocarboxylates counterparts [1]. Palladium phosphine carboxylates are active catalyst precursors especially in Heck-type reactions [11]. Their ready decomposition to Pd(0) species and its relationship to the electronic and molecular structure of the complex as well as the catalytic mechanism is a subject of contemporary interest [12]. In this paper, we examine two thiocarboxylate analogues of this system in an attempt to understand its structural behavior. The choice of monothiocarboxylate as a model is logical due to its resemblence to carboxylates and the higher stability it brings to the Pd(II) system. Two representative phosphines are chosen—PPh$_3$, which is commonly use as a stabilizer in the catalytic system, and Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$ [dppf], whose catalytic function is a subject of our recent review [13].

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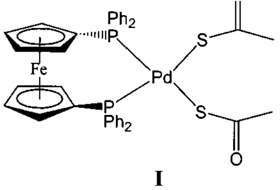
Table 1
IR and NMR spectroscopic data of Pd(κ*S*-S{O}CMe)$_2$(dppf) (**I**) and *trans*-Pd(S{O}CMe)$_2$(PPh$_3$)$_2$ (**II**)

Complex	ν(C=O) cm^{-1}	ν(C–S) cm^{-1}	δ_H (ppm)	δ_P (ppm)
I	1614 vs	947 s	1.87 (s, Me, 6H); 4.29 (dd, Cp–H$_\alpha$, 4H); $^3J_{HH}$ = 1.60 Hz; $^3J_{HP}$ = 1.60 Hz; 4.31 (d, Cp–H$_\beta$, 4H); $^3J_{HH}$ = 1.60 Hz; 7.34–7.40 (m, Ph, 8H); 7.41–7.48 (m, Ph, 4H); 7.80–7.88 (m, Ph, 8H)	25.75 (s)
II	1620 vs	948 s	1.33 (s, Me, 6H); 7.32–7.43 (m, Ph, 18H); 7.71–7.79 (m, Ph, 12H)	28.79 (s)

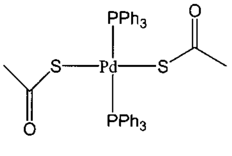
IR spectra were recorded in KBr and NMR in CDCl$_3$.

2. Results and discussion

Although metathesis reaction of PdX$_2$(dppf) with alkali salts of carboxylate were unsuccessful with the starting materials largely recover unreacted [14], similar reactions of PdBr$_2$(P$_2$) [P$_2$ = dppf; P = PPh$_3$] with excess potassium thioacetate gave Pd(S{O}CMe)$_2$(P$_2$) in moderate yields. The spectroscopic data of Pd(κ*S*-S{O}CMe)$_2$(dppf) (**I**), and *trans*-Pd(κ*S*-S{O}CMe)$_2$-(PPh$_3$)$_2$ (**II**) are given in Table 1. The presence of the thioacetate ligands is inferred by the strong IR absorption bands in the 1500–1650 cm^{-1} (C–O) and 900–950 cm^{-1} (C–S) regions [2,10,15]. Both complexes display IR bands in ~1600 and 940 cm^{-1} that characterize strong Pd–S and weak Pd–O interactions [10]. This is the first indication for a unidentate coordination of thioacetates via the S atom, thus ruling out an O-donation or bridging formation. The ^{1}H- and ^{31}P-NMR data are consistent with that expected from the complex Pd(κ*S*-S{O}CMe)$_2$(P$_2$) [P$_2$ = dppf, **I**; P = PPh$_3$, **II**]. An unexpected feature is the higher shielding effect of the Me group of thioacetate in **II** (δ_H 1.33 ppm). This has also been observed in similar acetate complexes, viz. Pt(O$_2$CMe)$_2$(P$_2$) [P = PPh$_3$ 1.35 ppm; P$_2$ = dppm 1.96 ppm, dppf 1.93 ppm] [16]. This could be explained by the proximity effect of the neigboring Ph rings due to steric congestion. Examination of the methyl shift trend in Pd(O$_2$CMe)$_2$(PPh$_3$)$_2$ (0.85 ppm [10]), Pd(O$_2$CMe)$_2$-(PMePh$_2$)$_2$ (1.64 ppm) [10] and Pd(O$_2$CMe)$_2$(PMe$_2$Ph)$_2$ (2.00 ppm) [10] tends to support this postulate. The ROSEY spectrum of **II** (Fig. 1) gives the clearest indication that spatial interaction between the Me and Ph protons is active. Shielding of the Me group originates from the delocalised electrons of the Ph rings of PPh$_3$.



I



II

The solid-state structures of both complexes have been examined by X-ray single-crystal crystallography (Tables 2 and 3; Figs. 2 and 3) and found to be consistent with the solution structures. Both are mononuclear with thioacetate opts for an *S*-coordination with a pendant O site. The two pendant oxygen atoms in both cases adopts the sterically more favorable *anti* conformation. The chelating dppf imposes a *cis* configuration on **I** whereas the *trans* configuration in **II** is promoted by the sterically demanding PPh$_3$ in **II**. The preference for thioacetate to use the S site for donation is not surprising considering that *trans*-Ni(κ*S*-S{O}CMe)$_2$(PPh$_3$)$_2$ [7] and [Pd(κ*S*-S{O}CPh)$_2$-(L$_2$)] (L = PPh$_3$, PMePh$_2$, PMe$_2$Ph, AsPh$_3$, SbPh$_3$, py; L$_2$ = bipy, PPh$_2$CH$_2$PPh$_2$, PPh$_2$(CH$_2$)$_2$PPh$_2$) [10] have been reported to behave similarly. Although there are reports suggesting that some Pd(II) monothiobenzoate could show dimeric or monothiocarboxylates bridging structures with both Pd–O and Pd–S functionalities [10], this is not observed in our system. The reluctance for the thioacetate to use the O site despite some favourable steric factors also points to a softer character for Pd(II). The isolation of these complexes suggests that the geometric isomeric preference of Pd(II) can be dictated by the phosphine. The Pd–X (X = P, S)

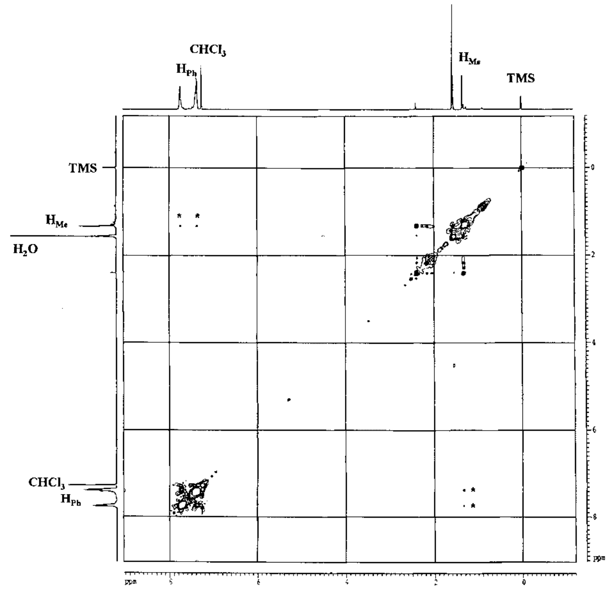


Fig. 1. ROSEY spectra of *trans*-Pd(κ*S*-S{O}CMe)$_2$(PPh$_3$)$_2$ (**II**). NOE contacts are mark by the * signs.

Table 2
Crystallographic data and refinement details for Pd(κS–S{O}CMe)$_2$-(dppf) (**I**) and *trans*-Pd(κS-S{O}CMe)$_2$(PPh$_3$)$_2$ (**II**)

	I	**II**
Empirical formula	$C_{38}H_{34}FeO_2P_2PdS_2$	$C_{40}H_{36}O_2P_2PdS_2$
M_r	810.96	781.15
Temperature (K)	223(2)	
Diffractometer	Bruker AXS	Bruker AXS
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	10.458(1)	8.071(1)
b (Å)	18.326(1)	10.796(2)
c (Å)	17.834(1)	11.116(2)
α (°)	90	114.500(2)
β (°)	90.661(2)	95.761(3)
γ (°)	90	95.806(3)
V (Å^3)	3417.7(4)	865.9(2)
Z	4	1
μ (mm^{-1})	1.200	0.784
Crystal size (mm^3)	0.24 × 0.20 × 0.16	0.20 × 0.20 × 0.14
θ range (°)	2.22 to 30.01	2.04 to 30.02
h, *k*, *l*	−14 to 14, −14 to 25, −23 to 25	−11 to 11, −15 to 13, 0 to 15
Reflections collected	28126	4997
Independent reflections	9907 [$R_{int} = 0.0441$]	10327 [$R_{int} = 0.0515$]
Completeness to θ (%)	99.3	98.6
Absorption correction	SADABS (Sheldrick, 1996)	SADABS (Sheldrick, 1996)
Max./min. transmission	0.8522, 0.6359	0.8981, 0.8589
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	9907/0/417	4997/0/227
Goodness-of-fit on F^2	1.061	1.016
Final *R* indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0356$, $wR_2 = 0.0858$	$R_1 = 0.0435$, $wR_2 = 0.0962$
R indices (all data)	$R_1 = 0.0481$, $wR_2 = 0.0921$	$R_1 = 0.0510$, $wR_2 = 0.1009$
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.732, −0.578	1.224, −1.384

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma w[(F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$.

lengths are within expectations [17]. The influence of the Ph ring on the methyl protons in II is exemplified in the close contact of the Me and Ph groups (3.172 Å for nearest $H_{Me}\cdots C_{Ph}$).

The Pd(II) phosphine carboxylates are valuable precatalysts but they are usually too unstable to be isolated or stored. The higher stability of the thiocarboxylate analogues could provide some solutions although their catalytic activities, which are largely unknown, may be sacrificed. The potential for an in situ S–O switching in a monothiocarboxylate entity, thereby offering a natural protection to a catalytically active functionality is intriguing. We are currently investigating this system in this direction in together with their chemical and thermal stabilities.

3. Experimental

3.1. General procedures

All reactions were performed under pure dry argon using standard Schlenk techniques. The products are stable and hence recrystallizations were done in air. All solvents and reagents were of reagent grade obtained from commercial sources and used without further purification.

PdBr$_2$(dppf) and PdBr$_2$(PPh$_3$)$_2$ were prepared using literature method [18].

All ^{1}H- and ^{31}P-NMR spectra except ROSEY spectrum were recorded at ca. 300 K at operating frequency

Table 3
Selected bond lengths (Å) and bond angles (°)

Pd(κS-S{O}CMe)$_2$(dppf) (**I**)			
Bond lengths			
Pd(1)–P(1)	2.2996(6)	Pd(1)–P(2)	2.3168(6)
Pd(1)–S(1)	2.3231(7)	Pd(1)–S(2)	2.3542(6)
S(1)–C(11)	1.727(3)	S(2)–C(13)	1.746(3)
O(1)–C(11)	1.209(3)	O(2)–C(13)	1.214(3)
C(11)–C(12)	1.490(4)	C(13)–C(14)	1.511(4)
Bond angles			
P(1)–Pd(1)–P(2)	99.55(2)	P(1)–Pd(1)–S(1)	89.88(2)
P(2)–Pd(1)–S(1)	169.97(2)	P(1)–Pd(1)–S(2)	173.77(2)
P(2)–Pd(1)–S(2)	83.56(2)	S(1)–Pd(1)–S(2)	87.37(2)
C(1)–P(1)–Pd(1)	113.63(8)	C(6)–P(2)–Pd(1)	123.04(7)
C(11)–S(1)–Pd(1)	102.71(9)	C(13)–S(2)–Pd(1)	100.22(9)
O(1)–C(11)–C(12)	121.1(3)	O(1)–C(11)–S(1)	125.3(2)
C(12)–C(11)–S(1)	113.6(2)	O(2)–C(13)–C(14)	122.3(2)
O(2)–C(13)–S(2)	124.4(2)	C(14)–C(13)–S(2)	113.3(2)
P(1)$\cdots\chi_A\cdots\chi_B\cdots$P(2) [a]	37.2	$\chi_A\cdots$Fe$\cdots\chi_A$	177.04
Trans-Pd(κS-S{O}CMe)$_2$(PPh$_3$)$_2$ (**II**)			
Bond lengths			
Pd–S(1–1A)	2.3264(7)	Pd–P(1–1A)	2.3343(7)
S(1)–C(1)	1.748(3)	O(1)–C(1)	1.219(3)
C(1)–C(2)	1.508(4)	P(1)–C(1A)	1.826(3)
P(1)–C(1B)	1.815(3)	P(1)–C(1C)	1.822(3)
Bond angles			
S(1)–Pd(1)–S(1A)	180.00(3)	S(1A)–Pd(1)–P(1)	92.51(3)
S(1)–Pd(1)–P(1)	87.49(3)	S(1A)–Pd(1)–P(1A)	87.49(3)
S(1)–Pd(1)–P(1A)	92.51(3)	P(1)–Pd(1)–P(1A)	180.0
C(1)–S(1)–Pd(1)	104.01(10)	O(1)–C(1)–C(2)	120.6(3)
O(1)–C(1)–S(1)	125.1(2)	C(2)–C(1)–S(1)	114.3(2)

[a] χ_A and χ_B is the centroid of C(1)–C(5) and C(6)–C(10), respectively.

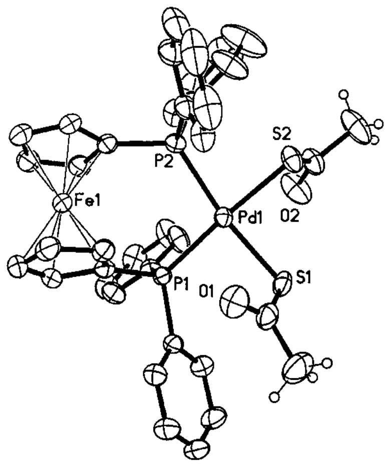


Fig. 2. ORTEP drawing of the molecular structure of Pd(κ*S*-S{O}CMe)$_2$(dppf) (**I**).

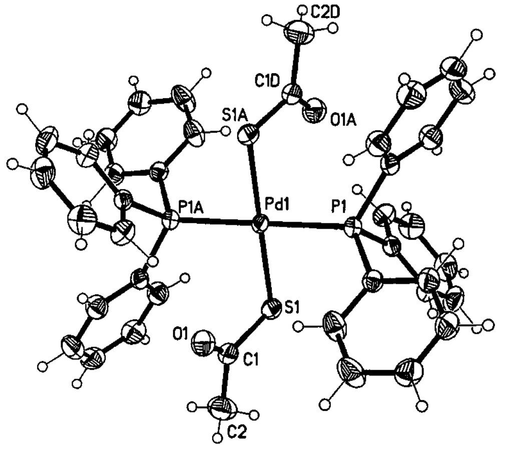


Fig. 3. ORTEP drawing of the molecular structure of *trans*-Pd(κ*S*-S{O}CMe)$_2$(PPh$_3$)$_2$ (**II**).

of 299.96 and 121.49 MHz, respectively. ^{1}H and ^{31}P chemical shifts are quoted in ppm downfield of Me$_4$Si and external 85% H$_3$PO$_4$, respectively. The ROSEY spectra were recorded at ca. 300 K at operating frequency of 500 MHz. All IR spectra were recorded in its solid state on a Bio-Rad FT-IR spectrometer using KBr disk. Elemental analyses were performed by the Elemental Analysis Laboratory of our Department. The X-ray structure determinations were carried out at our X-ray Diffraction Laboratory.

3.2. *Pd(κS-S{O}CMe)$_2$(dppf) (**I**)*

PdBr$_2$(dppf) (0.150 g, 0.183 mmol) and KS{O}CMe (0.044 g, 0.385 mmol) in CH$_2$Cl$_2$ (50 cm^3) were stirred at room temperature (r.t.) for ca. 20 h. The resulting orange suspension was filtered to obtain an orange filtrate, to which hexane was added to precipitate the product Pd(κ*S*-S{O}CMe)$_2$(dppf). Yield, 0.133 g (90%). Anal Calc.: C, 56.28; H, 4.23. Found: C, 55.35; H, 4.18%.

3.3. *Pd(κS-S{O}CMe)$_2$(PPh$_3$)$_2$ (**II**)*

cis-PdBr$_2$(PPh$_3$)$_2$ (0.200 g, 0.253 mmol) and KSC{O}CH$_3$ (0.064 g, 0.560 mmol) in CH$_2$Cl$_2$ (50 cm^3) were stirred at r.t. for ca. 20 h. The resulting lime-yellow suspension was filtered, and hexane added to crystallize the compound, Pd(κ*S*-S{O}CMe)$_2$(dppf). Yield, 0.192 g (97%). Anal Calc.: C, 61.50; H, 4.64. Found: C, 61.01; H, 4.58%.

4. Supplementary material

Crystallographic data (CIF files) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 155772 for **I** and CCDC no. 155773 for **II**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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