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Reaction of $(Ph_3P)_2PtS_4$ with $MeO_2CC{=}CCO_2Me$: synthesis and structure of (dimethyldimercaptomaleato(2–)-*S*,*S*′)bis(triphenylphosphine)platinum(II)

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Abstract

Addition of excess dimethyl acetylene dicarboxylate to $(PPh_3)_2PtS_4$ gave a black–dark-red solution. Purple crystals obtained from this solution were shown by single crystal X-ray crystallography to be the title compound; the sulfur has added to the acetylene to give dimethyldimercaptomaleate coordinated to Pt. The purple is attributed to an intensely colored impurity. Space group $P\bar{1}$; $a=11.713(5)$; $b=14.733(5)$; $c=15.774(6)$ Å; $\alpha=129.35(2)$; $\beta=106.40(3)$; $\gamma=93.44(3)°$; $V=1912(1)$ Å^3; $Z=2$; $R=0.0339$ and $R_w=0.0326$ for 6177 reflections with $F_o \geqslant 3\sigma(F_o)$ and 388 parameters.

Introduction

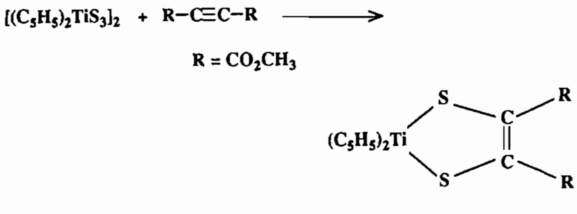
The electrophilic acetylene dimethylacetylenedicarboxylate, dmad, will react with compounds containing sulfur chains [1, 2], such as $(Cp_2TiS_3)_2$ [3], to form dimethyldimercaptomaleate [4], Scheme 1. This maleate can be transferred to platinum(II) in an exchange reaction that takes advantage of the halophilicity of titanium, Scheme 2 [5].

The compound $(PPh_3)_2PtS_4$ [6] contains an MS_4 ring [7]. Here we report that it will react with dmad to give $(PPh_3)_2Pt(S_2C_2(CO_2CH_3)_2)$ directly, Scheme 3. We also report the crystal structure of this compound.

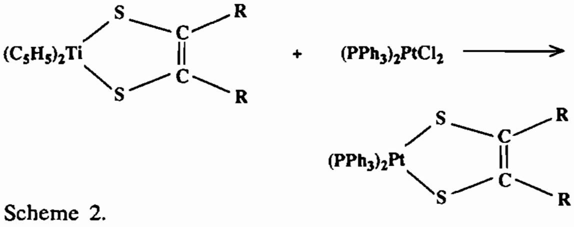
Experimental

Preparation

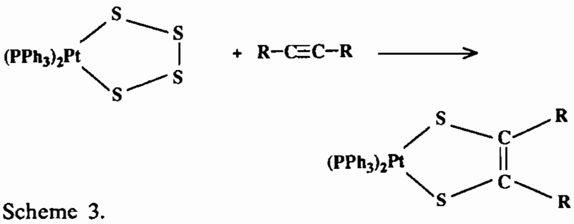
A solution of 0.21 g (0.25 mmol) $(PPh_3)_2PtS_4$ [6] and about 0.8 ml (7 mmol) dmad in about 30 ml of chloroform was refluxed under an inert atmosphere. The solution became dark after 15 min. After 14 h the solvent was evaporated from the black–dark-red solution. The red–black residue was redissolved in a $CHCl_3/CCl_4$ mixture and was placed in a freezer. The volume was reduced every few days with a stream of dry nitrogen until purple crystals formed. The compound has the same ^{1}H NMR and IR spectra as do lemon–yellow crystals of the same compound provided by Bolinger and Rauchfuss [5].



Scheme 1.



Scheme 2.



Scheme 3.

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TABLE 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)[a] for (S,S'-$H_3CO_2C(S)C{=}C(S)CO_2CH_3$)$Pt(PPh_3)_2$

Atom	x	y	z	U_{iso}[b]
Pt	4812(1)	4969(1)	2535(1)	25(1)*
S(1)	4720(1)	3027(1)	1835(1)	36(1)*
S(2)	2662(1)	4215(1)	1469(1)	34(1)*
P(1)	4833(1)	6922(1)	3325(1)	29(1)*
P(2)	6959(1)	5401(1)	3341(1)	28(1)*
O(1)	1782(4)	46(4)	−767(5)	86(4)*
O(2)	3683(4)	419(4)	384(4)	60(3)*
O(3)	166(4)	1606(4)	189(5)	72(4)*
O(4)	432(4)	1782(4)	−1012(4)	70(3)*
C(1)	2797(5)	775(5)	58(5)	41(4)*
C(2)	3154(5)	2128(4)	814(4)	34(3)*
C(3)	2292(4)	2650(4)	694(4)	32(3)*
C(4)	906(5)	1944(5)	−133(5)	46(4)*
C(5)	670(7)	1878(8)	1299(7)	81(7)*
C(6)	3423(7)	−894(6)	−350(7)	76(6)*
C(11)	2425(3)	6586(3)	1991(3)	46(4)*
C(12)	1232(3)	6717(3)	1817(3)	57(6)*
C(13)	913(3)	7439(3)	2796(3)	66(7)*
C(14)	1786(3)	8030(3)	3949(3)	61(6)*
C(15)	2979(3)	7900(3)	4123(3)	49(5)*
C(16)	3298(3)	7178(3)	3144(3)	35(4)*
C(21)	5804(4)	6611(3)	1772(2)	44(4)*
C(22)	6287(4)	6980(3)	1285(3)	63(6)*
C(23)	6364(4)	8153(3)	1692(3)	72(6)*
C(24)	5958(4)	8956(3)	2586(3)	65(5)*
C(25)	5476(4)	8587(3)	3074(3)	46(4)*
C(26)	5398(4)	7414(3)	2667(3)	33(3)*
C(31)	6591(3)	9215(3)	5617(3)	42(4)*
C(32)	7215(3)	10018(3)	6868(3)	58(4)*
C(33)	6975(3)	9671(3)	7459(3)	65(5)*
C(34)	6110(3)	8520(3)	6800(3)	57(5)*
C(35)	5485(3)	7717(3)	5550(3)	46(4)*
C(36)	5726(3)	8064(3)	4958(3)	35(3)*
C(41)	8349(3)	7550(3)	4074(2)	41(4)*
C(42)	9219(3)	8739(3)	4894(2)	56(5)*
C(43)	9821(3)	9353(3)	6107(2)	64(5)*
C(44)	9553(3)	8779(3)	6502(2)	56(4)*
C(45)	8683(3)	7591(3)	5682(2)	46(4)*
C(46)	8081(3)	6776(3)	4469(2)	32(3)*
C(51)	8871(3)	4921(3)	2535(2)	50(4)*
C(52)	9346(3)	4315(3)	1658(2)	60(6)*
C(53)	8525(3)	3434(3)	440(2)	57(5)*
C(54)	7229(3)	3158(3)	98(2)	50(5)*
C(55)	6754(3)	3765(3)	975(2)	38(4)*
C(56)	7575(3)	4646(3)	2193(2)	32(3)*
C(61)	8085(4)	4039(4)	3819(4)	65(6)*
C(62)	8362(4)	3636(4)	4427(4)	98(10)*
C(63)	7893(4)	4002(4)	5283(4)	99(10)*
C(64)	7148(4)	4770(4)	5531(4)	81(7)*
C(65)	6872(4)	5173(4)	4923(4)	57(5)*
C(66)	7340(4)	4807(4)	4067(4)	39(4)*

[a] e.s.d.s in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic U is defined as 1/3 of the trace of the U_{ij} tensor.

TABLE 2. Bond lengths (Å) and angles (°)[a] for (S,S'-$H_3CO_2C(S)C{=}C(S)CO_2CH_3$)$Pt(PPh_3)_2$

Pt–S(1)	2.304(2)	Pt–S(2)	2.304(2)
Pt–P(1)	2.293(2)	Pt–P(2)	2.308(2)
S(1)–C(2)	1.745(4)	S(2)–C(3)	1.734(6)
P(1)–C(16)	1.840(4)	P(1)–C(26)	1.825(6)
P(1)–C(36)	1.826(3)	P(2)–C(46)	1.832(3)
P(2)–C(56)	1.821(4)	P(2)–C(66)	1.819(8)
O(1)–C(1)	1.209(6)	O(2)–C(1)	1.313(9)
O(2)–C(6)	1.437(8)	O(3)–C(4)	1.333(12)
O(3)–C(5)	1.438(14)	O(4)–C(4)	1.191(11)
C(1)–C(2)	1.474(8)	C(2)–C(3)	1.348(9)
C(3)–C(4)	1.516(6)		
S(1)–Pt–S(2)	87.8(1)	S(1)–Pt–P(1)	175.6(1)
S(2)–Pt–P(1)	90.8(1)	S(1)–Pt–P(2)	84.5(1)
S(2)–Pt–P(2)	170.5	P(1)–Pt–P(2)	97.3(1)
Pt–S(1)–C(2)	104.0(2)	Pt–S(2)–C(3)	103.6(2)
Pt–P(1)–C(16)	116.0(1)	Pt–P(1)–C(26)	115.3(1)
Pt–P(1)–C(36)	110.7(2)	C(16)–P(1)–C(36)	102.7(2)
C(26)–P(1)–C(36)	109.8(2)	Pt–P(2)–C(46)	123.3(2)
Pt–P(2)–C(56)	112.4(1)	C(46)–P(2)–C(56)	101.1(2)
Pt–P(2)–C(66)	109.6(2)	C(46)–P(2)–C(66)	103.0(2)
C(56)–P(2)–C(66)	106.0(2)	C(1)–O(2)–C(6)	116.6(4)
C(4)–O(3)–C(5)	120.9(5)	O(1)–C(1)–O(2)	121.9(6)
O(1)–C(1)–C(2)	124.6(7)	O(2)–C(1)–C(2)	113.5(4)
S(1)–C(2)–C(1)	118.6(5)	S(1)–C(2)–C(3)	121.0(4)
C(1)–C(2)–C(3)	120.4(4)	S(2)–C(3)–C(2)	123.1(3)
S(2)–C(3)–C(4)	112.6(5)	C(2)–C(3)–C(4)	124.3(5)
O(3)–C(4)–O(4)	118.4(5)	O(3)–C(4)–C(3)	119.5(7)
O(4)–C(4)–C(3)	121.7(8)	P(1)–C(16)–C(11)	118.6(1)
P(1)–C(16)–C(15)	121.3(1)	P(1)–C(26)–C(21)	118.7(1)
P(1)–C(26)–C(25)	121.3(1)	P(1)–C(36)–C(31)	124.9(2)
P(1)–C(36)–C(35)	115.1(2)	P(2)–C(46)–C(41)	117.8(2)
P(2)–C(46)–C(45)	122.2(2)	P(2)–C(56)–C(51)	119.8(1)
P(2)–C(56)–C(55)	120.2(1)	P(2)–C(66)–C(61)	123.0(2)
P(2)–C(66)–C(65)	117.0(2)		

[a] e.s.d.s in the least significant digits are given in parentheses.

Structure determination

The equipment, procedures and programs (Syntex $P2_1$ diffractometer, SHELXTL 5.0) have been previously described [8]. The unit cell dimensions of a $0.28 \times 0.33 \times 0.34$ crystal, $a = 11.713(5)$, $b = 14.733(5)$, $c = 15.774(6)$ Å, $\alpha = 129.35(2)$, $\beta = 106.40(3)$ $\gamma = 93.44(3)$° and $V = 1912(1)$ $Å^3$, were determined from 15 reflections with $20° < 2\theta < 25°$ (293 K, monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The space group is $P\bar{1}$ with $Z = 2$. For $C_{42}H_{36}O_4P_2PtS_2$, $M_r = 925.9$, $D_{calc} = 1.61$ g/cm^3, $F(000) = 920$, and μ(Mo Kα) $= 40.84$ cm^{-1}. A total of 6760 unique reflections collected in the range $2° < 2\theta < 50°$ in the $\theta/2\theta$ mode gave 6177 reflections with $F_o > 3\sigma(F_o)$. Three check reflections every 50 showed only random variation. Corrections for Lorentz and polarization effects were applied. No absorption correction was applied. The structure was solved by the Patterson method. All non-hydrogen atoms were refined anisotropically. Phenyl rings were refined as idealized hexagons (C–C = 1.395 Å). Hydrogen atoms were placed at idealized positions (C–H = 0.96 Å) with isotropic thermal parameters 1.2 greater than that of the attached carbon. Refinement of 388 parameters gave $R=0.0339$, $R_w=0.0326$, and goodness-of-fit $=$ 1.36. ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_w=[\Sigma\sqrt{w}||F_o|-|F_c||]/\Sigma\sqrt{w}|F_o|$; $w^{-1}=[\sigma^2(|F_o|+0.00044|F_o|^2]$.) The largest peak in the final difference map, 1.8 e Å^{-3}, was 0.94 Å from Pt.

Atomic coordinates are given in Table 1. Bond lengths and angles are given in Table 2.

Results and discussion

Addition of excess dmad to $(PPh_3)_2PtS_4$ gave a black–dark-red solution. One of the compounds formed in this reaction is $(PPh_3)_2PtS_2C_2(CO_2CH_3)_2$ (**1**) in which sulfur has added to dmad to give a dimercaptomaleate coordinated to platinum, Fig. 1. The C(2)–C(3) bond, 1.348(9) Å, may be formulated as a double bond. As can be seen from the Figure, one carbonyl group is coplanar with this double bond and the other is not. The shorter distance for C(1)–C(2) compared with C(3)–C(4) may reflect this conjugation. The dithiolene ligand atoms S(1), S(2), C(1), C(2), C(3) and C(4) are planar to within 0.05 Å; that plane forms a 9.1° angle with the Pt–P(1)–P(2) plane. The shortest intermolecular separation between non-hydrogen atoms is 3.29 Å for O(3)–C(53). The only other mono(dithiolene)platinum complexes that have been crystallographically characterized are (4,5-dimercapto-1,3-dithia-2-thione-*S,S′*)(1,2-bis(diphenylphosphinoethane-*P,P′*)platinum(II) [9], and (2,2′-bipyrimidine-*N,N′*)(1,2-dicyanoethylene-1,2-dithiolato-*S,S′*)platinum(II) [10].

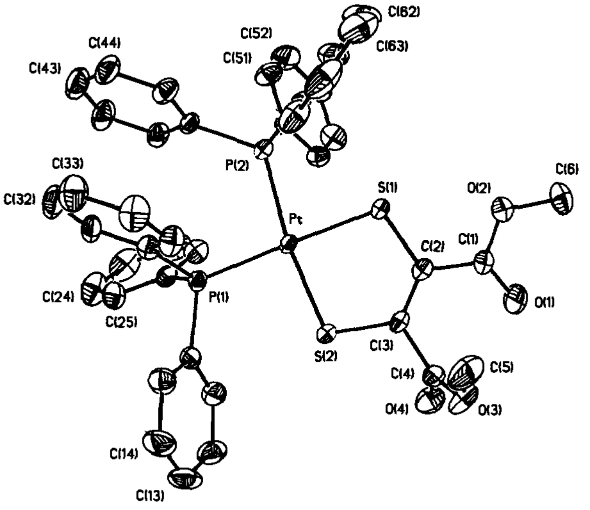

Fig. 1. Structure of $(PPh_3)_2Pt(S_2C_6O_4H_6)$ (**1**) with 40% thermal ellipsoids viewed through the best fitting plane through Pt, S(1), S(2), P(1), P(2), C(1), C(2), C(3) and C(4). Hydrogen atoms are omitted.

Compound **1** is reported [5] to be lemon–yellow; $(PPh_3)_2PtS_2C_2(CN)_2$ and $(PPh_3)_2PtS_2C_2(CF_3)_2$ are reported [11] to be lemon–yellow and brilliant yellow, respectively. The crystals obtained in the presence of excess dmad were purple. The color is attributed to the presence of a small amount of intensely-colored impurity. (Recrystallization to remove the impurity was not attempted.) Both the purple crystals and the yellow crystals of **1** provided by Rauchfuss and coworkers had the same ^{1}H NMR and IR spectra.

The fate of the rest of the sulfur has not been determined. A species such as $S_2C_2(CO_2CH_3)_2$ [2] may have formed from the excess acetylene. Addition of excess $S_2C_2(CF_3)_2$ to $(PPh_3)_2Pt(S_2C_2(CF_3)_2)$ is reported [11] to give a purple solution from which red–purple needles of $Pt(S_2C_2(CF_3)_2)_2$ were obtained. Formation of the analogous $Pt(S_2C_2(CO_2CH_3)_2)_2$ might account for the dark solution color.

Supplementary material

Anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters (5 pages), and structure factor tables (40 pages) have·been deposited with the British Library Document Supply Centre as a Supplementary Publication. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, U.K.

Acknowledgements

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