Crystal Structure of the 1:1 Adduct formed between Bis(*cis*-1,2-diphenylethylene-1,2-dithiolato)palladium and Cyclohexa-1,3-diene

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Crystals of the title adduct are triclinic, space group $P\bar{1}$, with $a = 14{\cdot}347 \pm 0{\cdot}004$, $b = 13{\cdot}194 + 0{\cdot}002$, $c = 9{\cdot}461 \pm 0{\cdot}001$ Å, $\alpha = 72{\cdot}50 \pm 0{\cdot}02$, $\beta = 114{\cdot}70 \pm 0{\cdot}01$, $\gamma = 114{\cdot}12 \pm 0{\cdot}02°$, $Z = 2$. The structure was refined by least-squares methods to R 0·047 for 2829 observed intensities measured by diffractometer. The analysis shows that a 1,8-addition reaction has occurred between donor and acceptor resulting in the formation of two new carbon–sulphur bonds.

THE formation of 1 : 1 adducts between bisdiphenylethylene-1,2-dithiolato-complexes of the nickel group and certain unsaturated hydrocarbons has been reported.[1] From i.r. spectral evidence interaction between hydrocarbon and complex to produce carbon–sulphur bonds has been postulated with co-ordination of the olefinic bond to the metal being additionally suggested in some instances. More recently this latter claim has been disproved by an *X*-ray analysis [2] of the donor–acceptor complex formed between norbornadiene and bis(*cis*-1,2-perfluoromethylethylene-1,2-dithiolato)nickel which shows that no interaction is possible between the remaining double bond in the olefin and the metal of the nickel dithiolate. The structural analysis also shows that 1,8-addition of the olefin to the nickel complex has occurred and not 1,4 as was originally suggested. This is in accord with the later view [3,4] that the two electrons remaining on formation of the new sulphur–carbon bonds reside in the π system of the nickel dithiolate, and that greater stability results if both chelate rings are equally affected. However, identification of the products of the reaction between norbornadiene and bis(*cis*-1,2-diphenylethylene-1,2-dithiolato)nickel [5] suggests that under certain conditions an unstable intermediate involving 1,4-addition forms but is not isolated. From a model it can be seen that if 1,4-addition occurred then with cyclohexa-1,3-diene as the olefin, the remaining double bond in the unsaturated hydrocarbon should lie in a position suitable for co-ordination to the metal and thus this interaction might have a stabilising effect. Since palladium olefinic complexes are considerably more stable [6] than those of nickel, substitution of this metal might allow the 1,4-addition product to be isolated. Accordingly we have undertaken a three-dimensional *X*-ray structural analysis of the 1 : 1 adduct formed between cyclohexa-1,3-diene and bis(*cis*-1,2-diphenylethylene-1,2-dithiolato)palladium.

EXPERIMENTAL

Crystal Data.—$C_{34}H_{28}PdS_4$, $M = 671{\cdot}3$, Triclinic, $a = 14{\cdot}347 \pm 0{\cdot}004$, $b = 13{\cdot}194 \pm 0{\cdot}002$, $c = 9{\cdot}461 \pm 0{\cdot}001$ Å,

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[1] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1965, **87**, 1483.

[2] R. M. Wing, G. C. Tustin, and W. H. Okamura, *J. Amer. Chem. Soc.*, 1970, **92**, 1935.

[3] R. D. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, 1968, **90**, 2288.

[4] J. R. Baker, A. Hermann, and R. M. Wing, *J. Amer. Chem. Soc.*, 1971, **93**, 6486.

[5] G. N. Schrauzer, R. K. Y. Ho, and R. P. Murillo, *J. Amer. Chem. Soc.*, 1970, **92**, 3508.

[6] M. L. H. Green, 'Organometallic Compounds,' vol. 2, Methuen, London, 1968, p. 30.

$\alpha = 72{\cdot}50 \pm 0{\cdot}02$, $\beta = 114{\cdot}70 \pm 0{\cdot}01$, $\gamma = 114{\cdot}12 \pm 0{\cdot}02°$, $U = 1467$ Å^3, $D_m = 1{\cdot}51$, $Z = 2$, $D_c = 1{\cdot}52$, $F(000) = 684$, Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 9·2 cm^{-1}. The cell parameters quoted are related to the standard triclinic cell ($a' = 9{\cdot}46$, $b' = 13{\cdot}19$, $c' = 13{\cdot}48$ Å, $\alpha' = 102{\cdot}93$, $\beta' = 104{\cdot}90$, $\gamma' = 107{\cdot}50°$), by the transformation matrix: $00\bar{1}|010|101$.

Intensity data were recorded on a Hilger and Watts four-circle automatic diffractometer, 2829 independent reflexions being considered observed, having $I > 3\sigma(I)$.

Positional parameters for palladium and four sulphur atoms consistent with space group $P\bar{1}$, were obtained from a ' sharpened ' Patterson. A structure-factor calculation based on these 5 atoms returned an R factor of 0·28 and the subsequent electron-density map revealed the atomic sites of the remaining non-hydrogen atoms. Inclusion of these in a second structure-factor calculation lowered R to 0·155. The atomic scattering factors of ref. 7 were used for palladium, with the real part of the anomalous dispersion correction being applied, those in ref. 8 were used for all other atoms. Four cycles of block-diagonal least-squares refinement assuming isotropic motion only, and with a weighting scheme of the form $w = 4\,F_o{}^2/\sigma^2(F^2)$, reduced R to 0·106. Positions for the 20 hydrogen atoms of the phenyl rings were calculated and their contributions included in the structure factors with isotropic thermal parameters (B 5·0 Å^2). Anisotropic thermal motion was then assumed for all non-hydrogen atoms other than those of the olefin and after 5 cycles of refinement R was 0·056. Probable positions for the hydrogens of the olefin were now calculated, confirmed from a difference-Fourier map and included in a structure-factor calculation with B 5·0 Å^2. Further least-squares refinement (except on the parameters for hydrogen atoms) gave a final R of 0·047. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20626 (8 pp., 1 microfiche).*

DISCUSSION

The numbering system for the molecule is shown in Figure 1. Final atomic parameters with their standard deviations are listed in Tables 1—3, bond distances and angles in Tables 4 and 5. A perspective diagram of the molecule is shown in Figure 2.

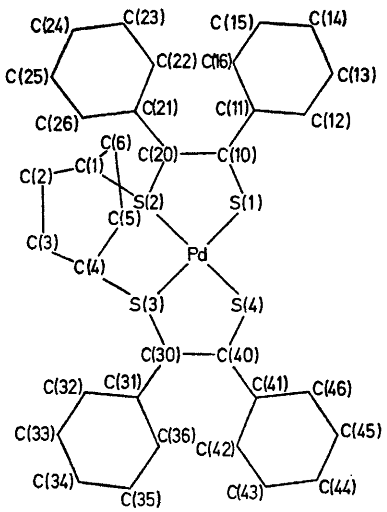

FIGURE 1 The numbering system used in the analysis. Hydrogen atoms are numbered according to the carbon atom to which they are attached

TABLE 1

Atomic co-ordinates for non-hydrogen atoms with standard deviations in parentheses

Atom	x/a	y/b	z/c
Pd	0·44088(5)	0·11519(5)	0·36356(7)
S(1)	0·3496(2)	0·0630(2)	0·5348(2)
S(2)	0·3373(1)	−0·0563(2)	0·2783(2)
S(3)	0·5293(2)	0·1859(2)	0·1838(2)
S(4)	0·5315(2)	0·2842(2)	0·4516(2)
C(10)	0·2456(6)	−0·0605(6)	0·4774(8)
C(20)	0·2342(6)	−0·1090(6)	0·3631(8)
C(30)	0·5913(6)	0·3329(6)	0·1935(8)
C(40)	0·5943(5)	0·3682(6)	0·3149(8)
C(11)	0·1741(6)	−0·1126(6)	0·5751(8)
C(12)	0·1563(7)	−0·2231(7)	0·6488(10)
C(13)	0·0916(8)	−0·2688(8)	0·7441(10)
C(14)	0·0446(8)	−0·2062(9)	0·7656(11)
C(15)	0·0608(7)	−0·0972(9)	0·6927(11)
C(16)	0·1267(7)	−0·0499(8)	0·5989(10)
C(21)	0·1405(5)	−0·2060(6)	0·2952(8)
C(22)	0·0374(6)	−0·1966(7)	0·2167(10)
C(23)	−0·0483(6)	−0·2846(8)	0·1481(11)
C(24)	−0·0328(7)	−0·3826(7)	0·1583(11)
C(25)	0·0680(7)	−0·3946(7)	0·2378(11)
C(26)	0·1554(6)	−0·3046(7)	0·3062(11)
C(31)	0·6373(6)	0·3997(6)	0·0661(8)
C(32)	0·6349(6)	0·5082(6)	−0·0014(9)
C(33)	0·6764(7)	0·5664(7)	−0·1227(9)
C(34)	0·7136(7)	0·5152(8)	−0·1838(9)
C(35)	0·7151(7)	0·4074(8)	−0·1220(10)
C(36)	0·6769(6)	0·3493(7)	0·0031(10)
C(41)	0·6589(6)	0·4859(6)	0·3526(8)
C(42)	0·7698(6)	0·5275(7)	0·3824(9)
C(43)	0·8293(7)	0·6336(8)	0·4266(10)
C(44)	0·7778(8)	0·6955(7)	0·4418(10)
C(45)	0·6670(8)	0·6545(7)	0·4115(10)
C(46)	0·6084(6)	0·5477(6)	0·3708(8)
C(1)	0·2612(6)	−0·0234(6)	0·0653(8)
C(2)	0·3293(7)	−0·0197(7)	−0·0225(9)
C(3)	0·3992(6)	0·0795(7)	−0·0684(9)
C(4)	0·4193(7)	0·1835(7)	−0·0126(9)
C(5)	0·3175(7)	0·1898(7)	−0·0099(10)
C(6)	0·2339(6)	0·0836(7)	0·0240(9)

The crystal structure shows that a chemical reaction has occurred between cyclohexa-1,3-diene and bis-(*cis*-1,2-diphenylethylene-1,2-dithiolato)palladium to produce a single monomeric unit. Two new sulphur–carbon bonds have been formed by 1,8-addition of the olefin. Within the monomer the palladium atom is surrounded by an approximately square planar arrangement of four sulphur atoms. To accommodate the olefin the two dithiolate chelate rings have been pushed apart so that the angle S(2)–Pd–S(3) is 96·32(8) compared with 88·21(9) found for S(1)–Pd–S(4). From the data in Table 6 it can be seen that the palladium dithiolate moiety is curved such that the palladium atom is displaced 0·07 Å below the plane of best fit through the four sulphur atoms whereas the carbon atoms of the chelate rings lie 0·3 [C(10) and C(40)] and 0·4 Å [C(20) and C(30)] above it and in the direction of the olefin. The four sulphur atoms are not truly coplanar, there

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[7] D. T. Cromer and J. A. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] ' International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, p. 202.

TABLE 2

Anisotropic thermal parameters (× 10⁴) for non-hydrogen atoms,* with standard deviations in parentheses

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pd	49·2(2)	47·4(3)	93·5(5)	1·4(5)	34·4(6)	−22·3(6)
S(1)	83(1)	58(1)	135(2)	−26(2)	101(3)	−62(3)
S(2)	51(1)	51(1)	127(2)	15(2)	43(3)	−37(3)
S(3)	60(1)	50(1)	118(2)	21(2)	54(3)	−28(3)
S(4)	69(1)	57(1)	115(2)	−10(2)	84(3)	39(3)
C(10)	53(4)	44(5)	122(10)	−5(8)	59(10)	−29(11)
C(20)	49(4)	36(4)	113(9)	3(7)	31(10)	−33(10)
C(30)	58(4)	39(4)	112(9)	17(7)	54(10)	−16(10)
C(40)	36(4)	57(5)	105(9)	17(7)	18(9)	−48(10)
C(11)	47(4)	63(5)	114(9)	−1(8)	43(10)	−65(11)
C(12)	72(5)	60(6)	151(11)	23(9)	64(12)	−17(13)
C(13)	92(7)	78(7)	152(12)	−22(12)	106(13)	−15(15)
C(14)	74(6)	128(9)	183(13)	−12(12)	97(13)	−100(17)
C(15)	66(6)	127(8)	203(13)	37(11)	69(13)	−108(16)
C(16)	58(5)	97(7)	154(12)	32(10)	32(13)	−48(15)
C(21)	46(4)	51(5)	118(9)	−1(7)	63(9)	−54(10)
C(22)	68(5)	78(6)	180(12)	39(9)	76(12)	−59(13)
C(23)	39(4)	96(7)	238(14)	7(9)	72(12)	−91(16)
C(24)	55(5)	81(7)	212(13)	−17(10)	72(13)	−109(14)
C(25)	73(6)	57(5)	252(14)	19(9)	83(14)	−100(13)
C(26)	48(5)	60(6)	222(14)	19(8)	72(12)	−45(14)
C(31)	53(4)	59(5)	92(8)	14(7)	49(9)	−43(10)
C(32)	57(5)	57(5)	128(10)	30(8)	50(11)	−10(12)
C(33)	74(6)	77(7)	125(11)	19(10)	73(12)	4(14)
C(34)	71(6)	112(8)	131(11)	−11(12)	95(12)	−42(16)
C(35)	99(6)	98(7)	199(11)	20(10)	167(11)	−88(13)
C(36)	85(5)	58(6)	192(12)	28(9)	146(11)	−19(13)
C(41)	61(5)	52(5)	91(8)	−12(8)	62(10)	−31(11)
C(42)	61(5)	67(6)	147(11)	1(9)	71(11)	−32(13)
C(43)	70(6)	90(8)	148(12)	−44(12)	66(13)	−57(15)
C(44)	123(8)	60(6)	159(12)	−29(12)	89(16)	−74(14)
C(45)	120(7)	66(6)	147(12)	59(10)	66(14)	−37(13)
C(46)	74(5)	58(5)	111(9)	24(8)	45(11)	−58(11)
C(1)	52(5)	62(5)	121(9)	−8(8)	49(10)	−79(11)
C(2)	99(6)	74(6)	158(10)	27(9)	115(11)	−81(12)
C(3)	71(5)	92(6)	150(10)	15(9)	84(10)	−124(12)
C(4)	72(5)	79(6)	95(9)	19(9)	44(11)	−40(12)
C(5)	77(6)	77(6)	131(12)	69(9)	29(13)	−5(14)
C(6)	49(5)	81(6)	123(11)	31(9)	21(11)	−20(14)

* The scattering factor is of the form $f = f_o \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{13}hl)]$.

TABLE 3

Atomic co-ordinates for hydrogen atoms

Atom	x/a	y/b	z/c
H(12)	0·191	−0·267	0·632
H(13)	0·078	−0·349	0·799
H(14)	0·000	−0·242	0·832
H(15)	0·025	−0·052	0·709
H(16)	0·140	0·030	0·545
H(22)	0·026	−0·124	0·207
H(23)	−0·122	−0·278	0·090
H(24)	−0·095	−0·445	0·110
H(25)	0·077	−0·469	0·246
H(26)	0·231	−0·312	0·364
H(32)	0·604	0·543	0·042
H(33)	0·678	0·645	−0·170
H(34)	0·740	0·558	−0·273
H(35)	0·745	0·372	−0·165
H(36)	0·677	0·270	0·049
H(42)	0·807	0·481	0·374
H(43)	0·908	0·666	0·449
H(44)	0·822	0·770	0·474
H(45)	0·628	0·701	0·419
H(46)	0·530	0·514	0·350
H(1)	0·186	−0·094	0·041
H(2)	0·332	−0·091	−0·036
H(3)	0·449	0·077	−0·113
H(4)	0·453	0·258	−0·090
H(51)	0·341	0·243	0·075
H(52)	0·280	0·235	−0·123
H(61)	0·214	0·090	0·119
H(62)	0·159	0·076	−0·077

being a slight distortion towards tetrahedral geometry. Similar distortions have been noted in an analogous donor–acceptor complex [2] involving nickel as the metal atom. On adduct formation with the palladium dithiolate the cyclohexa-1,3-diene is converted into a 1,4-substituted cyclohex-2-ene. The C(2)–C(3) bond length [1·36(1) Å] is decreased from that [1·465(2) Å]

TABLE 4

Bond lengths (Å) with standard deviations in parentheses

Pd–S(1)	2·275(3)	C(23)–C(24)	1·37(2)
Pd–S(2)	2·308(2)	C(24)–C(25)	1·37(2)
Pd–S(3)	2·292(3)	C(25)–C(26)	1·40(1)
Pd–S(4)	1·281(2)	C(30)–C(31)	1·49(1)
S(1)–C(10)	1·745(8)	C(31)–C(32)	1·39(1)
S(2)–C(20)	1·770(10)	C(31)–C(36)	1·40(1)
S(2)–C(1)	1·861(8)	C(32)–C(33)	1·39(1)
S(3)–C(30)	1·786(8)	C(33)–C(34)	1·37(2)
S(3)–C(4)	1·868(9)	C(34)–C(35)	1·37(2)
S(4)–C(40)	1·735(8)	C(35)–C(36)	1·39(2)
C(10)–C(20)	1·34(1)	C(40)–C(41)	1·51(1)
C(30)–C(40)	1·34(1)	C(41)–C(42)	1·39(1)
C(10)–C(11)	1·49(1)	C(41)–C(46)	1·37(1)
C(11)–C(12)	1·38(1)	C(42)–C(43)	1·39(1)
C(11)–C(16)	1·38(2)	C(43)–C(44)	1·37(2)
C(12)–C(13)	1·40(2)	C(44)–C(45)	1·38(2)
C(13)–C(14)	1·36(2)	C(45)–C(46)	1·39(1)
C(14)–C(15)	1·37(2)	C(1)–C(2)	1·50(2)
C(15)–C(16)	1·40(2)	C(1)–C(6)	1·52(1)
C(20)–C(21)	1·49(1)	C(2)–C(3)	1·36(1)
C(21)–C(22)	1·39(1)	C(3)–C(4)	1·49(1)
C(21)–C(26)	1·37(1)	C(4)–C(5)	1·51(2)
C(22)–C(23)	1·38(1)	C(5)–C(6)	1·48(1)

TABLE 5

Bond angles (°) with standard deviations in parentheses

S(1)–Pd–S(2)	87·84(8)	C(40)–C(41)–C(46)	119·3(8)
S(1)–Pd–S(4)	88·21(9)	C(12)–C(11)–C(16)	118·1(9)
S(2)–Pd–S(3)	96·32(8)	C(11)–C(12)–C(13)	120·3(9)
S(3)–Pd–S(4)	87·40(8)	C(12)–C(13)–C(14)	120·9(10)
Pd–S(1)–C(10)	103·6(3)	C(13)–C(14)–C(15)	119·4(11)
Pd–S(2)–C(20)	103·5(3)	C(14)–C(15)–C(16)	120·2(11)
Pd–S(2)–C(1)	105·8(3)	C(11)–C(16)–C(15)	121·0(10)
Pd–S(3)–C(30)	104·9(3)	C(22)–C(21)–C(26)	119·2(9)
Pd–S(3)–C(4)	105·0(3)	C(21)–C(22)–C(23)	120·4(9)
Pd–S(4)–C(40)	104·0(3)	C(22)–C(23)–C(24)	120·2(10)
S(1)–C(10)–C(20)	123·8(7)	C(23)–C(24)–C(25)	120·4(10)
S(1)–C(10)–C(11)	113·8(6)	C(24)–C(25)–C(26)	119·4(10)
S(2)–C(20)–C(10)	119·2(7)	C(21)–C(26)–C(25)	120·4(9)
S(2)–C(20)–C(21)	114·3(6)	C(32)–C(31)–C(36)	118·3(8)
S(3)–C(30)–C(40)	117·2(6)	C(31)–C(32)–C(33)	120·3(9)
S(3)–C(30)–C(31)	114·1(6)	C(32)–C(33)–C(34)	120·5(9)
S(4)–C(40)–C(30)	124·8(7)	C(33)–C(34)–C(35)	120·5(10)
S(4)–C(40)–C(41)	112·1(6)	C(34)–C(35)–C(36)	119·6(11)
S(2)–C(1)–C(2)	106·3(6)	C(31)–C(36)–C(35)	120·7(10)
S(2)–C(1)–C(6)	113·2(6)	C(42)–C(41)–C(46)	120·2(8)
S(3)–C(4)–C(3)	106·5(7)	C(41)–C(42)–C(43)	119·5(9)
S(3)–C(4)–C(5)	113·6(7)	C(42)–C(43)–C(44)	119·8(10)
C(20)–C(10)–C(11)	112·2(8)	C(43)–C(44)–C(45)	120·8(10)
C(10)–C(11)–C(12)	121·5(8)	C(44)–C(45)–C(46)	119·2(10)
C(10)–C(11)–C(16)	120·4(8)	C(41)–C(46)–C(45)	120·4(9)
C(10)–C(20)–C(21)	126·5(8)	C(2)–C(1)–C(6)	112·8(8)
C(20)–C(21)–C(22)	120·4(8)	C(1)–C(2)–C(3)	121·0(9)
C(20)–C(21)–C(26)	120·5(8)	C(2)–C(3)–C(4)	119·4(9)
C(40)–C(30)–C(31)	128·6(8)	C(3)–C(4)–C(5)	112·4(8)
C(30)–C(31)–C(32)	122·3(8)	C(4)–C(5)–C(6)	118·3(9)
C(30)–C(31)–C(36)	119·2(8)	C(1)–C(6)–C(5)	116·7(8)
C(30)–C(40)–C(41)	123·0(8)	C(1)–S(2)–C(20)	102·4(4)
C(40)–C(41)–C(42)	120·3(8)	C(4)–S(3)–C(30)	102·2(4)

found for cyclohexadiene in the gas phase[9] and the distances C(1)–C(2) and C(3)–C(4) are increased accordingly. The olefin adopts a skew-boat conformation; the more stable half-chair conformation[10] would not allow bond formation between C(1) and C(4) of the unsaturated hydrocarbon and two sulphur atoms of the chelate ring. That some strain is involved on adduct formation may be seen from the angles C(4)–C(5)–C(6) and C(1)–C(6)–C(5) [118·3(9) and 116·7(8)°] which deviate from the expected tetrahedral values.

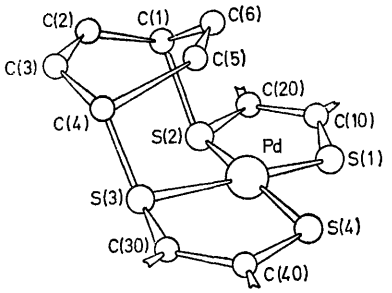

FIGURE 2 A perspective diagram of the molecule, with phenyl groups omitted

TABLE 6

Equations of planes, referred to orthogonal axes and given in the cosine form ($Ax + By + Cz + D = 0$, where A, B, and C are the direction cosines). Displacements (Å) of atoms from the plane are listed in square brackets

Plane (1):

S(1)—(4) $-0{\cdot}6893x + 0{\cdot}2700y - 0{\cdot}6723z - 4{\cdot}4384 = 0$

[S(1) 0·02, S(2) −0·02, S(3) 0·02, S(4) −0·02, Pd −0·07, C(10) 0·34, C(20) 0·41, C(30) 0·40, C(40) 0·30]

Plane (2):

Pd, S(1), S(2) $-0{\cdot}6586x + 0{\cdot}2974y - 0{\cdot}6912z - 4{\cdot}3856 = 0$

[S(3) 0·18, C(20) 0·36, S(4) 0·10, C(11) 0·29, C(10) 0·27, C(21) 0·74]

Plane (3):

Pd, S(3), S(4) $-0{\cdot}7168x + 0{\cdot}2405y - 0{\cdot}6545z - 0{\cdot}6274 = 0$

[C(40) 0·25, C(31) 0·62, S(2) 0·11, C(30) 0·33, C(41) 0·29, S(1) 0·18]

Plane (4):

C(1)—(4) $-0{\cdot}5223x + 0{\cdot}0698y - 0{\cdot}8499z - 2{\cdot}3901 = 0$

[C(1) 0·017, C(2) −0·036, C(3) 0·036, C(4) −0·017, C(5) 0·755, C(6) 0·822]

Within the palladium dithiolate moiety the mean palladium–sulphur distance involving sulphur bound to the olefin is 2·300(3) Å in contrast to the slightly shorter non-olefin bound sulphur–palladium distance, 2·278(3) Å. Both these values are relatively short but are comparable with similar distances (2·296 Å)[11,12] in compounds where multiple bonding is likely.[13] The two mean sulphur–carbon distances [1·778(9) and 1·740(8) Å] representing the sulphur respectively bonded and non-bonded to the olefin are comparable with the mean sulphur–carbon distance [1·75(2) Å] found for the dianion, $[\mathrm{Ni}(S_2C_2(CN)_2)_2]^{2-}$.[14] The longer palladium sulphur and sulphur–carbon distances observed where sulphur is linked to the olefin presumably arise from changes in the electron distribution about sulphur caused by the addition of the olefin. The carbon–carbon bonds of the dithiolate chelate rings [1·34(1) Å] compare with similar distances in the dianion [1·32(2) Å][13] and, as expected, indicate multiple bonding.

There is no evidence for any interaction between palladium and the double bond of the olefin as was originally postulated[1] and in spite of the i.r. band present at 1540 cm^{-1}. This is in accord with more recent findings[2] where this band is associated with the carbon–carbon multiple bond of the dithiolate chelate ring. Neither is there any evidence for any interaction between the metal and other carbon atoms of the adduct ring as shown by the intramolecular approaches listed in Table 7. Distortion from the ideal boat conformation occurs in order to avoid interaction between palladium and C(5) as may be seen by considering the ' plane of best fit ' (Table 6) through atoms C(1)—(4) and the asymmetric deviations from it of C(5) and C(6).

TABLE 7

Intramolecular approaches (Å) between palladium and the olefin

Pd · · · C(1)	3·34	Pd · · · C(4)	3·31
Pd · · · C(2)	3·97	Pd · · · C(5)	3·27
Pd · · · C(3)	4·02	Pd · · · C(6)	3·34

There are no intermolecular distances <3·5 Å involving non-hydrogen atoms. Pairs of monomeric units are arranged back-to-back throughout the crystal so that the two palladium atoms are separated by 3·82 Å with S(2) of one molecule approaching to within 3·69 Å of the palladium in the second. However these distances are too great to represent any significant interactions.

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