1974) and thymine (Neidle & Stuart, 1976). The O(1C)—Os(1)—O(1D) angle of the *trans*-oxoosmyl group was found to be 163·8 (2)°, compared to 164 and 162° for the adenosine and thymine esters, respectively.

The mechanism of formation of osmate esters was long thought to proceed *via* oxygen attack on the double bond in a [3 + 2] cycloaddition. Compelling evidence now shows that a four-membered heterocyclic organoosmium intermediate is formed initially, and this rearranges to give the osmate ester (Sharpless, Teranishi & Backväll, 1977; Tomioka, Nakajima, Iitaka & Koga, 1988). In addition to this thermal synthesis, osmate esters can be prepared photochemically by irradiation of charge-transfer bands [OsO_4^-, Ar^+] observed upon mixing of OsO_4 with various arene or alkene substrates (Wallis & Kochi, 1987). An X-ray structure determination of the resulting 2:1 adducts of benzene and also of anthracene likewise showed a *trans* orientation of the osmate groups (Wallis & Kochi, 1988).

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Structure of the Protonated Pentamethylcyclopentadienylrhodium Dimethylbutadiene Complex, a Compound with an Agostic $M\cdots H\cdots C$ Interaction

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Abstract. (2,3-Dimethylbutenyl)(pentamethylcyclopentadienyl)rhodium tetrafluoroborate, [Rh($C_{10}H_{15}$)(C_6H_{11})][BF_4], $M_r = 408\cdot10$, monoclinic, Cc, $a = 8\cdot418$ (3), $b = 14\cdot185$ (3), $c = 14\cdot840$ (3) Å, $\beta = 91\cdot98$ (2)°, $V = 1771$ (1) Å^3, $Z = 4$, $D_x = 1\cdot531$ g cm^{-3}, μ(Mo $K\alpha$) = 8·89 cm^{-1}, $\lambda = 0\cdot71073$ Å, $F(000) = 832$, $R = 0\cdot032$ for 3609 observed reflections. The compound has the typical appearance of a sandwich complex with two parallel π-bonded ligands. An Rh⋯H⋯C bond to one of the methyl groups of the butenyl ligand is indicated by the bond parameters Rh⋯H = 1·88 (3), H—C = 1·12 (2) and Rh⋯C = 2·351 (5) Å, making this molecule a further typical example of an organometallic compound with an 'agostic' metal-to-hydrogen bond.

Introduction. The stoichiometric activation of carbon–hydrogen bonds by transition-metal complexes has received considerable attention in recent years. A similar activation is also encountered in many catalytic transformations of hydrocarbons and as such is of vast industrial importance. Complexes with $M\cdots H\cdots C$ interactions are thought to be important intermediates in such conversions. This has to some extent been verified by the observation that complexes with an $M\cdots H\cdots C$ moiety can, under special circumstances, be isolated and spectroscopically as well as structurally characterized. This type of bonding is sometimes referred to as 'agostic'

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(Brookhart & Green, 1983). In most cases, such complexes are highly fluxional, confirming the ease with which $M \cdots H \cdots C$ interactions can convert into classical C—H or M—H bonding situations.

Typical spectroscopic and structural parameters that have been derived for such $M \cdots H \cdots C$ moieties include: chemical shifts of hydrogen resonances to high fields (typically -5 to -15 p.p.m.) and reduced coupling constants $^1J(C,H)$ (75–100 Hz) in the NMR, vibrational frequencies at low wave numbers ($\nu_{CH} = 2700$–2300 cm^{-1}) in the infrared as well as elongated C—H and M—H bonds as determined by X-ray or neutron diffraction studies (Elschenbroich & Salzer, 1989).

It has been previously shown that $M \cdots H \cdots C$ interactions are also observed in the protonated diolefin complexes $[CpM(H)(diolefin)]^+$ (M = Co, Rh, Ir; Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl) and that NMR spectroscopy provides a convenient tool for observing the dynamic behaviour of these complexes in solution and to determine their ground-state structure at low temperatures. It was found that these complexes have a ground state either with an M—H bond (M = Ir) or with an $M \cdots H \cdots C$ bridge, both forms rapidly interconverting at ambient temperatures in all molecules (Buchmann, Piantini, von Philipsborn & Salzer, 1987). Activation parameters for the various dynamic processes occurring consecutively and concurrently were derived from kinetic measurements and these were correlated with other physical data obtained via NMR spectroscopy, e.g. chemical shifts and C—H coupling constants. This was the first comparative study of such 'agostic' interactions in which three homologous transition metals were involved.

It seemed worthwhile additionally to characterize at least one of these complexes in the solid state to show that the characteristic features of $M \cdots H \cdots C$ moieties were also found in the above-referenced system. The X-ray structure analysis of the protonated complex [(pentamethylcyclopentadienyl)Rh(2,3-dimethylbutenyl)] tetrafluoroborate, [RhC$_5$(CH$_3$)$_5$-(C$_6$H$_{11}$)][BF$_4$], has been undertaken in order to gain further insight into the nature of the 'agostic' interactions in transition-metal complexes.

Experimental. *Preparation.* All reactions were carried out under N$_2$, using dry and deoxygenated solvents. The starting material [RhCl$_2${C$_5$(CH$_3$)$_5$}]$_2$ was synthetized following the procedure of Booth, Haszeldine & Hill (1969). An excess of 2,3-dimethylbutadiene (5 mmol) and Na$_2$CO$_3$ (5 mmol) was added to a suspension of [RhCl$_2${C$_5$(CH$_3$)$_5$}]$_2$ (0·05 mmol) in ethanol. The mixture was refluxed for 3 h, the solvent evaporated and the residue chromatographed with hexane (Alox, grade IV) after Lee & Maitlis (1975). 90% of the (pentamethylcyclo-

pentadienyl)(2,3-dimethylbutadiene)rhodium complex was obtained as pale-yellow crystals. This complex was protonated with HBF$_4$ in propionic anhydride and precipitated by the addition of ether. A saturated solution of the (pentamethylcyclopentadienyl)(2,3-dimethylbutenyl)rhodium tetrafluoroborate salt was prepared in propionic anhydride at room temperature. The solution was slowly cooled to 243 K. After a week, red, plate-shaped crystals up to 2 mm in length and suitable for X-ray crystallography could be isolated from the solution.

Crystallographic studies. A crystal of dimensions 0·4 × 0·4 × 0·09 mm was selected for measurement and protected from oxygen and moisture by covering its surface with a thin film of araldite. Precession photographs showed monoclinic symmetry and systematic absences typical of the space groups $C2/c$ and Cc. Lattice parameters were determined on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. θ values of 25 automatically centered reflections in the range $12\cdot2 < \theta < 18\cdot0°$ were used for the refinement of the cell parameters. Intensities of 4727 reflections up to $2\theta \le 74°$ [$(\sin\theta)/\lambda = 0\cdot847$ Å^{-1}] were recorded using the ω–2θ scan technique, zigzag mode and variable scan speeds between 1·82 and 6·67° min^{-1}. Miller indices ranged: $0 \le h \le 14$, $0 \le k \le 24$, $-25 \le l \le 25$. Six standard reflections (533, 08$\bar{3}$, 083, 247, 337, 33$\bar{7}$) monitored every three hours of measuring time showed no significant (0·2%) loss of intensities. Six orientation control reflections were remeasured every 300 recorded data. Lorentz–polarization and a numerical absorption correction were applied on eight crystal faces, min. and max. transmission factors 0·6974 and 0·9252. Data reduction of all measured reflections led to 4494 unique data, $R_{int} = 1·2\%$. 3609 reflections considered observed [$I > 3\sigma(I)$].

The structure was solved using the Patterson interpretation routine in *SHELXS*86 (Sheldrick, 1985) applying the non-centrosymmetric space group Cc on the basis of data statistics, and refined by full-matrix least-squares calculations, minimizing $\Sigma w(||F_o| - |F_c||)^2$ with *SHELX*76 (Sheldrick, 1976) on F_{hkl} with anisotropic thermal parameters. The BF$_4^-$ group appeared to be disordered, as unusually high temperature factors (up to $B_i = 32$ Å^2) were observed. Eight peaks from the difference map were chosen as split positions for the F atoms, their site occupation factors set to 0·5 each. All B—F bond lengths were constrained at 1·370 Å within the e.s.d. of 0·005 Å and refined isotropically (B_{iso} varied between 7·4 and 17·7 Å^2). All H atoms were localized on the difference map; however, the refinement for some methyl H atoms converged with some incorrect positional parameters. Therefore, the methyl hydrogens on the cyclopentadienyl and on C(5) of the

Table 1. *Positional and thermal parameters for* [Rh{C₅(CH₃)₅}(C₆H₁₁)][BF₄]

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}/U_{iso}(Å²)
Rh	0·0000	0·08724 (2)	0·0000	0·03290 (4)
C(1)	0·1270 (7)	−0·0403 (4)	−0·0380 (4)	0·0634 (8)
C(2)	−0·0368 (6)	−0·0452 (2)	−0·0691 (2)	0·0509 (7)
C(3)	−0·1547 (6)	−0·0322 (3)	−0·0069 (3)	0·0481 (7)
C(4)	−0·1081 (8)	−0·0311 (3)	0·0903 (3)	0·0680 (8)
C(5)	−0·3359 (6)	−0·0305 (4)	−0·0307 (3)	0·0723 (8)
C(6)	−0·0743 (7)	−0·0526 (3)	−0·1697 (3)	0·0727 (8)
C(7)	0·0407 (5)	0·1995 (2)	−0·0918 (2)	0·0424 (6)
C(8)	−0·1135 (5)	0·2173 (4)	−0·0549 (3)	0·0351 (7)
C(9)	−0·0875 (5)	0·2266 (2)	0·0398 (2)	0·0400 (7)
C(10)	0·0782 (6)	0·2190 (4)	0·0600 (3)	0·0425 (7)
C(11)	0·1581 (5)	0·2042 (3)	−0·0201 (3)	0·0479 (7)
C(12)	0·0706 (7)	0·1910 (4)	−0·1909 (3)	0·0728 (8)
C(13)	−0·2629 (6)	0·2235 (4)	−0·1091 (3)	0·0604 (7)
C(14)	−0·2117 (6)	0·2461 (4)	0·1079 (3)	0·0681 (8)
C(15)	0·1541 (7)	0·2329 (4)	0·1553 (3)	0·0757 (8)
C(16)	0·3374 (5)	0·1959 (4)	−0·0299 (4)	0·0808 (9)
B	−0·5669 (5)	−0·0105 (3)	−0·2776 (3)	0·0645 (8)
F(1A)*	−0·4877 (10)	0·0693 (4)	−0·2483 (6)	0·098 (2)
F(2A)	−0·4424 (11)	0·0498 (8)	−0·2901 (9)	0·177 (2)
F(3A)	−0·7217 (6)	0·0058 (5)	−0·3059 (5)	0·096 (2)
F(4A)	−0·4527 (8)	−0·0780 (5)	−0·2862 (6)	0·102 (2)
F(1B)	−0·6477 (10)	0·0102 (7)	−0·3554 (5)	0·141 (2)
F(2B)	−0·6443 (13)	0·0021 (10)	−0·2004 (6)	0·225 (2)
F(3B)	−0·6068 (9)	−0·0707 (5)	−0·2112 (5)	0·094 (2)
F(4B)	−0·4995 (11)	−0·0713 (5)	−0·3356 (6)	0·136 (2)

* F atoms refined isotropically with s.o.f. 0·5.

Table 2. *Selected interatomic bond distances* (Å)

Rh—C(1)	2·186 (5)	C(1)—H(11)	1·03 (3)
Rh—C(2)	2·157 (4)	C(1)—H(12)	0·79 (3)
Rh—C(3)	2·137 (5)	C(4)—H(41)	1·02 (3)
Rh—C(4)	2·351 (5)	C(4)—H(42)	0·96 (3)
Rh—C(7)	2·132 (4)	C(4)—H(43)	1·12 (2)
Rh—C(8)	2·219 (6)	C(7)—C(8)	1·448 (6)
Rh—C(9)	2·198 (4)	C(8)—C(9)	1·421 (7)
Rh—C(10)	2·164 (6)	C(9)—C(10)	1·420 (7)
Rh—C(11)	2·154 (6)	C(10)—C(11)	1·402 (7)
Rh—H(43)	1·88 (3)	C(11)—C(7)	1·428 (6)
C(1)—C(2)	1·440 (8)	C(7)—C(12)	1·505 (6)
C(2)—C(3)	1·392 (7)	C(8)—C(13)	1·472 (7)
C(2)—C(6)	1·517 (6)	C(9)—C(14)	1·505 (6)
C(3)—C(4)	1·481 (7)	C(10)—C(15)	1·543 (7)
C(3)—C(5)	1·554 (7)	C(11)—C(16)	1·526 (6)
B—F	1·363*		

* This is the mean bond length of four averaged B—F bonds of the two split sites with occupation factors set to 0·5 each.

Table 3. *Interatomic angles* (°)

C(1)—C(2)—C(3)	118·5 (4)	C(12)—C(7)—C(8)	124·5 (4)
C(1)—C(2)—C(6)	118·9 (5)	C(13)—C(8)—C(9)	129·4 (4)
C(2)—C(3)—C(4)	118·5 (5)	C(14)—C(9)—C(10)	124·9 (5)
C(4)—C(3)—C(5)	116·5 (5)	C(15)—C(10)—C(11)	126·9 (5)
C(7)—C(8)—C(9)	106·3 (4)	C(16)—C(11)—C(7)	125·9 (5)
C(8)—C(9)—C(10)	108·5 (4)	C(2)—C(6)—H(61)	109·6 (3)
C(9)—C(10)—C(11)	109·2 (5)	C(2)—C(6)—H(62)	109·6 (3)
C(10)—C(11)—C(7)	107·4 (4)	C(2)—C(6)—H(63)	109·6 (3)
C(11)—C(7)—C(8)	108·4 (4)	C(3)—C(5)—H(51)	109·9 (3)
H(11)—C(1)—C(2)	126 (2)	C(3)—C(5)—H(53)	109·3 (3)
H(12)—C(1)—C(2)	119 (2)	H(41)—C(4)—H(42)	116 (2)
H(11)—C(1)—H(12)	109 (2)	H(42)—C(4)—H(43)	100 (2)
H(41)—C(4)—C(3)	124 (2)	H(41)—C(4)—H(43)	91 (2)
H(42)—C(4)—C(3)	106 (2)		
H(43)—C(4)—C(3)	113 (1)		
C(4)—H(43)—Rh	99 (2)		

butenyl group were fixed at calculated positions (1·08 Å) and refined as a rigid group. Their temperature factors were refined with a common isotropic temperature parameter of $B_{iso} = 11·97$ (17) Å². The positional parameters of all the other hydrogens were refined with fixed $B_{iso} = 6·32$ Å².

The number of reflections in the final refinement cycle used was $m = 3609$; 236 parameters, consisting of 100 positional and 18 rotational parameters, 108 anisotropic displacement parameters, eight different isotropic displacement parameters, one common temperature factor for 18 H atoms, and the scale factor converged with a maximum shift/e.s.d. ratio of 0·24 for a rotational parameter at an R value of 3·23% and $wR = 3·03\%$.
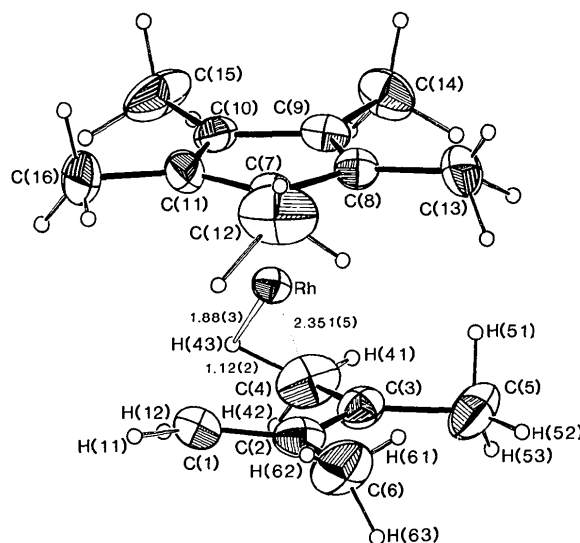

Fig. 1. *ORTEP* drawing of the coordination polyhedron of the (2,3-dimethylbutenyl)(pentamethylcyclopentadienyl)rhodium complex with numbering scheme.
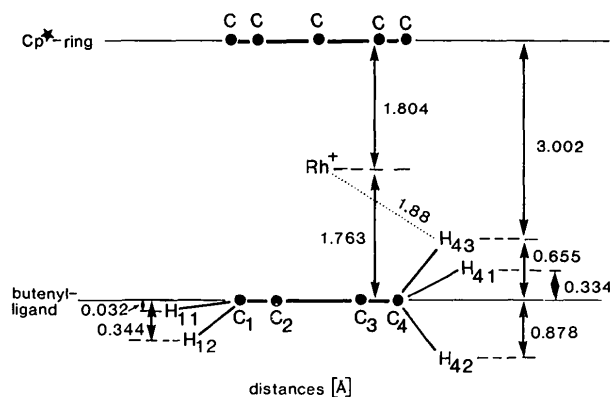

Fig. 2. Schematic frontview of geometry and distances of [Rh{C₅(CH₃)₅}(C₆H₁₁)][BF₄].

Table 4. *Comparison of distances in* $M\cdots H\cdots C$ *bonds* (Å)

Complex	M—H	H—C	M—C	Literature
[Rh(C₅CH₃)₅(C₆H₁₁)][BF₄]	1·88 (3)	1·12 (2)	2·351 (5)	This work
[Fe(C₈H₁₃){P(OCH₃)₃}₃][BF₄]*	1·874 (3)	1·164 (3)	2·384 (4)	Brown, Williams, Schultz, Stucky, Ittel & Harlow (1980)
Mn(C₆H₈CH₃)(CO)₃	1·84 (1)	1·19 (1)	2·34 (1)	Brookhart, Lamanna & Humphrey (1982)
[Cr(C₇H₁₀)(CO)₂P(CH₃)₃]	1·85 (2)	1·16 (2)	2·355 (2)	Michael, Kaub & Kreiter (1985a)
[Cr(C₇H₁₂)(CO)₂{P(OCH₃)₃}]	1·94 (3)		2·399 (4)	Michael, Kaub & Kreiter (1985b)
[(C₅H₅)Mo(C₁₁H₁₅)Mo(C₅H₅)]⁺	1·88 (8)	0·89 (7)	2·196 (5)	Green, Norman & Orpen (1981)
[Ru(C₄H₇){P(CH₃)₂(C₆H₅)}₃]⁺	1·84†	1·08	2·38 (3)	Ashworth, Chalmers, Meintjies, Oosthuizen & Singleton (1985)

* Data from neutron diffraction.
† Calculated distance.

Table 5. *Comparison of* M—C *distances* (Å)

Complex	M—C(1)	M—C(2)	M—C(3)	M—C(4)	Literature
[Rh(C₅CH₃)₅(C₆H₁₁)]⁺	2·186 (5)	2·157 (4)	2·137 (5)	2·351 (5)	This work
[Ru(C₄H₇){P(CH₃)₂(C₆H₅)}₃]⁺	2·26 (2)	2·17 (2)	2·14 (2)	2·38 (2)	Ashworth et al. (1985)
Mn[(C₆H₈CH₃)CO]₃	2·168 (3)	2·092 (2)	2·053 (3)	2·301 (2)	Booth et al. (1969)
[Fe(C₈H₁₃){P(OCH₃)₃}₃]⁺	2·170 (5)	2·081 (5)	2·053 (5)	2·362 (3)	Brown et al. (1980)
[Ru(C₈H₁₃){P(OCH₃)(C₆H₅)₂}₃]⁺	2·246 (7)	2·216 (8)	2·197 (8)	2·592 (9)	Ashworth, Singleton, Laing & Pope (1978)

The weighting scheme $w = k/\sigma(F^2)$ based on intensity statistics, k was finally set to 1·414. Atomic scattering factors from *SHELX*76 (C,H,B,F) and from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102) for the Rh atom. Maximum and minimum heights in final difference Fourier synthesis were 0·67 and −0·45 e Å⁻³. Other computer program used: *ORTEP* (Johnson, 1971).

The refined coordinates and vibrational parameters are listed in Table 1,* and interatomic bond distances and angles are given in Tables 2 and 3.

Discussion. The rhodium complex [Rh{C₅(CH₃)₅}-(C₆H₁₁)][BF₄], shown in Fig. 1, has the general appearance of a normal sandwich complex. The five C atoms of the cyclopentadienyl as well as the four C atoms of the diene moiety lie virtually in two parallel planes separated by a distance of 3·567 Å. The distance of the gravicenter of the ring plane to the Rh atom is 1·804 (1) Å and that of the diene plane 1·763 (1) Å (Fig. 2). It is noteworthy that the distances from rhodium to the cyclopentadienyl-ring C atoms vary significantly within the limits 2·132–2·219 Å and that the carbon–carbon distances also vary from 1·402 to 1·440 Å within the ring ligand without there being a clear correlation between these distances and the metal-to-ring-carbon distances. This has been noted before with other C₅Me₅–Rh complexes (Hursthouse, Malik, Mingos & Willoughby, 1980).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bonding distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53429 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The atoms H(11) and H(12) are both bent out of the diene plane opposite to the metal site. The distance to the diene plane is 0·032 Å for H(11) and 0·344 Å for H(12). This demonstrates again the phenomenon of rehybridization at C(1), the terminal C atom of the diene, which has already been observed in many other examples of allyl and diolefin complexes.

A more significant deviation from the diene plane is observed with the atoms H(41), H(42) and H(43), where the H atom introduced by protonation is located. H(41) and H(43) deviate from the plane defined by C(1)–C(4) by 0·334 and 0·655 Å, respectively, pointing towards the side of the metal, while H(42) points away from the metal and shows the largest deviation of 0·878 Å. The distance Rh—H(43) is 1·88 Å, in good agreement with that found in other 'agostic' bonds (Table 4). The bond C(4)—H(43) is correspondingly elongated to 1·12 Å, again a value quite characteristic for $M\cdots H\cdots C$ interactions. This is also clearly seen by comparison with other complexes with $M\cdots H\cdots C$ interactions, for which the solid-state structures have been determined either by X-ray or neutron diffraction.

A further consequence of the $M\cdots H\cdots C$ bridge is the asymmetric coordination of the four carbons of the diolefin to the rhodium metal, as the distance M—C(1) is 2·186 Å, while the M—C distance to C(4), the carbon involved in the $M\cdots H\cdots C$ bridge, is moderately elongated to 2·351 Å. The shortest bond lengths are found for M—C(2) and M—C(3). This again appears to be quite characteristic, as a comparison with other complexes shows (Table 5).

As the [Rh(C₁₀H₁₅)(C₆H₁₁)] cation is chiral, both enantiomers are found in the unit cell in equal amounts. The unit cell contains four molecules. The two enantiomers are found in alternate layers, one
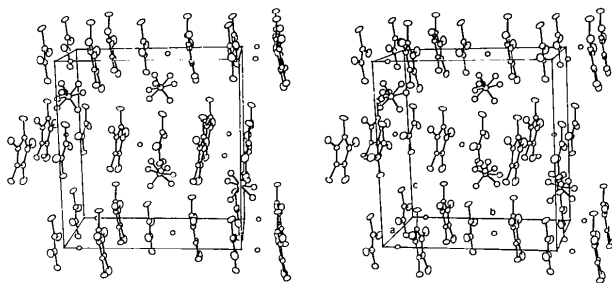
Fig. 3. Stereoscopic *ORTEP* (Johnson, 1971) drawing of the packing of [Rh(C₅H₅)(C₆H₁₁)][BF₄] with the split positions of the BF₄ groups.

layer being on the face of the unit cell and the other at the center (Fig. 3).

In conclusion, it can be said that the X-ray structure of [(RhC₅Me₅)(C₆H₁₁)][BF₄] fully confirms the structural assignment based on spectroscopic measurements and that the complex constitutes a typical example of a compound with an 'agostic' hydrogen bridge.

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Structure of Di[3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] Di-μ-iodo-bis[diiodocadmate(II)], (BEDT-TTF)₂[Cd₂I₆]

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Abstract. (C₁₀H₈S₈)₂[Cd₂I₆], $M_r = 1755.60$, triclinic, $P\bar{1}$, $a = 9.067$ (2), $b = 10.515$ (1), $c = 12.441$ (2) Å, $\alpha = 97.12$ (1), $\beta = 103.43$ (1), $\gamma = 106.13$ (1)°, $V = 1085$ (1) Å³, $Z = 1$, $D_x = 2.69$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 59.6$ cm⁻¹, $F(000) = 806$, room temperature, $R(F) = 0.051$, $wR = 0.061$ for 2761 unique reflections. The structure consists of pairs of BEDT-TTF cations [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] with an interplanar separation of 3.53 Å and $Cd_2I_6^{2-}$ anions formed by two CdI_4^{2-} tetrahedra sharing one common edge. π–π molecular overlap exists within each pair of BEDT-TTF molecules, while different pairs are linked *via* S⋯S contacts, which are as short as 3.339 (3) Å.

Introduction. Organic salts based on BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] and related molecules are among the most interesting solid-state materials. A salt of BEDT-TTF, (BEDT-TTF)₂-[Cu(NCS)₂] (Urayama *et al.*, 1988), has the highest T_c value of the known organic superconductors, while other highly conducting salts are based on the related cation BEDO-TTF [bis(ethylenedioxo)tetrathiafulvalene] (Suzuki, Yamochi, Srdanov, Hinkelman & Wudl, 1989; Wudl *et al.*, 1990; Beno *et al.*, 1990). The salts of these cations show enormous variety, as illustrated in a recent survey (Williams *et al.*, 1987). The present study is part of a program of synthesis of new organic salts by electrocrystal-