The Crystal and Molecular Structure of *trans*-Bis(trimethylphosphine)propynyl-1-(4'-dicyanomethylene-cyclohexa-2',5'-dien-1-yliden)-3,3-dicyano-2-methyl-prop-2-en-1-ylplatinum, a Reaction Product of *trans*-Bis(trimethylphosphine)bis(propynyl)platinum and 7,7,8,8-Tetracyanoquinodimethane

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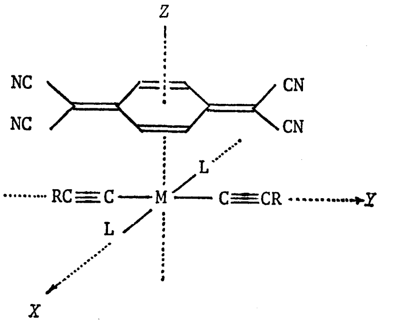
The molecular structure of the title complex has been determined from three-dimensional X-ray diffraction data. The crystal belongs to the monoclinic system, space group $P2_1/c$, $a=14.934(2)$, $b=8.997(1)$, $c=20.221(3)$Å, $\beta=97.44(2)°$, $Z=4$. The molecular structure showed that the tetracyanoquinodimethane (TCNQ) molecule has reacted with one of the propynyl groups of *trans*-$\{(PMe_3)_2Pt(C{\equiv}CMe)_2\}$: part of the TCNQ is bonded to the α-carbon atom and the other part to the β-carbon of the propynyl ligand. The platinum atom has a square-planar geometry; Pt–P=2.302(5) and 2.290(5), Pt–C($C{\equiv}CMe_3$)=2.009(15) and Pt–C(reacted)=2.057(15) Å.

Recently, it has been found that *trans*-bis(tertiary-phosphine)dialkynyl complexes of transition metals (Ni, Pd or Pt) react with 7,7,8,8-tetracyanoquinodimethane (TCNQ) to form stable complexes.[1] Spectroscopic studies suggested that these might be charge-transfer complexes although no other π-acceptors such as tetracyanoethylene, chloranil, bromanil or pyromellitic dianhydride show the charge-transfer interaction with the transition metal complexes mentioned above. This peculiar property of the TCNQ was explained by the possible overlapping of π system of the TCNQ and ethynyl ligands. The structure shown below has been proposed.[1]



(1) M=Pt, L=PMe_3, R=H,
(2) M=Pt, L=PMe_3, R=Me,
(3) M=Pt, L=PEt_3, R=Me.

In order to verify this hypothesis, an X-ray crystallographic study of [*trans*-$\{(PMe_3)_2Pt(C{\equiv}CMe)_2\}\cdot$(TCNQ)] (2) has been carried out. However, as the crystal suffered from an X-ray damage, the standard deviations for all variable parameters were high and consequently the structure is not well-defined.

Experimental

Crystal Data. $C_{24}H_{28}N_4P_2Pt$, *F.W.*=629.56, monoclinic, $a=14.934(2)$, $b=8.997(1)$, $c=20.221(3)$ Å, $\beta=97.44(2)°$, $U=2694.0(7)$ Å^3, $D_m=1.56$ g·cm^{-3} (by flotation), $Z=4$, $D_c=1.55$ g·cm^{-3}, $F(000)=1232$, Space group $P2_1/c$, Mo$K\alpha$ radiation ($\lambda=0.71069$ Å), μ(Mo)=56.14 cm^{-1}.

The crystals are purple-black and long prismatic. Initially, a freshly prepared crystal (approximate dimensions 0.17×0.19×0.17 mm) was used. Accurate cell parameters were obtained by least-squares refinement of 22 high angle reflections. Intensity data were collected on a Rigaku automated, four-circle diffractometer using the θ-2θ scan technique[2] with Zr-filtered Mo$K\alpha$ radiation.

A total of 2666 (2332 non-zero) independent reflections was collected at room temperature. Intensities of three standard reflections, 060, 500, and 006, were measured every 50 reflections, and these were used to detect any crystal decay or mispositioning. The magnitudes for the structure factors of these reflections decreased at an approximately linear rate with time. At the end of the data collection ($(\sin\theta)/\lambda \leqq 0.458$) they were 85.2% of the original values and a linear decay correction was applied. Another set of 1011 (887 non-zero) higher order reflections ($0.457 \leqq (\sin\theta)/\lambda \leqq 0.527$) was collected with a second crystal (*ca.* 0.23×0.17×0.23 mm) with standard reflections decreasing by 2.7%. A linear decay correction was also applied. All these data were placed on the same scale as the first set by collecting common 1117 non-zero reflections ($(\sin\theta)/\lambda \leqq 0.350$). The interset scale factor was 1.157. No absorption correction was applied to either set of data.

Structure Solution and Refinement

The structure was solved and refined using the intensity data from the first crystal. Three-dimensional Patterson synthesis revealed the positions of platinum and phosphorous atoms. All the nonhydrogen atoms were found from subsequent Fourier and difference electron density syntheses. Block-diagonal least-aquares refinement of positional and thermal parameters was carried out using HBLS-V program[3] in three steps: three cycles of isotropic, three cycles of partial anisotropic (Pt and P), and four cycles of anisotropic parameters for nonhydrogen atoms. The second data set was then added and the refinement continued. After the final three cycles, the R was 0.060 ($R_2=0.071$) for non-zero reflections.

The positional and thermal parameters are given in Tables 1 and 2, respectively. The observed and calculated structure factors are listed in Table 3.[4] Throughout the refinement, neutral atomic scattering factors were taken from those given by Hanson and co-workers.[5]

Table 1. Fractional coordinates of atoms along with their estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Pt	0.20891(4)	0.30728(6)	0.26981(3)	C(41)	0.2863(10)	0.3007(17)	0.3617 (7)
P (1)	0.2919 (3)	0.1230 (5)	0.2274 (2)	C(42)	0.3560(10)	0.4210(18)	0.3691 (7)
P (2)	0.1126 (3)	0.4843 (5)	0.3012 (2)	C(43)	0.4164(12)	0.4480(23)	0.3155 (9)
N (1)	0.3833(14)	−0.1592(24)	0.6615(10)	C(44)	0.2875 (9)	0.1929(17)	0.4084 (7)
N (2)	0.1060(12)	−0.2278(25)	0.5781(11)	C(45)	0.3577(10)	0.1665(17)	0.4638 (8)
N (3)	0.4589(12)	0.7477(23)	0.4296(10)	C(46)	0.3540(11)	0.0664(17)	0.5109 (8)
N (4)	0.2620(16)	0.4961(23)	0.5159 (8)	C(47)	0.2725(12)	−0.0172(19)	0.5113 (7)
C(11)	0.3788(12)	0.0232(21)	0.2837 (9)	C(48)	0.1996(11)	−0.0056(19)	0.4549 (8)
C(12)	0.3518(13)	0.1894(24)	0.1590 (9)	C(49)	0.2093(10)	0.0950(18)	0.4064 (7)
C(13)	0.2213(13)	−0.0266(20)	0.1893(10)	C(50)	0.2626(12)	−0.1087(21)	0.5634 (8)
C(21)	0.0661(16)	0.4423(28)	0.3756(11)	C(51)	0.3297(13)	−0.1329(23)	0.6178(10)
C(22)	0.1631(14)	0.6671(20)	0.3206(12)	C(52)	0.1736(14)	−0.1778(21)	0.5721 (9)
C(23)	0.0153(13)	0.5276(23)	0.2388(11)	C(53)	0.3592(11)	0.5149(19)	0.4216 (8)
C(31)	0.1409 (9)	0.3028(17)	0.1774 (7)	C(54)	0.4135(12)	0.6442(23)	0.4267(11)
C(32)	0.1026(11)	0.2972(20)	0.1242 (8)	C(55)	0.3030(14)	0.5036(21)	0.4731 (9)
C(33)	0.0581(16)	0.2919(31)	0.0514(10)				

Table 2. Thermal parameters along with their estimated standard deviations in parentheses

Anisotropic thermal parameters ($\times 10^4$) are expressed in the form:

$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	31.4(3)	112.0(8)	22.6(2)	−4.8(8)	0.9(3)	1.5(6)
P (1)	40 (2)	149 (7)	28 (1)	29 (6)	5 (3)	−14 (5)
P (2)	42 (2)	112 (6)	37 (1)	18 (6)	8 (3)	−11 (5)
N (1)	104(14)	351(44)	62 (8)	−134(42)	−57(17)	142(31)
N (2)	68(11)	367(46)	90(10)	−138(38)	−6(17)	155(36)
N (3)	80(11)	292(38)	72 (8)	−109(36)	10(16)	−34(29)
N (4)	176(20)	290(37)	33 (5)	−102(47)	43(17)	−36(24)
C(11)	57(10)	191(31)	46 (7)	119(31)	−13(13)	13(23)
C(12)	67(11)	258(38)	36 (6)	7(35)	32(13)	−24(25)
C(13)	65(11)	151(28)	55 (7)	−1(30)	−0(15)	−65(24)
C(21)	106(16)	288(46)	56 (8)	110(46)	82(20)	−24(32)
C(22)	71(12)	111(26)	81(10)	−16(30)	−34(18)	−43(27)
C(23)	62(11)	223(36)	56 (8)	111(34)	−48(15)	−45(28)
C(31)	37 (7)	150(23)	20 (4)	−8(22)	17 (9)	3(16)
C(32)	48 (9)	183(28)	33 (5)	48(27)	23(11)	31(20)
C(33)	97(16)	382(57)	37 (7)	−87(51)	−39(17)	22(32)
C(41)	47 (8)	136(23)	19 (4)	−8(23)	−6 (9)	−8(15)
C(42)	44 (8)	153(25)	29 (5)	1(24)	−34(10)	−12(18)
C(43)	52(10)	240(36)	44 (6)	−97(32)	35(13)	−7(25)
C(44)	33 (7)	155(24)	24 (4)	−6(22)	6 (9)	12(17)
C(45)	40 (8)	115(22)	35 (5)	−22(22)	−10(10)	−12(17)
C(46)	50 (9)	114(22)	34 (5)	−27(23)	−23(11)	21(18)
C(47)	73(11)	161(27)	23 (4)	−32(29)	−3(11)	31(18)
C(48)	61(10)	156(26)	29 (5)	−18(27)	−8(11)	−2(19)
C(49)	44 (8)	149(25)	28 (5)	−17(24)	12(10)	−5(18)
C(50)	59(10)	189(30)	35 (5)	−66(30)	−15(12)	4(21)
C(51)	75(12)	219(35)	48 (7)	−77(35)	−45(15)	82(26)
C(52)	99(14)	178(31)	38 (6)	26(35)	−31(15)	108(23)
C(53)	61(10)	158(26)	29 (5)	−65(27)	−30(11)	−0(19)
C(54)	53(10)	197(33)	61 (8)	−40(31)	−29(15)	−2(27)
C(55)	99(14)	165(29)	32 (5)	−32(34)	−11(14)	−17(21)

Results and Discussion

A perspective view of the molecule is given in Fig. 1 with the numbering system of atoms. A stereographic drawing of the molecule is shown in Fig. 2.

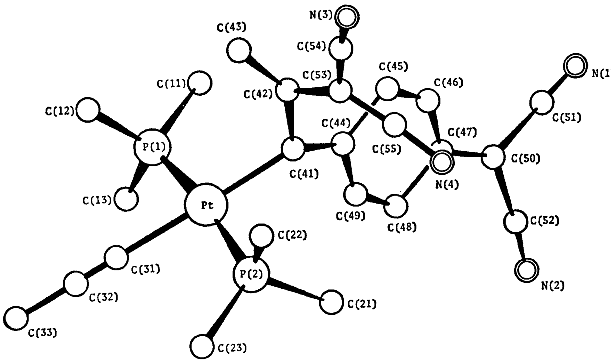
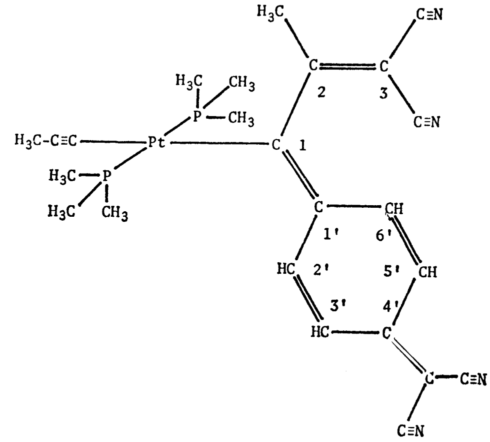


Fig. 1. Perspective view of the molecule with the numbering system of atoms.

The molecular structure determined is entirely different from that proposed¹⁾ as no charge-transfer complex had been formed. The TCNQ molecule had reacted with one of the propynyl groups of *trans*-$\{(PMe_3)_2Pt(C{\equiv}CMe)_2\}$ (Pt-complex), and, as a result, part of the TCNQ is bonded to the α-carbon atom (C(41)) and the remaining part to the β-carbon (C(42)) of the propynyl ligand. The product is, therefore, *trans*-bis(trimethylphosphine)propynyl-1-(4′-dicyanomethylene-cyclohexa-2′,5′-dien-1′-yliden)-3,3-dicyano-2-methyl-prop-2-en-1-ylplatinum.

Bond distances and bond angles are listed in Table 4. The environment of the platinum atom is essentially square-planar and the phosphine groups are mutually *trans*. The Pt–P distances observed [2.290(5) and 2.304(5) Å] are normal as found in the related platinum(II) complexes.⁶,⁷⁾ Both the Pt–C(31)(sp) and Pt–C(41)(sp^2) distances [2.009(15) and 2.057(15)Å] are equal to the respective sum of the covalent radii [Pt–C(sp)=2.00 and Pt–C(sp^2)=2.07 Å]. However, the former is longer than the Pt–C(CNR) distances in *cis*-$\{PtCl_2(PEt_2Ph)(C{\equiv}NEt)\}$ [1.83(4) Å]⁸⁾ and *cis*-$\{PtCl_2(C{\equiv}NPh)_2\}$ [av. 1.986(16) Å],⁹⁾ and it is also longer than the Pt–C(CO) distance in *trans*-$\{PtCl(CO)(PEt_3)_2\}$ [1.78 Å].¹⁰⁾ This may be caused by the reduced basicity of the σ-bonded carbon atoms. The C(31)–C(32) distance of the unreacted propynyl ligand [1.15(3) Å] is shorter than in *trans*-$\{(PEt_3)_2Ni(C{\equiv}CPh)_2\}$¹¹⁾ [1.22(2) Å] although the difference is not fully significant.



The skeleton around the resulted propyl group is shown in Fig. 3. The C(41)–C(42) and C(42)–C(43) links [1.50(2) and 1.52(3) Å] are single bonds, while the C(41)–C(44) and C(42)–C(53) [both 1.35(2) Å] are double bonds. The sum of bond angles around the C(41) and C(42) atoms are both equal to 360° within the range of experimental error. These facts suggest that both the C(41) and C(42) are sp^2 carbon atoms. The significant distortions of Pt–C(41)–C(42) and Pt–C(41)–C(44) angles from 120° [111.9(10) and 127.3(12)°] are probably due to the Pt...C(44) non-bonded interaction, and the concomitant steric strains are relieved by the distortion of the cyclohexadiene ring.

The geometry around the C(41), C(42), C(44) and C(53) atoms suggests that the C(41), C(42) and C(43) atoms are from the original propynyl ligand of the Pt-complex and the remaining C(44) to C(55) and N(1) to N(4) from the TCNQ. Of the two possibilities to arrange a triple bond of the Pt-complex and a double bond of the TCNQ approximately parallel the scheme (1) in Fig. 4 is supported from the structure determined. The charge-transfer complex proposed by Masai and co-workers¹⁾ may be considered as an

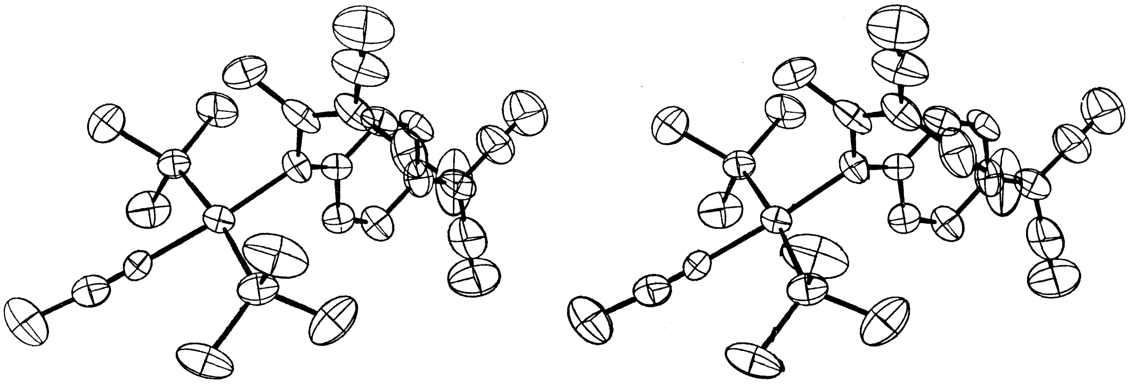


Fig. 2. Stereographic drawing of the molecule. Non-hydrogen atoms are represented by thermal ellipsoids of 50% probability.

Table 4. Bond distances and bond angles along with their estimated standard deviations in parentheses

Bond distances [Å]

Pt-P(1)	2.302 (5)	Pt-P(2)	2.290(5)	Pt-C (31)	2.009(15)
Pt-C (41)	2.057(15)	P (1)-C (11)	1.84 (2)	P (1)-C (12)	1.84 (2)
P (1)-C (13)	1.82 (2)	P (2)-C (21)	1.78 (3)	P (2)-C (22)	1.83 (3)
P (2)-C (23)	1.84 (2)	N (1)-C (51)	1.14 (3)	N (2)-C (52)	1.13 (3)
N (3)-C (54)	1.15 (3)	N (4)-C (55)	1.13 (3)	C (31)-C (32)	1.15 (3)
C (32)-C (33)	1.54 (3)	C (41)-C (42)	1.50 (2)	C (41)-C (44)	1.35 (2)
C (42)-C (43)	1.52 (3)	C (42)-C (53)	1.35 (2)	C (44)-C (45)	1.45 (2)
C (44)-C (49)	1.46 (2)	C (45)-C (46)	1.32 (2)	C (46)-C (47)	1.43 (2)
C (47)-C (48)	1.48 (2)	C (47)-C (50)	1.36 (3)	C (48)-C (49)	1.36 (3)
C (50)-C (51)	1.41 (3)	C (50)-C (52)	1.50 (3)	C (53)-C (54)	1.41 (3)
C (53)-C (55)	1.42 (3)				

Bond angles [°]

P (1)-Pt-P (2)	172.9 (2)	P (1)-Pt-C (31)	82.6 (5)
P (1)-Pt-C (41)	92.8 (4)	P (2)-Pt-C (31)	90.7 (5)
P (2)-Pt-C (41)	93.9 (4)	C (31)-Pt-C (41)	175.3 (6)
Pt-P (1)-C (11)	119.4 (6)	Pt-P (1)-C (12)	112.6 (7)
Pt-P (1)-C (13)	112.4 (7)	C (11)-P (1)-C (12)	104.5 (9)
C (11)-P (1)-C (13)	103.0 (9)	C (12)-P (1)-C (13)	103.5(10)
Pt-P (2)-C (21)	114.5 (8)	Pt-P (2)-C (22)	115.3 (8)
Pt-P (2)-C (23)	115.2 (7)	C (21)-P (2)-C (22)	101.9(11)
C (21)-P (2)-C (23)	105.3(11)	C (22)-P (2)-C (23)	102.9(11)
Pt-C (31)-C (32)	178.5(15)	C (31)-C (32)-C (33)	175.9(20)
Pt-C (41)-C (42)	111.9(10)	Pt-C (41)-C (44)	127.3(12)
C (42)-C (41)-C (44)	120.2(14)	C (41)-C (42)-C (43)	120.9(14)
C (41)-C (42)-C (53)	119.0(15)	C (43)-C (42)-C (53)	119.8(15)
C (11)-C (44)-C (45)	126.8(15)	C (41)-C (44)-C (49)	118.4(14)
C (45)-C (44)-C (49)	114.7(14)	C (44)-C (45)-C (46)	125.2(15)
C (45)-C (46)-C (47)	118.6(15)	C (46)-C (47)-C (48)	120.1(15)
C (46)-C (47)-C (50)	120.0(16)	C (48)-C (47)-C (50)	119.9(16)
C (47)-C (48)-C (49)	117.9(15)	C (44)-C (49)-C (48)	122.9(15)
C (47)-C (50)-C (51)	124.2(18)	C (47)-C (50)-C (52)	122.0(17)
C (51)-C (50)-C (52)	113.3(17)	N (1)-C (51)-C (50)	176.9(23)
N (2)-C (52)-C (50)	178.8(23)	C (42)-C (53)-C (54)	122.3(17)
C (42)-C (53)-C (55)	124.4(17)	C (54)-C (53)-C (55)	113.0(17)
N (3)-C (54)-C (53)	178.1(23)	N (4)-C (55)-C (53)	176.8(23)

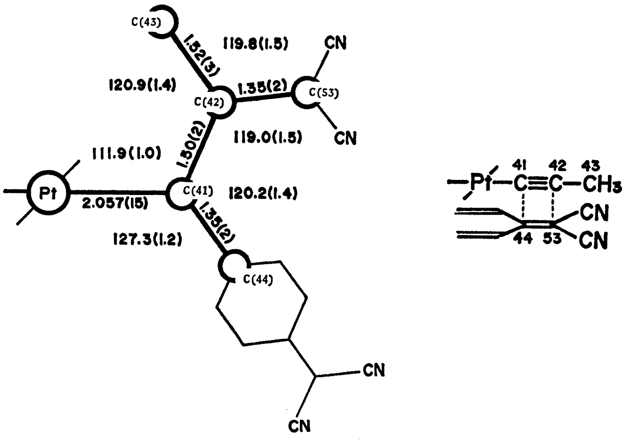


Fig. 3. Skeleton around the resulted propyl group.

intermediate. However, it is inconclusive whether both or one of the ethynyl bonds interact with a double bond of the TCNQ. The unreactivity of the other π-acceptors with the Pt-complex is supposed partly due to the steric hindrance of phosphine groups attached to the platinum atom.

Bond distances and bond angles in two dicyanomethylene groups are similar to those in TCNQ.[12]

A perspective drawing of the crystal structure along the b axis is shown in Fig. 5. No close intermolecular atomic contact less than the sum of the van der Waals radii is observed.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at Osaka University. Figures 2 and 4 were drawn on a NUMMERICON 7000 system at Osaka University with a local version of ORTEP.[13]

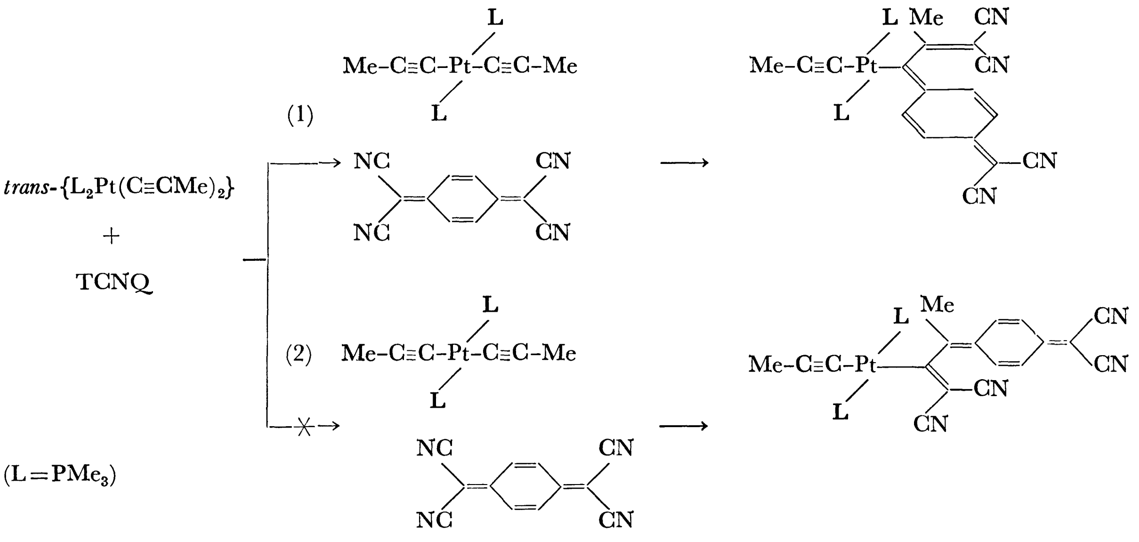


Fig. 4. Reaction scheme.

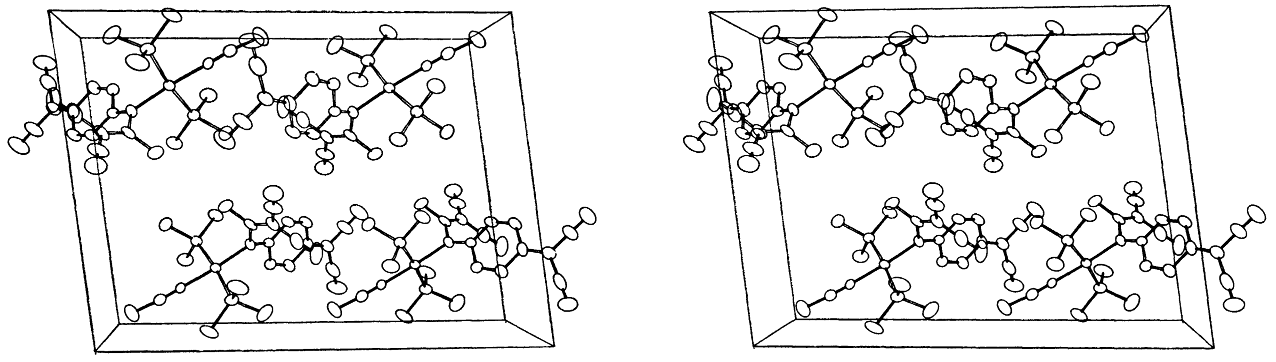


Fig. 5. Perspective drawing of the crystal structure along the b axis.

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