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STRUCTURAL CHEMISTRY OF TITANIUM AND ALUMINIUM BIMETALLIC HYDRIDE COMPLEXES

V *. CRYSTAL AND MOLECULAR STRUCTURE OF OCTONUCLEAR $\{[\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_3\overline{CH_2)Ti(\mu_2\text{-}H)_2Al}]_2\text{-}\mu_3\text{-}O\}_2 \cdot 2C_6H_6$

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Summary

$\{[(C_5Me_5)(C_5Me_4\overline{CH_2)TiH_2Al}]_2O\}_2 \cdot 2C_6H_6$ has been obtained by treating $(C_5Me_5)_2TiCl$ with $LiAlH_4$. The complex crystallized in a rhombic unit cell with parameters; *a* 24.647(8), *b* 26.575(9), *c* 13.519(4) Å, space group P_{nma}, $Z = 8$. The molecular structure incorporates four $(C_5Me_5)(C_5Me_4\overline{CH_2)TiH_2Al}$ moieties, interlinked by two oxygen-μ_3 atoms. Linkage between Ti and Al atoms is accomplished via the double hydrogen bridge and the η^5-$C_5Me_4CH_2$ methylene group of the ring.

Introduction

Certain authors [1–3] have shown that the activity of catalyst systems of the Ziegler type depends on small amounts of water added to the system. It has been determined that traces of water are also catalytic for the homolytic decomposition of the M–R bond [4]. However, the mechanism of water activation and the structure of the resultant metallic complexes are as yet unclear. In this light, we conducted X-ray structural analysis on the product, extracted from the $(C_5Me_5)_2TiCl/LiAlH_4$ system, which is catalytic for olefin hydrogenation and isomerization.

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* For Part IV see ref. 5.

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Results and discussion

The interaction of $(C_5Me_5)_2TiCl$ with lithium aluminiumhydride, depending on reagent ratio, results in the bimetallic hydride complexes $[(C_5Me_5)_2TiAlH_4]_2$ and $(C_5Me_5)_2Ti_2AlH_4Cl$ [5]. $[(C_5Me_5)_2TiAlH_4]_2$ was isolated and characterized using structural analysis [5]. An attempt to isolate the second compound at a ratio of reagents $(C_5Me_5)_2TiCl/LiAlH_4$ 2/1 unexpectedly yielded a small amount of greenish-black crystals of a compound containing no chlorine atoms. The composition and structure of this compound was identified by X-ray structural analysis as $\{[C_5Me_5)Ti(C_5Me_4\overline{CH_2)H_2Al}]_2O\}_2 \cdot 2C_6H_6$. The presence of oxygen atoms in the molecule is most likely to be caused by the partial hydrolysis of the reaction products by traces of water.

The crystal structure of the complex is a sandwich of $\{[(C_5Me_5)Ti(C_5Me_4\overline{CH_2)H_2Al}]_2O\}_2$ molecules (I) and two crystallochemically independent benzene molecules. There are no short intermolecular contacts between them. One benzene molecule is situated at the beginning of coordinates and has no symmetry. The other is located over the dense center of the cross-shaped molecule of I and has "*m*" symmetry.

The molecule of I consists of four identical $(C_5Me_5)Ti(C_5Me_4CH_2)H_2Al$ moieties bonded by two oxygen bridges (Fig. 1). It has a plane of symmetry that passes through the Ti(2), Ti(3), Al(2), Al(3) atoms, and several carbon atoms. The wedge-like $(C_5Me_5)Ti(C_5Me_4CH_2)$ sandwiches have a chessboard conformation with geometric parameters common to compounds with a $(C_5Me_5)_2Ti$ moiety. The coordination environment of the Ti atom is similar to that of the other known complexes of Ti^{III}. There are two hydrogen bridges in the bisector plane of the wedge-like sandwich, which link the Ti and the Al atoms. The geometry of the TiH_2Al system is close to that observed for $(Cp_2TiAlH_4)_2 \cdot TMEDA$ (II) [6], $Cp_2TiH_2AlCl_2 \cdot OEt_2$ (III) [7], $[Cp_2TiH_2AlH(\eta^1:\eta^5\text{-}C_5H_4)TiCp(\mu\text{-}H)]_2$ (IV) [8] and $[(C_5Me_5)_2TiH_2AlH_2]_2$ (V) [5]. Thus, the $Ti-H_{av.}$ distance (1.7 Å) and the $H-Ti-H_{av.}$ angle (70°) are close to the corresponding parameters in complexes II (1.6 Å and 71°) [6], III (1.8 Å and 75°), IV (1.8 Å and 72°, 76°) [8], and V (1.9 Å and 73°) [5]. At the same time, the Al–H distance in I is somewhat larger than those in compounds II–V, because the Al atoms in I are out of the bisector plane of the wedge-like sandwich because of the formation of a σ-bond with a CH_2 group in one of the rings. This is one of the most remarkable features of this rather unusual molecule. Although the cyclopentadienyl $\eta^5:\eta^1$ groups bonded to the Al atom are well known (cf., for instance, [8] and references therein), there is as yet no description of the C_5Me_5 groups in this respect. Only one structure – $(C_5Me_5)Ti(C_5Me_4\overline{CH_2)(\mu\text{-}O_2)Ti}(C_5Me_5)$ (VI) [9] – is known which has the bifunctional $C_5Me_4CH_2$ group linked via a σ-bond with the Ti atom. In I as in VI, the M atom deviates towards the ring, forming a C–M bond, which leads to folding of the TiX_2M diamond along the line X–X, at an angle of 150° in I and 158.8° in VI [9]. Only the Cp–Ti–Cp angle is different, being almost 7° greater in I than in VI (148° and 140.6°, respectively [9]). This is because of shortening of the X bridges, on moving from VI to I. It is noteworthy that in V and in $[Cp_2TiH_2AlH(OMe)]_2$ (VII) [10], where there is no Al–ring bond, and the $Ti \cdots Al$ distance is short, the Cp–Ti–Cp angle is also much smaller (142.2° for V and $138^{\circ}_{av.}$ for VII thus avoiding short non-valent contacts, $Al \cdots H-C$.

Al atoms in the molecule of I are non-equivalent in pairs with coordination

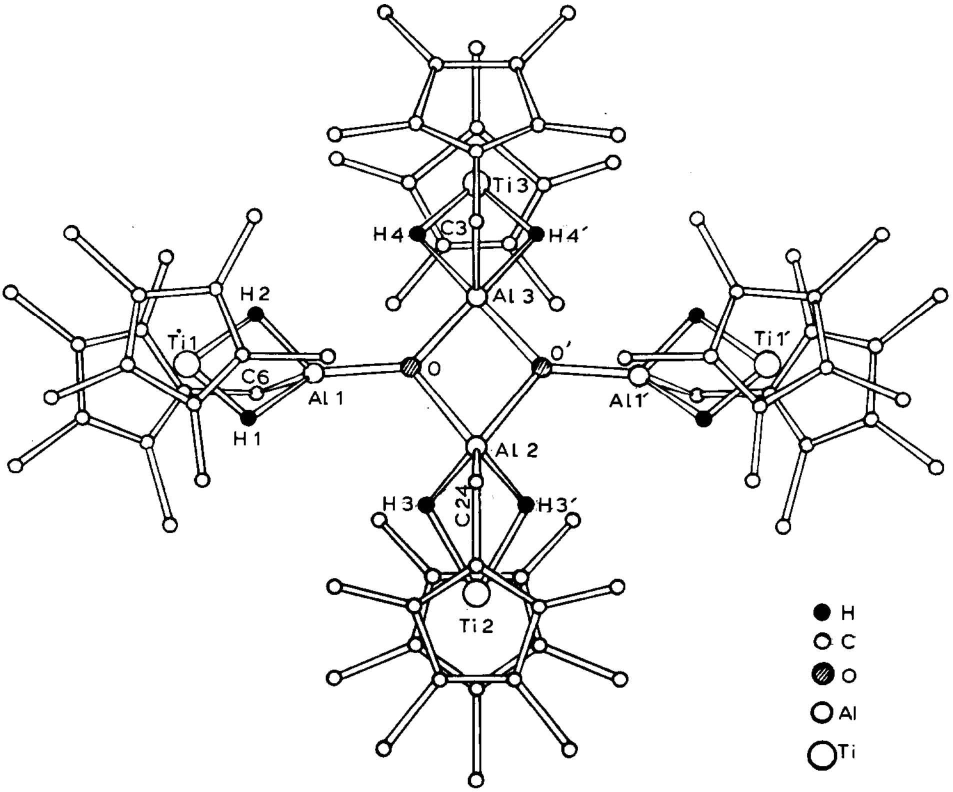


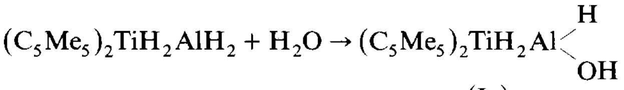
Fig. 1. Molecular structure of the complex $\{[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4CH_2)Ti(\mu_2\text{-}H)_2Al]_2\text{-}\mu_3\text{-}O\}_2 \cdot 2C_6H_6$.

numbers of 4 and 5. Coordination polyhedrons differ radically from those described for Group I and II metal aluminiumhydrides (distorted tetrahedron) and titanium aluminium hydride complexes II–V [5–8] or yttrium complexes [11–12] (distorted trigonal bipyramid). Thus, the Al(1) and Al(1′) atoms have environments that approach trigonal pyramids with axial oxygen atoms, while the polyhedra of Al(2) and Al(3) atoms are best described as tetragonal pyramids, each with two O atoms at the base and an axial C atom. It should be mentioned that such a pentahedral configuration is unique to aluminium coordination chemistry. All bond lengths in the polyhedron at the Al(1) coordination atom, as well as the Ti · · · Al distances, are naturally smaller than those for the penta-coordinated Al(2) and Al(3) atoms (Table 2). It is also noteworthy that the Ti · · · Al distance for penta-coordinated Al atoms in I is considerably larger (Table 2) than that found in the structures of complexes II–V and VII (2.75–2.79 Å) [5–8,10], although additional bonding does exist via the μ-$C_5Me_4CH_2$ group. It may be assumed that this is because the Al atoms are out of the bisector plane of the wedge-like sandwich $(C_5Me_5)Ti(C_5Me_4CH_2)$; greater Ti · · · Al distance corresponds to a greater Al atom diviation from the bisector plane, which should result in reduced overlapping of Ti and Al atom orbitals and, therefore, in a weakened Ti–Al interaction. Earlier [7], we had assumed the existence of a direct weakened interaction, on the strength of the remarkable consistency of the Ti · · · Al distances and their near-equivalence to the sum total of metal covalent radii.

The central unit of molecule I forms as a result of the dimerization of the monomer, $[(C_5Me_5)Ti(C_5Me_4\overline{CH_2)H_2Al}]_2O$, brought about by the donor–acceptor, and covalent O → Al bonds. This is a cross-shaped system of four Al atoms bonded by oxygen μ_3 bridges. The Al(2)–O–Al(3)–O diamond is virtually planar, with trigonal O atom coordination. Similar bonding is realized in VII, and the $[Al_4O_2Cl_{10}]^{2-}$ ion [13]; in fact, Al–O bond lengths in these ions are very close to those in I, although slight asymmetry of the AlO_2Al diamond in VII is observed.

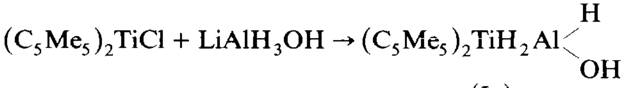
The formation of the polynuclear complex I is very interesting. There is no difficulty in describing the scheme of the reactions that leads to the alumoxane cycle, provided terminal Al–H bond hydrolysis is accepted as basic (oxidation is hardly likely, as, Ti^{III} atoms in this case, would have been the first to be oxidized). On this condition, the first stage of the process is the hydrolysis of the Ti and Al hydride complex already formed (from reaction 1), or more likely, direct interaction of $(C_5Me_5)_2TiCl$ with partially hydrolyzed lithium aluminiumhydride (eq. 3). The unusual stability of the alumoxane AlO_2Al cycle is illustrated by the formation of

$$(C_5Me_5)_2TiCl + LiAlH_4 \rightarrow (C_5Me_5)_2TiH_2AlH_2 + LiCl \qquad (1)$$



$$(C_5Me_5)_2TiH_2AlH_2 + H_2O \rightarrow (C_5Me_5)_2TiH_2Al{<}^{H}_{OH} \qquad (2)$$

(Ia)

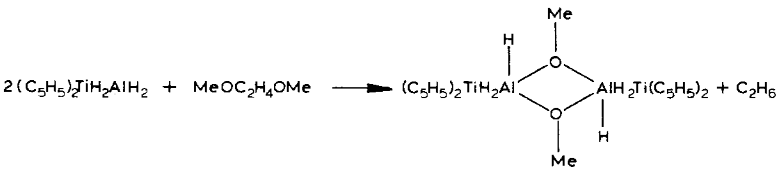


$$(C_5Me_5)_2TiCl + LiAlH_3OH \rightarrow (C_5Me_5)_2TiH_2Al{<}^{H}_{OH} \qquad (3)$$

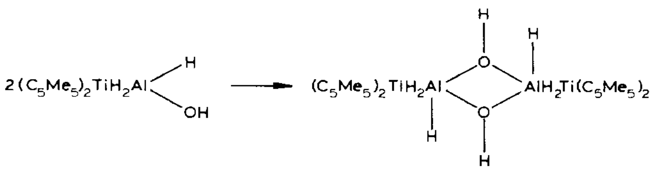
(Ia)

complex VII that occurs upon decomposition of the O–C bond in 1,2-dimethoxyethane [10] (eq. 4). It can naturally be assumed that Ia ring closure should take place under milder conditions, however, contrary to reaction 4, two acidic hydrogen atoms are retained in the alumoxane cycle of intermediate Ib, which can then participate in further transformations (eq. 5).

At the same time, to preserve the stoichiometry of complex I, there is a certain



(4)



(5)

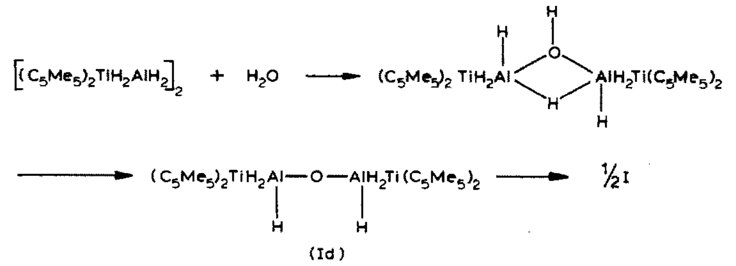
(Ib)

quantity of non-hydrolyzed complex $(C_5Me_5)_2TiH_2AlH_2$, in the solution whose reaction with Ib leads to the hydride form of the octonuclear complex Ic (eq. 6).

$$[(C_5Me_5)_2TiH_2Al(H)(OH)]_2 + 2(C_5Me_5)_2TiH_2AlH_2 \rightarrow \underset{(1c)}{\{[(C_5Me_5)_2TiH_2Al(H)]_2O\}_2} + H_2 \qquad (6)$$

To explain the simultaneous transformation of Ic into the final product with the Al–C bond is difficult. It is probable that the formation of the σ-bond is the result of a fortuitous combination of geometric (close proximity of the weakly acidic H atom of the methyl group to the hydride H atom), and electronic (changing charges of interacting H atoms upon formation of alumoxane cycle), factors. The former is indicated by the absence of H^+ and H^- interaction in complex VII [10], and the latter by the absence of similar interaction in the $[(C_5Me_5)_2TiH_2AlH_2]_2$ [5].

The fact that $(C_5Me_5)_2TiH_2AlH_2$ is a dimer in the crystal state [5] points to another possible route to the formation of I, with the first stage as described in eq. 7. This scheme is possible because it explains the formation of the Al–C σ-bond (second stage) in the coordination-unsaturated intermediate Id with equivalent Al atoms; Al atoms in Ic are non-equivalent in pairs.



(7)

It should be pointed out that the schemes discussed above on the formation of I are assumptions, however, it is our belief that they provide a realistic account of the way this compound is formed and, moreover, can be useful in the discussion of the reasons behind stronger or weaker catalytic activity of compounds and systems of the Ziegler type upon activation with water. Hence, in accordance with [14], the intermediate Ic should possess high catalytic activity in reactions of olefin izomerization, as two coordination-unsaturated Al atoms (coordination number 4) and two mobile terminal H atoms are combined in its structure.

Experimental

Synthesis of $\{[(C_5Me_5)Ti(C_5Me_4\overline{CH_2)H_2Al}]_2O\}_2 \cdot 2C_6H_6$. $(C_5Me_5)_2TiCl$ (0.253 g, 0.715 mmol) synthesized according to ref. 15 was dissolved in 22 ml of benzene to this was added 0.357 mmol of $LiAlH_4$ in 1.4 ml of ether. The dark-green solution was evaporated to 4 ml in vacuo and kept under argon for four days. During this time, a small amount of dark-green crystals precipitated. They were separated out and dried in vacuo.

The crystal was placed in a thin-walled glass capillary. The periods of the rhombic unit cell are *a* 24.647(8), *b* 26.575(9), *c* 13.519(4) Å, space group P_{nma},

TABLE 1. ATOMIC COORDINATES (10^3 for H, A[a]; 10^4 for non-H atoms) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS[b]

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ti(1)	1528(1)	510(1)	8599(2)	4.9	C(27)	4311(7)	2500	9091(16)	6.7
Ti(2)	3397(1)	2500	8492(3)	5.3	C(28)	4057(6)	2069(4)	9422(12)	8.3
Ti(3)	865(1)	2500	1900(3)	5.1	C(29)	3658(5)	2232(5)	99(12)	6.3
Al(1)	1844(1)	1390(1)	9480(4)	5.5	C(30)	4856(8)	2500	8368(20)	14
Al(2)	2250(2)	2500	8777(5)	4.9	C(31)	4262(6)	1533(6)	9301(12)	10
Al(3)	1328(2)	2500	9998(4)	4.0	C(32)	3351(6)	1879(6)	798(12)	11
O	1801(2)	2048(2)	9429(6)	4.3	C(33)	274(6)	2500	492(17)	3.6
C(1)	2085(9)	493(6)	44(14)	8.0	C(34)	161(5)	2086(4)	1137(14)	6.5
C(2)	2372(6)	279(6)	9273(15)	7.1	C(35)	−77(5)	2234(4)	2090(13)	8.4
C(3)	2128(9)	−177(7)	8978(15)	9.7	C(36)	552(6)	2500	9485(17)	4.1
C(4)	1644(10)	−258(7)	9559(20)	11	C(37)	198(4)	1523(4)	781(10)	7.0
C(5)	1629(6)	131(10)	154(16)	6.8	C(38)	−341(6)	1875(6)	2829(12)	12
C(6)	2271(6)	999(5)	475(11)	7.3	C(39)	941(12)	2500	3697(30)	22
C(7)	2917(5)	409(5)	8773(12)	8.2	C(40)	1257(9)	2081(10)	3244(19)	12
C(8)	2310(6)	−647(6)	8267(13)	11	C(41)	1668(8)	2256(5)	2746(13)	8.6
C(9)	1239(6)	−677(5)	9782(13)	11	C(42)	584(15)	2500	4519(24)	28
C(10)	1258(7)	289(6)	1108(13)	10	C(43)	1206(10)	1488(8)	3531(20)	24
C(11)	1211(7)	123(5)	7205(13)	8.1	C(44)	2142(8)	1962(8)	2207(16)	17
C(12)	754(6)	195(7)	7791(13)	8.0	A(1)	250(1)	250	469(2)	
C(13)	676(5)	677(7)	7885(12)	8.5	A(2)	279(1)	205(1)	453(2)	
C(14)	1058(6)	921(5)	7336(12)	7.2	A(3)	331(1)	205(1)	423(2)	
C(15)	1394(6)	565(6)	6892(12)	7.7	A(4)	358(1)	250	411(2)	
C(16)	1353(8)	−453(6)	6710(17)	17	A(5)	27(3)	46(2)	514(6)	
C(17)	351(6)	−250(7)	8179(17)	15	A(6)	50(2)	8(4)	414(5)	
C(18)	174(6)	881(9)	8396(15)	16	A(7)	−3(3)	34(2)	572(5)	
C(19)	1073(8)	1503(5)	7176(16)	18	A(8)	8(4)	41(3)	524(8)	
C(20)	1870(8)	674(10)	614(14)	17	A(9)	−33(3)	26(2)	577(4)	
C(21)	2831(7)	2500	7151(14)	6.0	A(10)	44(2)	26(3)	471(8)	
C(22)	3151(5)	2058(5)	7052(9)	5.2	H(1)	132(2)	100(2)	919(6)	1
C(23)	3694(5)	2235(4)	6883(10)	5.7	H(2)	199(2)	104(2)	834(5)	1
C(24)	2205(6)	2500	7265(11)	7.5	H(3)	287(3)	216(2)	897(6)	1
C(25)	2953(5)	1521(5)	7014(10)	7.8	H(4)	117(3)	212(3)	110(6)	2
C(26)	4165(4)	1891(5)	6473(10)	7.7					

[a] A(1)–A(10) are the centroids of the C_5H_5 and C_6H_6 groups. [b] $B_{eq} = 4/3\Sigma_i\Sigma_j b_{ij}\bar{a}_i\bar{a}_j$ (Å^2).

TABLE 2

THE MAIN BOND LENGTHS (Å) AND VALENCE ANGLES (°) OF THE COMPLEX $\{[(C_5Me_5)(C_5Me_4\overline{CH_2)Ti(\mu_2\text{-}H)_2Al}]_2\text{-}\mu_3\text{-}O\}_2\cdot 2C_6H_6$

(Ti–C)	2,36(4) [a]	(C–C)	1,39(6) [a]	(C–C)	1,56(6) [a]
Ti(1)–H(1)	1,63(6)	Al(1)–H(1)	1,70(6)	Al(1)–O	1,752(6)
Ti(1)–H(2)	1,84(5)	Al(1)–H(2)	1,84(7)	Al(2)–O	1,857(7)
Ti(2)–H(3)	1,72(6)	Al(2)–H(3)	1,70(6)	Al(3)–O	1,843(7)
Ti(3)–H(4)	1,66(7)	Al(3)–H(4)	1,84(8)	Al(2) ··· Al(3)	2,809
Al(1)–C(6)	2,00(1)	Al(2)–C(24)	2,05(2)	Al(3)–C(36)	2,03(2)
Ti(1) ··· Al(1)	2,739	Ti(2) ··· Al(2)	2,854	Ti(3) ··· Al(3)	2,681(2)
H(1)–Ti(1)–H(2)	71(3)	Al(1)–O–Al(2)	128,9(4)	Al(1)–C(6)–C(1)	92(1)
H(3)–Ti(2)–H(3)	63	Al(1)–O–Al(3)	132,3(4)	Al(2)–C(24)–C(21)	93(1)
H(4)–Ti(3)–H(4)	75	Al(2)–O–Al(3)	98,8(3)	Al(3)–C(36)–C(33)	97(1)
O–Al(1)–H(1)	123(2)	O–Al(2)–O	80,7	O–Al(3)–O	81,4
O–Al(1)–H(2)	119(2)	O–Al(2)–C(24)	116,2(4)	O–Al(3)–C(36)	116(1)
O–Al(1)–C(6)	125,3(5)	O–Al(2)–H(3)	96(2)	O–Al(3)–H(4)	97(2)
C(6)–Al(1)–H(1)	104(2)	O–Al(2)–H(3)	139	O–Al(3)–H(4)	146
C(6)–Al(1)–H(2)	101(2)	C(24)–Al(2)–H(3)	102(3)	C(36)–Al(3)–H(4)	94(2)
H(1)–Al(1)–H(2)	70(3)	H(3)–Al(2)–H(3)	60	H(1)–Al(3)–H(4)	67
Ti(1) [b]	147,6	Ti(2) [b]	148,6	Ti(3) [b]	147,8

[a] E.s.d. in parentheses. [b] Dihedral angle of wedge-like sandwich at titanium atom.

$Z = 8$ (for $\{[(C_5Me_5)Ti(C_5Me_4\overline{CH_2)H_2Al}]_2O\}_2 \cdot 2C_6H_6$), $\rho_{\text{calcd.}}$ 1.18 g/cm^3 A CAD autodiffractometer was used to measure 2089 reflections (Mo-K_α, graphite monochromator, $\theta/2\theta$ scanning, $\theta_{\max}$ 22°), where 1223 reflections, with $I > 2\sigma(I)$, were used in the calculations. The small number of reflections is due to the small size of the crystal and its partial decomposition during analysis.

The structure was the solved by a combination of direct and Patterson methods and refined to $R = 0.07$. Hydride H atoms were found from Fourier syntheses. The remaining H atoms were excluded from calculations.

Atom coordinates and thermal parameters are presented in Table 1, the main interatomic distances and valent angles in Table 2.

References

1 L.A. Volkov, B.G. Gerasimov, G.B. Sakharovskaya and S.S. Medvedev, Vysokomolek. soed. 15 B (1973) 455.

2 A. Animoto J. Polym. Sci. 13 (1975) 549.

3 L.F. Borisova, E.A. Fushman, A.N. Shupik, Ye.I. Vizen, L.N. Sosnovskaya, and S.S. Lalayan, Vysokomol. Soedin., 23 A (1981) 1984.

4 O.M. Chukanova, N.E. Khrushch, V.V. Drobotenko F.S. D'yachkovsky and N.S. Enykolopyan, Izv. Akad. Nauk SSSR, Ser. Khim. (1984) 1856.

5 V.K. Bel'sky, A.I. Sizov, B.M. Bulychev, G.L. Soloveichik J. Organomet. Chem., 280 (1985) 67.

6 E.B. Lobkovskii, G.L. Soloveichik and B.M. Bulychev, J. Organomet. Chem., 265 (1984) 167.

7 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev, R.G. Gerr and Yu.T. Struchkov J. Organomet. Chem., 270 (1984) 45.

8 E.B. Lobkovskii, G.L. Soloveichik, A.I. Sizov and B.M. Bulychev J. Organomet. Chem., 280 (1985) 53.

9 F. Bottomley, I.J.B. Lin, and P.S. White, J. Amer. Chem. Soc., 103 (1981) 703.

10 V.K. Bel'sky, A.I. Sizov, B.M. Bulychev, G.L. Soloveichik, Koord. Chim., 17 (1985) 1003.

11 V.K. Bel'sky, A.B. Erofeev, B.M. Bulychev, G.L. Soloveichik. J. Organomet. Chem., 265 (1984) 123.

12 V.K. Bel'sky, B.M. Bulychev, A.B. Erofeev and G.L. Soloveichik J. Organomet. Chem., 268 (1984) 107.

13 D. Jentsch, P.G. Lones, E. Schwartzman and G.M. Scheldrick, Acta Cryst. C 39 (1983) 1173.

14 B.M. Bulychev, E.V. Evdokimova, A.I. Sizov, G.L. Soloveichik. J. Organomet. Chem., 239 (1982) 313.

15 S.A. Cohen, P.R. Aubern and J.E. Bercaw J. Amer. Chem. Soc., 105 (1983) 1136.