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THE CRYSTAL AND MOLECULAR STRUCTURE OF (π-METHYL BENZOATE)(TRIPHENYLPHOSPHINE)CHROMIUM DICARBONYL

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Summary

The crystal and molecular structure of the title compound was determined by the direct method on the basis of 2192 reflections measured by an automatic diffractometer. Least-squares anisotropic (isotropic for hydrogens) refinement led to $R = 0.040$. The bond lengths and angles are usual. The $Cr(CO)_2$-PPh_3 fragment is in an eclipsed orientation relative to the almost planar η^6-methyl benzoate ligand. The molecule has no specific conformational features to explain its unusually fast isotopic hydrogen exchange.

Introduction

Earlier we showed [1] that methyl and methoxyl substituents in an aromatic ligand in π-arenechromium complexes do not affect the rate of isotopic hydrogen exchange (IHE) to any considerable degree. Therefore it was surprising that the carbomethoxyl group in $(\eta^6\text{-}C_6H_5COOMe)Cr(CO)_2PPh_3$ (I) gave rise to the ten-fold increase of the IHE rate in CF_3COOH compared with that of $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$ (the rate constants at 27.7°C are $(4.7 \pm 0.4) \times 10^{-6}$ and $(5.0 \pm 0.5) \times 10^{-7}$ s^{-1} respectively [2]). At the same time the carbomethoxyl substituent in benzene derivatives is known to decrease the rate of electrophilic substitution.

In attempt to explain this anomaly of complex I we considered it useful to carry out its X-ray structural determination.

Experiment and solving the structure

Red, needle-shaped crystals of I are monoclinic. The unit cell parameters were determined by least-squares on the basis of 12 reflections with large θ-values measured in the 4-circle automatic Hilger—Watts diffractometer:

$a = 10.182(5)$, $b = 18.884(6)$, $c = 13.250(5)$ Å; $\gamma = 108.64(2)°$; $V = 2414$ Å^3; mol. wt. = 506.5 ($C_{28}H_{23}PO_4Cr$); $d_m = 1.40$, $d_c = 1.40$ g cm^{-3}; $Z = 4$; space group $P2_1/n$.

Intensities of ca. 2400 reflections were measured by the same diffractometer (λ(Cu-K_α), graphite monochromator, $\theta/2\theta$ scan, ordinate analysis [3]). Absorption was neglected, and for subsequent calculations 2192 reflections with $F^2 \geqslant 3\sigma(F^2)$ were used.

The structure was solved by the direct method and 24 (out of 34) non-hydrogen atoms were revealed by the E-synthesis. Positions of 10 more atoms were determined by the difference synthesis (Cr and P atoms being subtracted). The isotropic refinement led to $R = 0.108$. At this stage the next difference synthesis with subtraction of non-hydrogen atoms allowed all 23 hydrogens to be localized. The refinement of their coordinates lowered the R-factor to 0.092. Finally 5 cycles of block-diagonal anisotropic (isotropic for hydrogen atoms) refinement gave the final values $R = 0.040$ and $R_w = 0.036$. Atomic coordinates and temperature factors are given in Tables 1 and 2 respectively.

Molecular geometry and discussion of results

The configuration of the molecule I, the main bond lengths and angles are shown in the Fig. 1. As in related (η^6-arene)$Cr(CO)_3$ complexes the coordination of chromium is octahedral with angles P—Cr—C(O) and (O)C—Cr—C(O) close to the ideal value of 90°. Thus the substitution of one CO group by the bulky PPh_3 ligand does not cause any appreciable distortion of the coordination polyhedron, i.e., does not give rise to considerable overcrowding.

The mutual orientation of the methyl benzoate ligand and the $Cr(CO)_2$-PPh_3 fragment is shown in the Fig. 2 (a projection on the coordinated benzene ring plane). Evidently these molecular parts are in an "eclipsed" conformation. A similar configuration is found in all related complexes where arene ligands have electronegative substituents [4]. It is also obvious from Fig. 2 that in accordance with a *meta*-orienting effect of the carbomethoxyl group 3 octahedral orbitals of the Cr atom (collinear with Cr—CO bonds) are directed towards the atoms C(3), C(5) and C(7) of the benzene ring.

The average Cr—C(arene) distance 2.198(4) Å is the same as found in chromium tricarbonyl complexes of benzene (2.22 Å) [5], anizole (2.23 Å) [6], methyl benzoate (2.22 Å) [7] and other arene ligands.

The methyl benzoate ligand is almost planar (the dihedral angle between the benzene ring and the planes of the carbomethoxyl groups is 3.2°). Its bond lengths and angles are in good agreement with those found in the structure of (η^6-C_6H_5COOMe)$Cr(CO)_3$ [7].

Comparison of Cr—CO bond lengths in octahedral complexes shows their pronounced sensitivity to *trans*-ligands. Some geometrical parameters of a series of such complexes are given in Table 3. In $Cr(CO)_6$ all Cr—CO distances are equal [8], and substitution of one or more CO groups by weaker π-acceptors L gives rise both to a general shortening of Cr—CO bonds and to the more essential contraction of those bonds which are *trans* to ligands L. In I the average Cr—CO distance 1.823(3) Å is shorter than in complexes with phosphine (or phosphite) ligands in *trans*-positions to CO groups (with the exception of the

TABLE 1

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF HYDROGEN ATOMS

Atom	x	y	z	Atom	x	y	z	B_j (Å^2)
Cr	0.45318(5)	0.32330(3)	0.03614(4)	C(22)	0.63801(34)	0.48946(18)	0.30459(26)	
P	0.56626(7)	0.35338(4)	0.19143(6)	C(23)	0.52397(30)	0.28076(16)	0.28948(23)	
O(1)	0.35286(24)	0.45562(13)	0.04425(19)	C(24)	0.45446(35)	0.20691(18)	0.26449(27)	
O(2)	0.18759(24)	0.24719(14)	0.14354(19)	C(25)	0.42227(42)	0.15197(20)	0.33771(33)	
O(3)	0.43618(42)	0.10467(17)	0.02771(34)	C(26)	0.45848(38)	0.16993(22)	0.43635(31)	
O(4)	0.65150(35)	0.17221(20)	0.07226(30)	C(27)	0.52749(37)	0.24283(22)	0.46272(26)	
C(1)	0.39641(31)	0.40563(17)	0.04305(24)	C(28)	0.55945(34)	0.29829(19)	0.38985(25)	
C(2)	0.29260(32)	0.27570(17)	0.10252(23)	H(4)	0.7202(31)	0.2989(16)	0.0075(23)	1.1(6)
C(3)	0.52274(35)	0.23105(18)	−0.02152(26)	H(5)	0.7039(40)	0.4084(22)	−0.0767(30)	4.1(9)
C(4)	0.63461(34)	0.29724(19)	−0.02474(24)	H(6)	0.4987(46)	0.3982(24)	−0.1493(33)	5.8(1.1)
C(5)	0.62602(39)	0.36087(20)	−0.07456(27)	H(7)	0.3057(46)	0.2903(23)	−0.1488(33)	4.8(1.1)
C(6)	0.49996(51)	0.35746(26)	−0.12020(27)	H(8)	0.3243(39)	0.1859(21)	−0.0649(29)	3.4(8)
C(7)	0.38853(47)	0.29222(29)	−0.11948(30)	H(12)	0.7803(30)	0.2899(16)	0.2702(23)	1.2(6)
C(8)	0.39634(39)	0.22949(23)	−0.06771(30)	H(13)	1.0199(39)	0.3380(20)	0.2542(29)	3.6(8)
C(9)	0.53195(52)	0.16269(24)	0.02779(38)	H(14)	1.1479(31)	0.4517(17)	0.1720(24)	1.7(6)
C(10)	0.65285(101)	0.10127(53)	0.12368(78)	H(15)	1.0164(35)	0.5188(19)	0.0954(26)	2.4(7)
C(11)	0.75639(29)	0.38198(16)	0.18855(22)	H(16)	0.7754(32)	0.4783(17)	0.1024(25)	2.2(7)
C(12)	0.83172(33)	0.34092(19)	0.23374(26)	H(18)	0.3241(28)	0.3832(15)	0.2644(22)	0.5(6)
C(13)	0.97564(36)	0.36548(23)	0.22647(28)	H(19)	0.2602(40)	0.4665(21)	0.3599(30)	4.0(9)
C(14)	1.04348(33)	0.43002(22)	0.17604(27)	H(20)	0.4459(40)	0.5753(22)	0.4206(31)	4.0(9)
C(15)	0.97101(34)	0.47065(19)	0.13048(25)	H(21)	0.6833(38)	0.5867(20)	0.3886(29)	3.7(9)
C(16)	0.82751(31)	0.44641(17)	0.13437(24)	H(22)	0.7429(31)	0.4917(17)	0.2910(24)	1.6(7)
C(17)	0.53506(30)	0.42920(16)	0.26401(23)	H(24)	0.4153(39)	0.1953(20)	0.1906(29)	4.0(9)
C(18)	0.39814(33)	0.42358(18)	0.28556(25)	H(25)	0.3629(50)	0.0951(26)	0.3156(37)	6.2(1.3)
C(19)	0.36544(37)	0.47647(21)	0.34289(28)	H(26)	0.4292(33)	0.1259(18)	0.4876(25)	2.1(7)
C(20)	0.46959(41)	0.53725(20)	0.37943(28)	H(27)	0.5544(37)	0.2567(20)	0.5315(26)	3.0(8)
C(21)	0.60592(40)	0.54339(19)	0.36068(30)	H(28)	0.6067(30)	0.3484(16)	0.4126(23)	1.7(6)

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS

Atom	$10^5 B_{11}$	$10^5 B_{22}$	$10^5 B_{33}$	$10^5 B_{12}$	$10^5 B_{13}$	$10^5 B_{23}$
Cr	746(6)	233(2)	397(3)	387(5)	−59(7)	−26(4)
P	651(9)	196(3)	414(5)	292(8)	−2(10)	22(6)
O(1)	1333(33)	332(9)	918(20)	733(29)	340(40)	265(21)
O(2)	1074(31)	484(10)	773(19)	282(29)	220(38)	292(23)
O(3)	3236(71)	356(12)	2098(45)	775(47)	2050(91)	108(37)
O(4)	2307(55)	747(16)	1728(36)	1854(52)	1216(72)	1026(41)
C(1)	779(38)	268(11)	525(23)	276(34)	82(45)	100(25)
C(2)	951(41)	273(12)	478(21)	426(35)	−152(47)	33(25)
C(3)	1168(47)	273(12)	622(24)	541(38)	335(53)	−60(28)
C(4)	979(44)	386(14)	489(22)	542(39)	323(49)	−89(28)
C(5)	1534(55)	394(14)	545(25)	640(46)	676(57)	68(31)
C(6)	2756(83)	639(20)	385(24)	1709(68)	355(70)	109(36)
C(7)	1959(67)	840(24)	548(27)	1676(69)	−750(67)	−536(42)
C(8)	1232(51)	507(17)	758(28)	544(48)	−15(61)	−681(37)
C(9)	2403(80)	427(17)	1185(43)	973(60)	1525(93)	60(43)
C(10)	5934(220)	1553(57)	3195(128)	5133(204)	3657(270)	2983(147)
C(11)	675(36)	241(10)	439(20)	328(31)	−77(42)	3(24)
C(12)	1056(45)	368(13)	574(23)	676(40)	158(51)	193(29)
C(13)	1015(46)	636(19)	672(26)	1041(49)	−46(56)	259(37)
C(14)	791(44)	563(17)	541(24)	386(44)	117(49)	−47(32)
C(15)	1011(44)	342(13)	563(23)	296(38)	232(51)	12(29)
C(16)	793(39)	288(11)	520(22)	364(34)	−55(47)	−37(27)
C(17)	865(39)	233(10)	418(20)	360(33)	−83(43)	3(23)
C(18)	898(41)	317(12)	578(23)	420(37)	−179(49)	−221(27)
C(19)	1227(49)	441(14)	667(26)	759(43)	−11(57)	−327(32)
C(20)	1769(60)	376(14)	611(25)	915(48)	−9(62)	−261(32)
C(21)	1412(52)	314(13)	805(29)	279(42)	−69(61)	−309(32)
C(22)	995(44)	286(12)	666(25)	269(37)	−10(53)	−223(28)
C(23)	769(37)	238(10)	493(21)	377(32)	70(44)	69(24)
C(24)	1210(46)	268(12)	658(26)	488(38)	−34(55)	185(29)
C(25)	1624(58)	302(13)	931(32)	414(45)	−112(70)	307(35)
C(26)	1281(51)	440(16)	841(29)	664(46)	304(60)	639(36)
C(27)	1150(49)	538(17)	518(25)	738(47)	195(52)	296(32)
C(28)	1110(45)	328(13)	487(23)	379(39)	60(50)	58(27)

β-isomer of $Cr(CO)_5[Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2]Mn(CO)_3Br$ [9]).

It is to be noted that the Cr—P bond in I is the shortest [2.337(1) Å] of all found in chromium complexes with phosphine ligands, where these bonds are 2.360-2.422 Å in length. This fact is explained naturally by the different character of ligands *trans* to a phosphorus atom: in I this is methyl benzoate, in all other complexes mentioned a carbonyl group. All the same the $Cr—PPh_3$ bond in I is somewhat longer than the $Cr—P(OPh)_3$ bond in $Cr(CO)_5P(OPh)_3$ (2.309 Å [11]). A contraction of the latter is specific for all phosphite complexes of transition metals and is due to the presence of more electronegative substituents at phosphorus because such groups facilitate back-donation M→P.

The configuration of the PPh_3 ligand is usual. The Cr—P—C bond angles are increased to 117.0(1)°, the C—P—C angles are decreased to 101.0(1)° in comparison with ideal tetrahedral values. The average bond lengths are P—C 1.836(3), C—C 1.382(5) Å. Planar phenyl rings make dihedral angles 96, 84 and 78° with each other.

Analysis of intramolecular non-bonded distances does not reveal any short

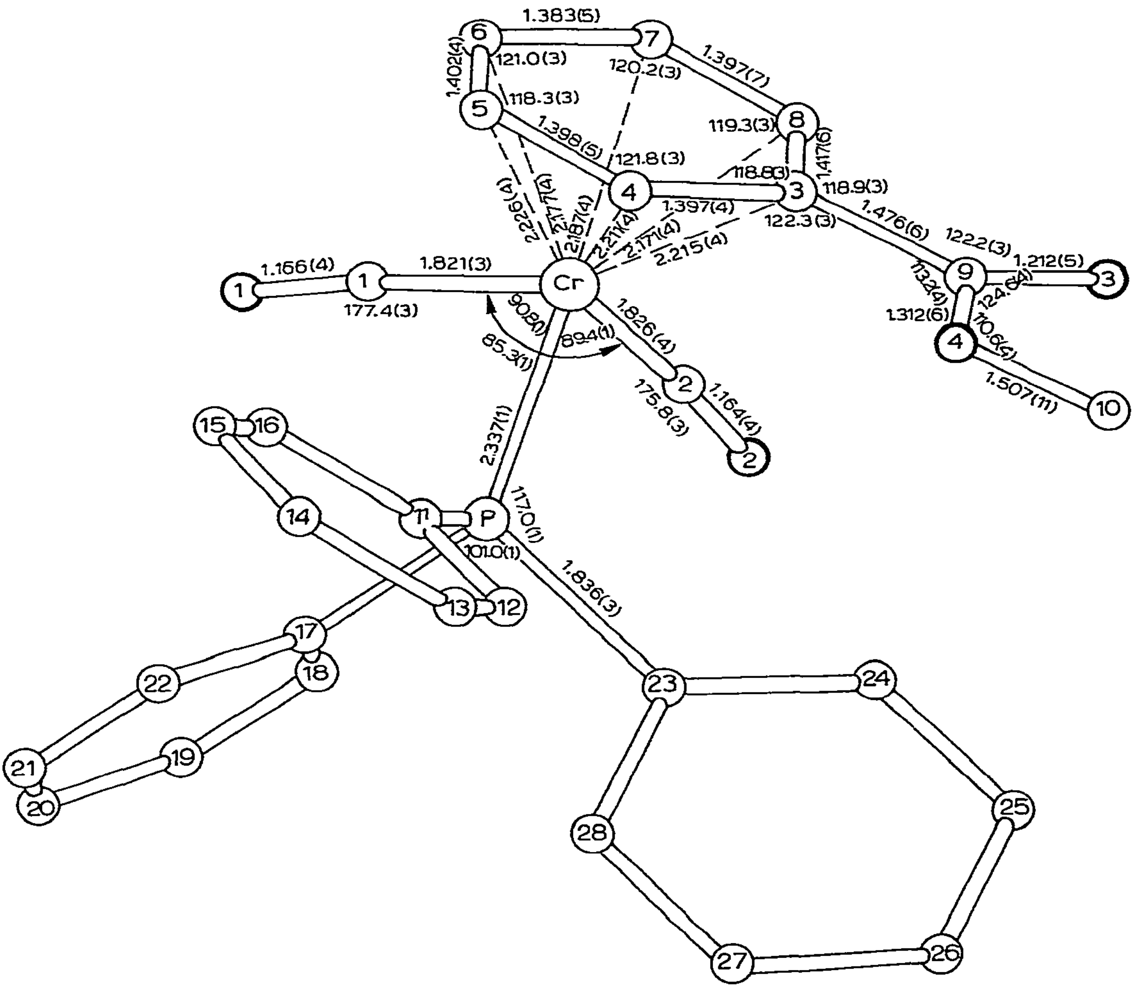

Fig. 1. A perspective view of the molecule with the main bond lengths and angles.

TABLE 3

BOND LENGTHS IN CHROMIUM CARBONYL PHOSPHINE COMPLEXES

Complex	*cis*-Cr—CO (Å)	*trans*-Cr—CO (Å)	Cr—P (Å)	Ref.
$Cr(CO)_6$	1.909		—	8
$Cr(CO)_5PPh_3$	1.880	1.844	2.422	10
$Cr(CO)_5P(OPh_3)_3$	1.896	1.861	2.309	10
β-$Cr(CO)_5[Ph_2PCH_2CH_2(Ph)PCH_2CH_2PPh_2]Mn(CO)_3Br$	1.84	1.77	2.376	9
$Cr(CO)_3[Ph_2PCH_2CH_2N(C_2H_5)CH_2CH_2PPh_2]$		1.827 [a] 1.804 [b]	2.381	11
$Cr(CO)_3(C_6H_5COOCH_3)$		1.85	—	7
$Cr(CO)_2PPh_3(C_6H_5COOCH_3)$		1.823	2.337	
$Cr(CO)_4(Ph_2PCH_2CH_2PPh_2)$	1.884	1.831	2.360	12

[a] *trans* to P. [b] *trans* to N.

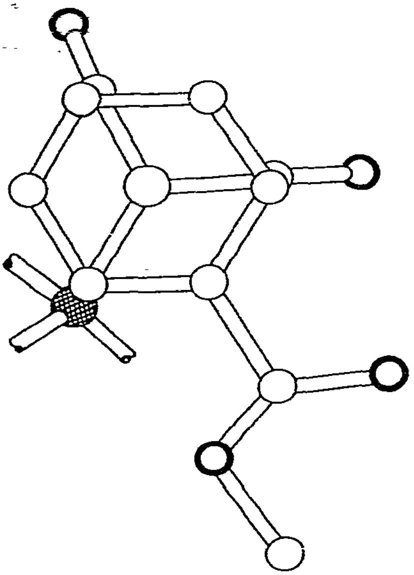

Fig. 2. A projection of the molecule on the plane of the coordinated benzene ring showing an eclipsed conformation.

contacts between the carbomethoxyl group and the phosphine ligand: the shortest P···C, P···O, C···O and C···C distances are even greater than corresponding Van der Waals radii sums. Thus the molecular structure of I does not contain any unusual features and there are no conformational reasons for its anomalous behaviour in the IHE reaction.

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