Journal of Organometallic Chemistry, 231 (1982) 315—321
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CARBONYL COMPLEXES OF 1,2,4-TRIAZOLES

II *. THE CRYSTAL STRUCTURE OF PENTACARBONYL-4-METHYL-1,2,4-TRIAZOLECHROMIUM(0), $Cr(CO)_5(C_3N_3H_5)$. CHROMIUM-TO-TRIAZOLE π-BONDING

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(Received December 7th, 1981)

Summary

The crystal structure of pentacarbonyl-4-methyl-1,2,4-triazolechromium $[Cr(CO)_5(C_3N_3H_5)]$ has been determined by single-crystal X-ray techniques. The compound crystallizes in the space group *Pbca* with *a* 10.899(2), *b* 17.572(2), *c* 11.877(2) Å and $Z = 8$. The compound consists of monomeric units in which the chromium atom is coordinated octahedrally to five CO groups and one monodentate coordinating 4-methyl-1,2,4-triazole ligand (Cr—N 2.111(2) Å). Full matrix least-squares refinement resulted in a final $R = 0.025$ ($R_w = 0.0324$). There appears to be no or little π-interaction between the triazole ligand and the chromium atom.

Introduction

During the last few years triazoles have attracted much attention because of their medical and biological applications [1—8], and, in addition, the coordination chemistry of triazoles has numerous interesting aspects. Different coordination modes result in a range of complexes with varying geometries. In most cases 1,2,4-triazole gives rise to layered coordination compounds in which the ligand is bridging via its 1,4-nitrogen atoms [9,10]. Earlier experiments showed that 4-substituted 1,2,4-triazoles, like 4-ethyl-1,2,4-triazole [11,12], form

* For Part I: See ref. 13. Requests for reprints should be sent to Dr. J.G. Haasnoot.

0022-328X/82/0000—0000/$02.75

dinuclear transition-metal compounds, with 1,2-bidentate bridging triazoles. Both classes of compounds have interesting magnetic properties because of their polynuclear nature.

Recently we have investigated Group VI metal pentacarbonyl complexes with 4-substituted 1,2,4-triazoles [13]. A wide range of metal carbonyl complexes with nitrogen donor ligands have been reported [14,15], but only very few with 1,2,4-triazoles [16]. Although the coordination chemistry of 1,2,4-triazoles with first-row transition-elements has been studied extensively [9—12, 17—19], there is little known about the coordination behaviour of these ligands towards low-valent Group VI metals [13,16]. The advantage of Group VI metal coordination compounds with triazoles is their solubility in a wide range of organic solvents, which facilitates the use of NMR spectroscopy in their investigation. In a preceding paper compounds of $Cr(CO)_5$ and $W(CO)_5$ with 4-phenyl-1,2,4-triazole (Phtrz) and 4-methyl-1,2,4-triazole (Metrz) were described [13]. In this paper we report the crystal structure of $Cr(CO)_5$(Metrz). The structural parameters are discussed with respect to the electronic nature of the N-donor ligand.

Experimental

Yellow crystals of $Cr(CO)_5$(Metrz) were prepared as described previously [13]. A single crystal, dimensions 0.3 × 0.3 × 0.4 mm, which, according to Weissenberg photographs, appeared to be of good quality, was mounted on a CAD-4 diffractometer. Mo-K_α radiation monochromated by graphite was used to determine the unit cell parameters and the space group and also to measure the reflection intensities.The data were corrected for Lorentz and polarisation effects, for absorption [20] and for extinction [21]. Reflections with intensities less than twice the standard deviation (calculated from counting statistics, inaccuracies of attenuation filters and absorption correction) were considered not significant. After reduction of the intensities to structure factors, a Wilson plot was calculated to obtain starting values for the scale factor and the initial thermal parameter B.

Solution and refinement of the structure

The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, $w = \sigma_F^{-2}$. The discrepancy indices are defined as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$. Scattering factors and anomalous-dispersion corrections were taken from International Tables for X-ray Crystallography [22]. A three dimensional Patterson synthesis revealed the position of the Cr atom. The other non-hydrogen atoms were also located by Patterson techniques. Four cycles of isotropic refinement yielded $R = 0.130$ ($R_w = 0.184$). A difference Fourier synthesis revealed the positions of the hydrogens of the triazole ring and of a hydrogen belonging to the methyl group. The positions of the remaining two hydrogen atoms were calculated. After another three cycles of isotropic refinement, including the hydrogen atoms, R decreased to 0.0695 (R_w = 0.0942). Six cycles of anisotropic refinement led finally to $R = 0.0250$ (R_w = 0.0324) (significant reflections only). Two cycles including all reflections

TABLE 1

CRYSTAL AND DIFFRACTION DATA FOR $Cr(CO)_5$(Metrz)

Space group	*Pbca*
Lattice constants	
a (Å)	10.899(2)
b (Å)	17.572(2)
c (Å)	11.877(2)
Crystal dimensions (mm)	0.3 × 0.3 × 0.4
θ-range (°)	2—27
Measured reflections	2026
Independent reflections	1765
Significant reflections	1722
Density (g cm^{-3})	1.61
Final *R* (R_w)	0.0250 (0.0324)

TABLE 2

FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FAÇTORS ($Å^2$) FOR $Cr(CO)_5$-(Metrz) [a]

	x	*y*	*z*	B_{iso}
Cr	0.46524(3)	0.33385(2)	0.38272(2)	3.04(1)
C(1)	0.5620(3)	0.2482(2)	0.3915(2)	3.80(7)
O(1)	0.6222(2)	0.1940(1)	0.3948(2)	5.14(6)
C(2)	0.3255(3)	0.2697(1)	0.3725(2)	4.01(7)
O(2)	0.2461(2)	0.2284(1)	0.3662(2)	6.37(7)
C(3)	0.4472(3)	0.3377(1)	0.5423(3)	3.85(7)
O(3)	0.4371(3)	0.3393(1)	0.6372(2)	5.95(7)
C(4)	0.4785(3)	0.3356(1)	0.2236(2)	3.77(7)
O(4)	0.4886(3)	0.3379(1)	0.1287(2)	5.79(2)
C(5)	0.6096(3)	0.3943(2)	0.3918(2)	4.33(8)
O(5)	0.6995(3)	0.4270(2)	0.3954(2)	7.19(8)
N(1)	0.3571(2)	0.4330(1)	0.3674(2)	3.36(2)
N(2)	0.3963(2)	0.4946(1)	0.3049(2)	5.01(7)
C(6)	0.3064(3)	0.5430(2)	0.3071(3)	4.83(9)
N(3)	0.2111(2)	0.5177(1)	0.3666(2)	3.47(5)
C(7)	0.2474(3)	0.4490(2)	0.4026(3)	3.56(3)
C(8)	0.0956(4)	0.5568(2)	0.3893(3)	4.81(9)
H(1)	0.308(3)	0.589(2)	0.275(2)	5
H(2)	0.205(2)	0.421(1)	0.443(2)	5
H(3)	0.032(3)	0.523(2)	0.380(2)	5
H(4)	0.101(4)	0.579(2)	0.455(3)	5
H(5)	0.874(4)	0.599(2)	0.330(3)	5

[a] The isotropic temperature factors of the hydrogen atoms were not refined.

yielded $R = 0.0689$ ($R_w = 0.0367$). The positional parameters of the atoms in the monomeric unit are listed in Table 2. Lists of the temperature factors and the observed and calculated intensities are available from the authors.

Description of the molecular structure

The compound has the expected octahedral coordination around the central chromium atom. It can be seen from Table 3, that the octahedron is slightly distorted. Distortions of this type have been observed before in substituted

TABLE 3

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) IN $Cr(CO)_5$(Metrz) EXCEPT Metrz RING

Cr—C(1)	1.841(3)	C(1)—O(1)	1.156(3)
Cr—C(2)	1.899(3)	C(2)—O(2)	1.132(3)
Cr—C(3)	1.907(3)	C(3)—O(3)	1.133(3)
Cr—C(4)	1.896(3)	C(4)—O(4)	1.133(3)
Cr—C(5)	1.902(3)	C(5)—O(5)	1.136(3)
Cr—N(1)	2.111(2)		
C(1)—Cr—C(2)	88.7(1)	C(4)—Cr—C(5)	89.1(1)
C(1)—Cr—C(3)	91.9(1)	C(4)—Cr—N(1)	86.75(9)
C(1)—Cr—C(4)	91.5(1)	C(5)—Cr—N(1)	90.3(1)
C(1)—Cr—C(5)	88.9(1)	Cr—C(1)—O(1)	178.6(2)
C(1)—Cr—N(1)	178.07(9)	Cr—C(2)—O(2)	176.5(3)
C(2)—Cr—C(3)	90.1(1)	Cr—C(3)—O(3)	179.2(2)
C(2)—Cr—C(4)	90.4(1)	Cr—C(4)—O(4)	178.4(2)
C(2)—Cr—C(5)	177.5(1)	Cr—C(5)—O(5)	176.2(3)
C(2)—Cr—N(1)	92.1(1)	Cr—N(1)—N(2)	121.4(2)
C(3)—Cr—C(4)	176.6(1)	Cr—N(1)—C(7)	131.7(2)
C(3)—Cr—C(5)	90.5(1)		
C(3)—Cr—N(1)	89.90(9)		

hexacarbonyl chromium compounds [23—27]. One complete $Cr(CO)_5L$ unit, showing the numbering of the atoms, is depicted in Fig. 1. Calculation of the Cr—N distance based on the covalent radii of Cr^0 (1.48 Å) [26] and nitrogen (0.70 Å) [28], yields a value of 2.18 Å. It thus seems probable that the observed Cr—N distance of 2.111(2) Å represents a single bond and that the nitrogen ligand is coordinated to the chromium atom predominantly by simple σ-donation, with a very small π-interaction if any. Further support for this conclusion can be derived from the Cr—C bond lengths in the molecule. It is generally accepted, that in compounds of the type $M(CO)_5L$ a lack of multiple bonding in the M—L bond allows greater π-interaction in the M—C bonds,

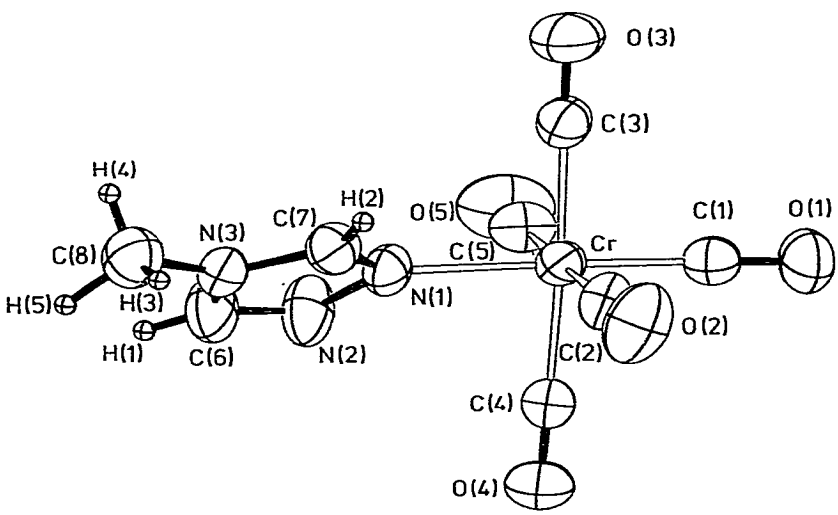

Fig. 1. ORTEP drawing of the mononuclear unit $Cr(CO)_5$(Metrz).

particularly for the CO ligand in the *trans* position [29]. A range of substituted derivatives of $Cr(CO)_6$ are known, in which the π-bonding ability of the ligand varies. In carbene derivatives, with appreciable Cr—L π-bonding, the *cis* and *trans* distances are very similar, with only a very slight shortening of the *trans* bond [23]. In a compound with diethylene triamine, which has no π-bonding ability, the shortening of the *trans* Cr—C bond is considerable [26]. In $Cr(CO)_5$-(Metrz), the four *cis* Cr—C bonds have lengths 1.896—1.907(3) Å, which are slightly shorter than that observed in $Cr(CO)_6$ (1.909(3) Å) [30]. The Cr—C bond *trans* to the triazole ligand has a length of 1.841(3) Å, which is considerably shorter than the *cis* Cr—C bonds and the Cr—C bonds in $Cr(CO)_6$. The *cis* and *trans* distances in $Cr[P(OPh)_3](CO)_5$ are 1.896(4) Å and 1.861(4) Å respectively [31]. This compound is known to involve little π-interaction between the metal and the phosphine ligand [31]. On the basis of the shorter *trans* Cr—C distance, the π-bonding ability of the Metrz ligand must be very small indeed.

Recently Frazier and Kisch [32] have suggested two possible orientations of the free nitrogen in diazine complexes of $M(CO)_5$. In the first orientation the N(2) is located between the two equatorial CO groups. This orientation is expected to have the lowest energy, since steric interactions are minimised. In the second orientation the N(2) is situated in the M—C—O plane. The steric hindrance between the nitrogen and the CO groups can in this case be balanced by a better overlap of the orbitals suitable for back donation. The structural parameters showed that the triazole ring makes an angle of about 45° with the plane containing Cr and the three other CO groups. This means that the uncoordinated nitrogen of the triazole ring is located between two CO groups. This orientation would imply that steric considerations alone dictate the position of the triazole ring with respect to the equatorial carbonyls and that there is no or very little back donation from the $M(CO)_5$ to the triazole ligand. The small difference between the four *cis* C—O bonds (1.132—1.136(3) Å) and the *trans*

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) IN THE Metrz RING IN $Cr(CO)_5$(Metrz) AND IN THE trz RINGS IN TWO OTHER trz COMPOUNDS

	$Cr(CO)_5$(Metrz)	$Mn_2(NCS)_4$(Metrz)$_5$ [19] [a]	Mn(trz)$SO_4(H_2O)_4$ [33]
N(1)—N(2)	1.380(3)	1.383(3)	1.357(3)
N(2)—C(6)	1.298(4)	1.306(3)	1.312(4)
C(6)—N(3)	1.332(3)	1.341(3)	1.355(4)
N(3)—C(7)	1.341(3)	1.341(3)	1.324(4)
C(7)—N(1)	1.297(3)	1.306(3)	1.311(4)
N(3)—C(8)	1.460(4)		
N(1)—N(2)—C(6)	105.7(2)	106.5(2)	102.2(3)
N(2)—C(6)—N(3)	112.3(2)	111.0(2)	114.6(3)
C(6)—N(3)—C(7)	103.9(2)	105.0(3)	102.5(3)
N(3)—C(7)—N(1)	111.4(2)	111.0(2)	110.4(3)
C(7)—N(1)—N(2)	106.8(2)	106.5(2)	110.4(3)
C(6)—N(3)—C(8)	127.8(3)		
C(7)—N(3)—C(8)	128.3(3)		

[a] The bond lengths and angles of the other Metrz rings in this compound are similar.

C—O bond (1.156(3) Å) is in agreement with the predicted behaviour, since an increase in the bond order of the *trans* Cr—C bond should be accompanied by a decrease in the bond order (and hence increase in bond length) of the associated C—O bond [29,31].

The carbonyl groups are coordinated in the usual angular fashion, the angles Cr—C—O ranging from 176.2(2) to 179.2(2)°. There is a good agreement between the geometry of the Metrz ring in this compound and the Metrz rings in $Mn_2(Metrz)_5(NCS)_4$ [19] (see Table 4). The differences with the trz rings in $Mn(trz)SO_4(H_2O)_4$ [33] and other unsubstituted 1,2,4-triazole coordination compounds [10,34] are more substantial. An explanation for this is the presence of the substituent on the 4-position of the triazole ring, which influences the double bond character in the ring. It is to be expected that in 4-substituted 1,2,4-triazoles the double bond character is located predominantly between N(1)—C(5) and N(2)—C(3), which makes these bonds shorter and the remaining bonds longer. The same phenomenon has been observed in other coordination compounds with 4-substituted 1,2,4-triazoles [10,12,35].

Acknowledgements

All calculations were carried out on an Amdahl V7B computer at Leiden University, using a set of computer programs written or modified by Mrs. E.W. Rutten-Keulemans and Dr. R.A.G. de Graaff. The investigations were supported in part by the Netherlands Organization for Chemical Research (SON) with financial aid of the Netherlands Organization for the Advancement of Pure Research (ZWO) (GV) and the Irish National Board for Science and Technology (JGV). CL wishes to thank the Department of Education, Republic of Ireland and Trinity College, Dublin, for research awards. The authors are indebted to Prof. Dr. J. Reedijk for his interest in this investigation.

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