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THE CRYSTAL AND MOLECULAR STRUCTURE OF ACETYLCYCLOPENTADIENYL-MANGANESE AND -RHENIUM TRICARBONYLS

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Summary

The X-ray investigation of the title compounds has shown that in $CH_3COC_5H_4Mn(CO)_3$ the orientation of CO groups with respect to the cyclopentadienyl ring is almost the same as in the unsubstituted manganese compound whereas in $CH_3COC_5H_4Re(CO)_3$ the orientation is different to that in $C_5H_5Re(CO)_3$, so that the molecule as a whole becomes less symmetrical. Unsubstituted cyclopentadienyl-manganese and -rhenium tricarbonyls are isostructural and entirely analogous; that the two acetyl derivatives are not isostructural is possibly caused by conformational differences. Both molecules have the "piano stool" configuration with the CH_3CO group almost coplanar with the cyclopentadienyl ring plane. Interatomic distances and bond angles in these molecules are typical for this type of compound.

Introduction

^{55}Mn and $^{185,187}Re$ NQR studies of the series of cyclopentadienyl-manganese and -rhenium tricarbonyls [1] show a significant increase in the asymmetry parameters η on introduction of COR substituents ($R = CF_3, C_6H_5, CH_3$) into the ring. This may be due either to a distortion or rearrangement of the molecule caused by introduction of a substituent, or to a direct interaction between the substituent and the metal atom. A comparison of the asymmetry parameters on Mn and Re atoms in analogous compounds gives an almost linear dependence described by the equation:

$$\eta_{Re} = [(3.0 + 3.4\,\eta_{Mn}) \pm 1.5]\%$$

The equation was derived for the compounds $(CO)_3MC_5H_4R$ [$M = Mn, Re$; $R = COC_6H_5, COCH_3, I, CH_3, Sn(C_6H_5)_3, H$].

This also confirms the conclusion about the intramolecular origin of the asymmetry parameters since for non-isostructural crystals one would not expect proportional changes in q_{xx} and q_{yy} [$\eta = |(q_{xx}-q_{yy})/q_{zz}|$] to be accounted for by intermolecular interactions. To elucidate the nature of the observed phenomenon we carried out an X-ray investigation of non-isomorphous crystals of two analogous compounds of Mn and Re: $C_5H_4COCH_3Mn(CO)_3$ (V) and $C_5H_4COCH_3Re(CO)_3$ (II).

Experimental

NQR parameters and crystallographic constants for six derivatives of $Mn(CO)_3C_5H_5$ and $Re(CO)_3C_5H_5$ are listed in Table 1.

X-ray intensities for II and V recorded in a de Young—Bouman camera (λ-Mo for II and λ-Cu for V) were estimated visually and converted to $F^2(hkl)$ values by applying the usual Lorentz and polarization corrections. Both structures were solved by the heavy atom method and refined by the full-matrix isotropic least-squares analysis to $R = 0.089$ (for 1480 non-zero independent reflections) for II and to $R = 0.12$ (for 627 non-zero independent reflections) for V.

Results and discussion

The atomic coordinates and isotropic thermal parameters for both compounds are listed in Table 2. The interatomic distances, bond and dihedral angles as well as several dihedral angles for unsubstituted compounds $CpMn(CO)_3$ and $CpRe(CO)_3$ are given in Table 3.

The molecular geometry is shown in Fig. 1. The molecules of both compounds possess the piano stool conformation. The cyclopentadienyl rings are regular, planar pentagons (the deviations from the "best" plane for both molecules do not exceed 0.009 Å) with the sides equal to 1.39 Å for the rhenium and to 1.43 Å for the manganese derivative. In $CH_3COC_5H_4Mn(CO)_3$ the cyclopentadienyl plane ($0.335x-12.224y + 0.926z + 1.705 = 0$) makes an angle of 1°06′ with the plane of the acetyl group ($0.457x-12.270y-0.818z + 1.786 = 0$). In the rhenium derivative the dihedral angle which the cyclopentadienyl ring plane ($4.961x + 0.894y-6.571z-1.114 = 0$) makes the acetyl group plane ($6.070x + 1.317y-6.519z-0.930 = 0$) is 5°23′. Thus the CH_3CO group in both compounds is nearly coplanar with the ring plane; the small departures from coplanarity, exceeding the experimental errors, are usually caused by packing forces (e.g. in nitrobenzene derivatives).

As it can be seen from Table 1, of three pairs of analogous compounds only $CpMn(CO)_3$ and $CpRe(CO)_3$ are isostructural (controlled by calculation of the molecular parameters of $CpRe(CO)_3$ using the atomic coordinates of $CpMn(CO)_3$). A comparison was made of dihedral angles between planes passing through the metal atom M, the carbon atom of a carbonyl group and the gravity centre of the ring, and those drawn through the metal atom, gravity centre and the carbon atom next to the corresponding CO group (angles ϕ_1, ϕ_2 and ϕ_3, Fig. 1). If one assumes the full coincidence of the relative atomic coordinates for $CpRe(CO)_3$ and $CpMn(CO)_3$ the orientation of carbonyl groups

(continued on p. 356)

TABLE 1

NQR AND CRYSTALLOGRAPHIC DATA FOR CYCLOPENTADIENYL-RHENIUM AND -MANGANESE TRICARBONYLS

Compound		e^2Qq_{zz} [a] (MHz)	η (%)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z	Space group	Remarks
I	$C_5H_5Re(CO)_3$	586.6	8.7	12.31	7.13	11.32		120		4	$P2_1/a$	crystallographic data [2]
II	$CH_3COC_5H_4Re(CO)_3$	548.8	30.5	14.22	11.71	6.59		110		4	$P2_1/a$	this work
III	$C_6H_5COC_5H_4Re(CO)_3$	464.7	41.9	12.13	9.88	6.27	108.8	108.2	89.8	2	$P\bar{1}$	crystallographic data [3]
IV	$C_5H_5Mn(CO)_3$	65.2	1.9	11.99	7.07	10.93		117.8		4	$P2_1/a$	full structure [4]
V	$CH_3COC_5H_4Mn(CO)_3$	61.6	6.8	13.19	12.39	6.26		95		4	$P2_1/c$	this work
VI	$C_6H_5COC_5H_4Mn(CO)_3$	62.4	11.8	12.47	6.42	16.49		96.7		4	$P2_1/c$	this work

[a] e^2Qq and η values taken from ref. 1.

TABLE 2. ATOMIC AND ISOTROPIC TEMPERATURE PARAMETERS FOR $C_5H_4COCH_3M(CO)_3$, WHERE M = Re OR Mn

Atom	*x/a*	*y/b*	*z/c*	*B* (A^2)
Re	0.12288	0.19160	−0.0079	1.8
C_1	0.1467	0.0632	−0.1600	2.8
C_2	0.1982	0.2936	−0.1201	3.4
C_3	0.0041	0.2191	−0.2486	3.2
C_4	0.1020	0.0810	0.2562	2.8
C_5	0.1978	0.1274	0.3375	3.0
C_6	0.1869	0.2455	0.3434	3.2
C_7	0.0865	0.2721	0.2717	3.2
C_8	0.0335	0.1688	0.2189	3.2
C_9	0.0424	0.3890	0.2607	3.3
C_{10}	−0.0687	0.4120	0.1619	4.2
O_1	0.1643	−0.0149	−0.2502	4.2
O_2	0.2480	0.3531	−0.1807	4.0
O_3	−0.0688	0.2364	−0.3922	4.3
O_4	0.1021	0.4722	0.3331	5.2
Mn	0.20171	0.02474	0.19070	1.4
C_1	0.0969	0.1114	0.2567	2.1
C_2	0.2011	0.0894	−0.0702	1.9
C_3	0.2993	0.1125	0.2990	2.0
C_4	0.1700	−0.1040	0.4030	3.3
C_5	0.1147	−0.1209	0.1999	4.1
C_6	0.1864	−0.1311	0.0430	1.9
C_7	0.2854	−0.1199	0.1487	1.7
C_8	0.2759	−0.1038	0.3716	1.9
C_9	0.3822	−0.1279	0.0514	1.7
C_{10}	0.4823	−0.1150	0.1889	2.6
O_1	0.0322	0.1635	0.3203	3.6
O_2	0.1954	0.1242	−0.2347	4.4
O_3	0.3575	0.1737	0.3774	3.6
O_4	0.3787	−0.1409	−0.1416	4.8

TABLE 3

BOND DISTANCES, BOND AND DIHEDRAL ANGLES IN $C_5H_4COCH_3M(CO)_3$, WHERE M = Re OR Mn

Atoms	Bond distances (Å)		Atoms	Bond angles (°)	
	M = Re	M = Mn		M = Re	M = Mn
$(C{-}C)_{av}$ (ring)	1.39	1.43	C_4—C_5—C_6	107°08′	107°58′
C_1—O_1	1.16	1.17	C_5—C_6—C_7	109°05′	107°58′
C_2—O_2	1.16	1.11	C_6—C_7—C_8	107°09′	108°19′
C_3—O_3	1.16	1.16	C_7—C_8—C_4	108°11′	107°45′
average	1.16	1.15	C_8—C_4—C_5	108°23′	107°57′
C_7—C_9	1.50	1.47	average	108°	108°
C_9—C_{10}	1.51	1.52	C_8—C_7—C_9	126°33′	124°45′
C_9—O_4	1.27	1.22	C_6—C_7—C_9	126°14′	126°50′
M—C_1	1.90	1.82	C_7—C_9—C_{10}	122°49′	120°11′
M—C_2	1.91	1.82	O_4—C_9—C_7	117°53′	117°35′
M—C_3	1.91	1.77	O_4—C_9—C_{10}	119°16′	122°10′
average	1.91	1.80	M—C_1—O_1	177°58′	173°04′
$(M{-}Cp)_{av}$	2.28	2.14	M—C_2—O_2	176°38′	175°07′
			M—C_3—O_3	178°48′	174°54′
			average	177°48′	174°22′
			C_1—M—C_2	93°49′	89°59′
			C_2—M—C_3	91°31′	91°07′
			C_3—M—C_1	87°49′	95°15′

TABLE 3 (continued)

Atoms	Standard deviations	
	M = Re	M = Mn
M...M	0.003 Å	0.006 Å
M...C	0.04	0.05
M...O	0.03	0.04
C...C	0.04	0.05
C...O	0.04	0.05
O...O	0.03	0.04
M...C...O	1°	2°
C...M...C	1	2
C...C...C	1.6	2.6
C...C...O	1.5	2.3

Planes	Dihedral angles (°)			
	M = Re	$ReC_5H_5(CO)_3$	M = Mn	$MnC_5H_5(CO)_3$
M, GT, C_1 M, GT, C_5	38	34	32	31
M, GT, C_2 M, GT, C_6	6	19	14	16
M, GT, C_3 M, GT, C_8	15	12	13	11

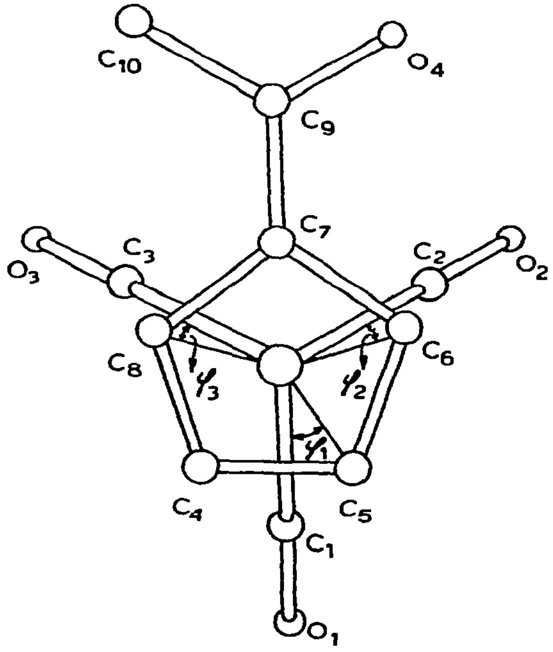

Fig. 1. The structure of $CH_3COC_5H_4Re(CO)_3$.

with respect to the cyclopentadienyl plane in $CpRe(CO)_3$, $CpMn(CO)_3$ and $CH_3COC_5H_4Mn(CO)_3$ appears to be identical to within experimental errors. It is interesting to note that for $CpMn(CO)_3$ derivatives where one carbonyl group is replaced by $P(C_6H_5)_3$ or SO_2 [5, 6] the orientation of the legs of the piano stool with respect to the seat is the same as in the original $CpMn(CO)_3$ molecule. On introducing an acetyl group in the $CpRe(CO)_3$ molecule the orientation of the legs of the piano stool differs from that in the unsubstituted molecule of $CpRe(CO)_3$ (see corresponding angles ϕ_1, ϕ_2, ϕ_3). Compared to $CpRe(CO)_3$, $CH_3COC_5H_4Re(CO)_3$ is much less symmetrical (see Fig. 1 and Table 3). The fact that analogues II and V (see Table 1) are not isostructural might possibly be explained by the differences in configuration.

High values of the asymmetry patameter η in these compounds are apparently caused by molecular asymmetry which is not significant in the Mn-derivative but rather appreciable in $CH_3COC_5H_4Re(CO)_3$.

References

1 A.N. Nesmeyanov, G.K. Semin, E.V. Bryukhova, T.A. Babushkina, K.N. Anisimov, N.E. Kolobova and Yu.V. Makarov, Tetrahedron Lett., 37 (1968) 3987.

2 Yu.T. Struchkov, K.N. Anisimov, O.P. Osipova, N.E. Kolobova and A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 172 (1967) 107.

3 A.N. Nesmeyanov, G.K. Semin, E.V. Bryukhova, K.N. Anisimov, N.E. Kolobova, Yu.V. Marakov and T.L. Khotsyanova, Izv. Akad. Nauk SSSR, Ser. Khim., 4 (1968) 929.

4 A.F. Berndt and R.E. Marsh, Acta Crystallogr., 16 (1963) 118.

5 C. Barbeau, K.S. Dichmann and L. Ricard, Can. J. Chem., 51 (1973) 3027.

6 C. Barbeau and R.J. Dubey, Can. J. Chem., 51 (1973) 3684.