Crystal and molecular structure of bis[tetracarbonyldiphenylphosphidomanganese(0)]

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Abstract

The crystal structure of bis[tetracarbonyldiphenylphosphidomanganese(0)] has been determined by an X-ray diffraction study. The complex crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions, a 15.714(4), b 16.446(5), c 12.016(4) Å, and β 101.25(2)°. The molecule has approximately centrosymmetric bi-octahedral D_{2h} structure. Each manganese atom is bonded to two phosphorus atoms of μ-diphenylphosphide groups and four carbonyl carbon atoms. The separation of the manganese atoms is 3.690(1) Å.

Introduction

We have recently described the photochemical decarbonylation of the title complex, $Mn_2(\mu\text{-PPh}_2)_2(CO)_8$ [1]. The crystal structure of the photochemical product showed that the decarbonylation was accompanied by an increase of the metal–metal bond order and distortion of the molecular framework by a semibridging carbonyl. Here we describe the structure of $Mn_2(\mu\text{-PPh}_2)_2(CO)_8$ as the starting material for the decarbonylation reaction and is compared with that of $Mn_2(\mu\text{-PMe}_2)_2(CO)_8$ [2].

Experimental

Preparation. The complex was prepared according to a published procedure [3]. Single crystals were obtained by careful recrystallization from toluene.

X-ray structure determination

Crystal data: $Mn_2P_2C_{32}H_{20}O_8$, M 704.33, monoclinic, space group $P2_1/n$, a 15.714(4), b 16.446(5), c 12.016(4) Å, β 101.25(2)°, U 3045.7(17) Å^3, Z 4, D_c 1.536 g cm^{-3}, $\bar{\lambda}$ 1.54178 Å, μ(Cu-K_α) 85.38 cm^{-1}.

Table 1

Final atomic fractional coordinates of the non-hydrogen atoms with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{eq} (Å^2) [a]
Mn(1)	0.9102(0)	0.1738(0)	0.4588(1)	2.70(2)
Mn(2)	0.7826(0)	0.3234(0)	0.2662(1)	2.60(2)
P(1)	0.7795(1)	0.2507(1)	0.4372(1)	2.40(4)
P(2)	0.9180(1)	0.2523(1)	0.2938(1)	2.46(4)
C(1)	0.8971(4)	0.1256(3)	0.5909(4)	4.03(25)
C(2)	1.0077(4)	0.1153(3)	0.4539(5)	4.16(24)
C(3)	0.9749(3)	0.2582(3)	0.5316(4)	3.74(22)
C(4)	0.8393(4)	0.0953(3)	0.3809(4)	3.59(22)
C(5)	0.8027(4)	0.3774(3)	0.1397(5)	4.16(24)
C(6)	0.6729(3)	0.3624(3)	0.2519(4)	3.81(22)
C(7)	0.8221(4)	0.4101(3)	0.3610(5)	3.83(24)
C(8)	0.7455(3)	0.2345(3)	0.1751(4)	3.57(19)
C(9)	0.7660(3)	0.3132(3)	0.5603(4)	2.79(18)
C(10)	0.8242(3)	0.3140(3)	0.6632(4)	3.43(20)
C(11)	0.8075(4)	0.3596(4)	0.7548(4)	4.22(25)
C(12)	0.7332(4)	0.4039(3)	0.7447(5)	4.08(22)
C(13)	0.6743(4)	0.4034(3)	0.6440(5)	4.37(27)
C(14)	0.6907(3)	0.3593(3)	0.5534(4)	3.92(22)
C(15)	0.6830(3)	0.1857(3)	0.4347(4)	2.91(20)
C(16)	0.6722(3)	0.1462(3)	0.5321(4)	3.78(22)
C(17)	0.6031(4)	0.0962(4)	0.5331(5)	4.91(27)
C(18)	0.5418(4)	0.0842(4)	0.4352(5)	5.17(29)
C(19)	0.5519(4)	0.1217(4)	0.3368(5)	4.47(27)
C(20)	0.6206(3)	0.1734(3)	0.3365(4)	3.71(22)
C(21)	1.0182(3)	0.3132(3)	0.3099(4)	3.15(20)
C(22)	1.0197(3)	0.3975(3)	0.3174(4)	3.71(24)
C(23)	1.0978(4)	0.4391(3)	0.3380(5)	4.69(27)
C(24)	1.1743(4)	0.3985(4)	0.3498(5)	5.09(27)
C(25)	1.1742(3)	0.3154(4)	0.3402(5)	4.64(27)
C(26)	1.0971(3)	0.2735(3)	0.3208(5)	3.94(24)
C(27)	0.9307(3)	0.1951(3)	0.1662(4)	3.00(20)
C(28)	0.9236(4)	0.1103(3)	0.1586(5)	3.80(22)
C(29)	0.9261(4)	0.0711(3)	0.0566(5)	4.98(30)
C(30)	0.9377(4)	0.1147(4)	−0.0368(5)	4.64(25)
C(31)	0.9481(4)	0.1966(4)	−0.0285(5)	4.63(25)
C(32)	0.9437(4)	0.2372(3)	0.0708(4)	3.86(22)
O(1)	0.8894(3)	0.0946(3)	0.6733(3)	6.44(25)
O(2)	1.0683(3)	0.0777(3)	0.4526(4)	6.82(20)
O(3)	1.0162(3)	0.3098(3)	0.5757(3)	5.54(18)
O(4)	0.7943(3)	0.0453(2)	0.3369(4)	5.46(19)
O(5)	0.8139(3)	0.4101(3)	0.0613(4)	6.41(22)
O(6)	0.6043(3)	0.3874(3)	0.2424(4)	5.81(20)
O(7)	0.8410(3)	0.4645(3)	0.4170(4)	6.42(24)
O(8)	0.7228(3)	0.1816(3)	0.1155(3)	5.57(20)

[a] B_{eq} is the equivalent isotropic temperature factor as defined by Hamilton [6].

Table 2

Bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses

Mn(1)–P(1)	2.383(2)	C(9)–C(10)	1.387(6)
Mn(1)–P(2)	2.389(2)	C(10)–C(11)	1.398(8)
Mn(2)–P(1)	2.386(2)	C(11)–C(12)	1.361(9)
Mn(2)–P(2)	2.394(2)	C(12)–C(13)	1.373(8)
Mn(1)–C(1)	1.821(5)	C(13)–C(14)	1.374(8)
Mn(1)–C(2)	1.820(6)	C(14)–C(9)	1.394(7)
Mn(1)–C(3)	1.838(5)	C(15)–C(16)	1.378(7)
Mn(1)–C(4)	1.838(5)	C(16)–C(17)	1.364(8)
Mn(2)–C(5)	1.840(6)	C(17)–C(18)	1.381(8)
Mn(2)–C(6)	1.816(5)	C(18)–C(19)	1.370(9)
Mn(2)–C(7)	1.855(5)	C(19)–C(20)	1.375(8)
Mn(2)–C(8)	1.851(5)	C(20)–C(15)	1.394(6)
P(1)–C(9)	1.847(5)	C(21)–C(22)	1.389(7)
P(1)–C(15)	1.851(5)	C(22)–C(23)	1.385(8)
P(2)–C(21)	1.844(5)	C(23)–C(24)	1.358(9)
P(2)–C(27)	1.843(5)	C(24)–C(25)	1.371(9)
C(1)–O(1)	1.141(7)	C(25)–C(26)	1.374(7)
C(2)–O(2)	1.138(8)	C(26)–C(21)	1.385(7)
C(3)–O(3)	1.135(6)	C(27)–C(28)	1.401(7)
C(4)–O(4)	1.144(6)	C(28)–C(29)	1.392(8)
C(5)–O(5)	1.128(8)	C(29)–C(30)	1.374(9)
C(6)–O(6)	1.138(7)	C(30)–C(31)	1.358(9)
C(7)–O(7)	1.124(7)	C(31)–C(32)	1.381(8)
C(8)–O(8)	1.139(6)	C(32)–C(27)	1.388(7)
P(1)–Mn(1)–P(2)	78.8(1)	Mn(1)–C(1)–O(1)	179.2(5)
P(1)–Mn(1)–C(1)	94.8(2)	Mn(1)–C(2)–O(2)	178.6(5)
P(1)–Mn(1)–C(2)	172.0(2)	Mn(1)–C(3)–O(3)	178.7(5)
P(1)–Mn(1)–C(3)	92.1(2)	Mn(1)–C(4)–O(4)	176.9(5)
P(1)–Mn(1)–C(4)	83.9(2)	Mn(2)–C(5)–O(5)	179.0(5)
P(2)–Mn(1)–C(1)	172.4(2)	Mn(2)–C(6)–O(6)	179.4(5)
P(2)–Mn(1)–C(2)	94.5(2)	Mn(2)–C(7)–O(7)	175.7(6)
P(2)–Mn(1)–C(3)	82.7(2)	Mn(2)–C(8)–O(8)	177.4(5)
P(2)–Mn(1)–C(4)	94.7(2)	P(1)–C(9)–C(10)	124.1(4)
C(1)–Mn(1)–C(2)	92.1(3)	P(1)–C(9)–C(14)	118.9(3)
C(1)–Mn(1)–C(3)	93.4(2)	C(10)–C(9)–C(14)	116.9(5)
C(1)–Mn(1)–C(4)	88.7(2)	C(9)–C(10)–C(11)	121.0(5)
C(2)–Mn(1)–C(3)	91.4(2)	C(10)–C(11)–C(12)	120.4(5)
C(2)–Mn(1)–C(4)	92.5(3)	C(11)–C(12)–C(13)	119.6(5)
C(3)–Mn(1)–C(4)	175.6(2)	C(12)–C(13)–C(14)	120.2(5)
P(1)–Mn(2)–P(2)	78.6(1)	C(13)–C(14)–C(9)	121.9(4)
P(1)–Mn(2)–C(5)	171.4(2)	P(1)–C(15)–C(16)	119.7(3)
P(1)–Mn(2)–C(6)	94.6(2)	P(1)–C(15)–C(20)	122.4(4)
P(1)–Mn(2)–C(7)	85.2(2)	C(16)–C(15)–C(20)	117.9(4)
P(1)–Mn(2)–C(8)	93.2(2)	C(15)–C(16)–C(17)	121.5(4)
P(2)–Mn(2)–C(5)	93.4(2)	C(16)–C(17)–C(18)	120.2(6)
P(2)–Mn(2)–C(6)	170.9(2)	C(17)–C(18)–C(19)	119.5(6)
P(2)–Mn(2)–C(7)	96.2(2)	C(18)–C(19)–C(20)	120.3(5)
P(2)–Mn(2)–C(8)	82.2(2)	C(19)–C(20)–C(15)	120.7(5)
C(5)–Mn(2)–C(6)	93.7(2)	P(2)–C(21)–C(22)	123.5(4)
C(5)–Mn(2)–C(7)	92.6(3)	P(2)–C(21)–C(26)	119.0(4)
C(5)–Mn(2)–C(8)	88.7(2)	C(22)–C(21)–C(26)	117.4(4)
C(6)–Mn(2)–C(7)	89.1(2)	C(21)–C(22)–C(23)	120.5(4)
C(6)–Mn(2)–C(8)	92.3(2)	C(22)–C(23)–C(24)	120.8(5)
C(7)–Mn(2)–C(8)	178.0(2)	C(23)–C(24)–C(25)	119.6(5)
Mn(1)–P(1)–Mn(2)	101.4(1)	C(24)–C(25)–C(26)	120.0(5)

Table 2 (continued)

Mn(1)–P(1)–C(9)	116.1(2)	C(25)–C(26)–C(21)	121.6(5)
Mn(1)–P(1)–C(15)	112.4(2)	P(2)–C(27)–C(28)	122.8(4)
Mn(2)–P(1)–C(9)	115.8(2)	P(2)–C(27)–C(32)	119.3(4)
Mn(2)–P(1)–C(15)	115.5(2)	C(28)–C(27)–C(32)	117.7(5)
Mn(1)–P(2)–Mn(2)	101.0(1)	C(27)–C(28)–C(29)	120.2(5)
Mn(1)–P(2)–C(21)	112.8(2)	C(28)–C(29)–C(30)	120.6(5)
Mn(1)–P(2)–C(27)	116.5(2)	C(29)–C(30)–C(31)	119.4(6)
Mn(2)–P(2)–C(21)	117.8(2)	C(30)–C(31)–C(32)	121.2(6)
Mn(2)–P(2)–C(27)	111.8(2)	C(31)–C(32)–C(27)	120.8(5)

The diffraction intensities were measured on a Rigaku AFC-5RU diffractometer with graphite-monochromated Cu-K_α radiation. The intensity data in the range $2\theta < 120°$ were collected in the ω–2θ scan mode with a 0.8° scan range and a scan rate of 4° min^{-1} on a crystal with dimensions of $0.15 \times 0.15 \times 0.10$ mm^3. During the course of data collection, three reflections were monitored every 56 reflections. The intensity data were converted to F_o data in the usual manner. Absorption correction was applied in the cylindrical approximation (μR 0.64). The standard deviations, $\sigma(F_o)$, were estimated by counting statistics. A total of 3714 independent reflections with $F_o > 3\sigma(F_o)$ were regarded as observed, and in solving and refining the structure.

The structure was solved by the heavy-atom method. The complete structure was elucidated through iterative synthesis of Fourier maps, and was refined by the block-diagonal least-squares method. Several cycles of the refinement including anisotropic thermal parameters were carried out with the weighting scheme $w^{-1} = (\sigma^2(F_o) + (0.023F_o)^2)$. Atomic scattering factors [4a] and anomalous dispersion terms [4b] were taken from the International Tables for X-Ray Crystallography IV. The hydrogen atoms were included as being isotropical in the last cycle; their positions were obtained from the difference Fourier synthesis. The final R and R_w values were 0.056 and 0.072, respectively. The final difference Fourier map showed no peaks greater than 0.4 e/Å^3; most of the largest peaks were around the manganese atoms. All computations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY [5].

The final coordinates and thermal parameters of the non-hydrogen atoms are given in Table 1. The bond distances and bond angles are listed in Table 2.

Results and discussion

The crystal structure of the title complex consists of discrete molecules Mn$_2$(μ-PPh$_2$)$_2$(CO)$_8$. The essential molecular geometry, with the numbering of the atoms, is shown in Fig. 1. Each manganese atom is octahedrally coordinated to the two μ-diphenylphosphido-phosphorus atoms and two carbonyl-carbon atoms at the equatorial positions and the two carbonyl-carbon atoms at the axial positions, in which the Mn–C$_{ax}$ bond distances are slightly longer than the Mn–C$_{eq}$ bond distances. The bi-octahedral structure resembles that of Mn$_2$(μ-PMe$_2$)$_2$(CO)$_8$ [2]. The structure, however, deviates slightly from the exact D_{2h} symmetry of the latter.
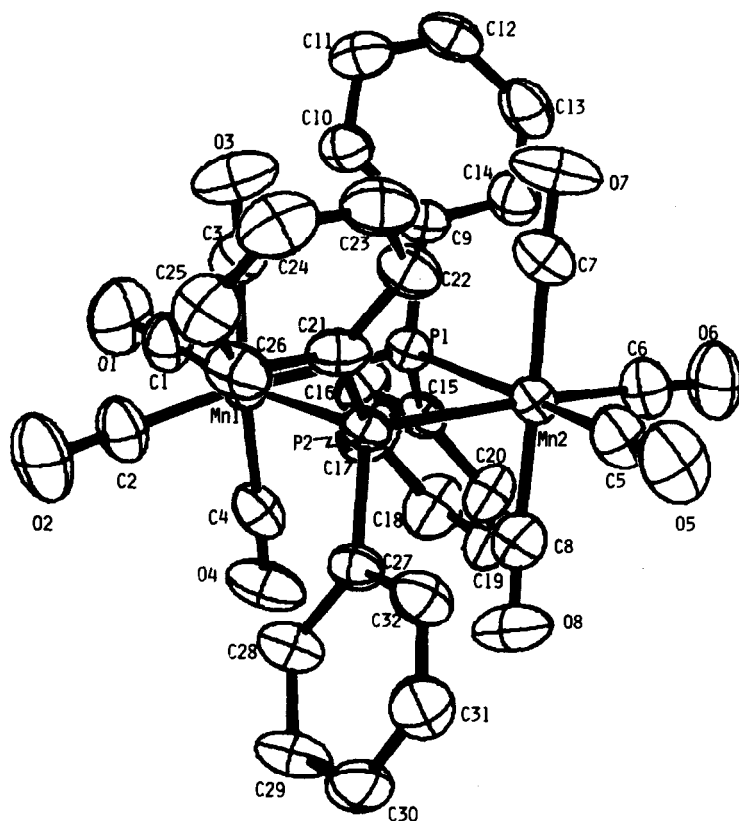
Fig. 1. The molecular structure of $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$. The thermal ellipsoids are drawn at the 50% probability level.

The following specific points may be noted. Firstly, the main distortion of the bi-octahedral structure is the tilting of the axial carbonyls. The axial carbonyls attached to the respective manganese atoms rotate from the eclipsed position around the $Mn \cdots Mn$ vector by ca. $17°$, and one of them is tilted outward from the normal direction resulting in the irregular tetrahedral coordination around the phosphorus atoms. The distortion is probably caused by the steric strain due to the bulky diphenylphosphido groups. As shown in Fig. 2, the axial carbonyls and phenyl groups have contacts; the some short non-bonding distances are listed in Table 3. Although the axial carbonyls are usually tilted inward for the molecular center owing to the repulsion by the equatorial carbonyls, the C(7)–O(7) carbonyl is bent outward, and the C(9)–P(1)–C(15) and C(21)–P(2)–C(27) angles are 96.5(2) and 97.8(2)°, respectively, which are smaller than the regular tetrahedral values. The phosphorus atoms are slightly displaced (0.03 Å) from the plane defined by two manganese and two phosphorus atoms in the opposite direction against the outward-bending carbonyl. Secondly, the present complex shows some expansion of the molecular framework in comparison with $Mn_2(\mu\text{-}PMe_2)_2(CO)_8$ [2]. The Mn–P distances, 2.383(2), 2.389(2), 2.386(2), and 2.394(2) Å, are significantly longer than those in $Mn_2(\mu\text{-}PMe_2)_2(CO)_8$ [2], 2.345(4) and 2.348(2) Å, presumably reflecting
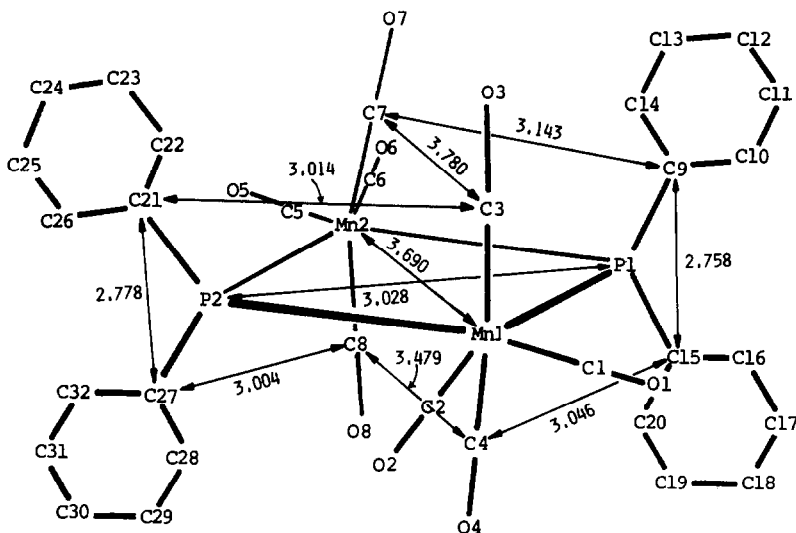
244

Fig. 2. Non-bonding intramolecular interactions in $Mn_2(\mu\text{-PPh}_2)_2(CO)_8$.

Table 3

Selected intramolecular non-bonded contacts (Å)

P(1) · · · C(1)	3.119	C(3) · · · C(26)	3.473	C(14) · · · C(16)	3.522
P(1) · · · C(3)	3.061	C(4) · · · C(16)	3.572	C(21) · · · C(32)	3.142
P(1) · · · C(4)	2.850	C(4) · · · C(20)	3.610	C(26) · · · C(27)	3.171
P(1) · · · C(6)	3.112	C(4) · · · C(27)	3.586	C(26) · · · C(32)	3.516
P(1) · · · C(7)	2.898	C(4) · · · C(28)	3.214	O(1) · · · C(10)	3.746
P(1) · · · C(8)	3.101	C(5) · · · C(6)	2.667	O(1) · · · C(16)	3.604
P(2) · · · C(2)	3.115	C(5) · · · C(7)	2.671	O(2) · · · C(26)	3.655
P(2) · · · C(3)	2.824	C(5) · · · C(8)	2.581	O(3) · · · C(10)	3.384
P(2) · · · C(4)	3.130	C(5) · · · C(21)	3.750	O(3) · · · C(21)	3.201
P(2) · · · C(5)	3.104	C(5) · · · C(22)	3.668	O(3) · · · C(22)	3.433
P(2) · · · C(7)	3.183	C(5) · · · C(27)	3.590	O(3) · · · C(26)	3.588
P(2) · · · C(8)	2.821	C(5) · · · C(32)	3.410	O(3) · · · O(7)	3.955
C(1) · · · C(2)	2.822	C(6) · · · C(7)	2.575	O(4) · · · C(15)	3.252
C(1) · · · C(3)	2.664	C(6) · · · C(8)	2.644	O(4) · · · C(16)	3.700
C(1) · · · C(4)	2.559	C(6) · · · C(9)	3.796	O(4) · · · C(20)	3.447
C(1) · · · C(9)	3.688	C(6) · · · C(14)	3.579	O(4) · · · C(28)	3.400
C(1) · · · C(10)	3.472	C(6) · · · C(15)	3.628	O(4) · · · O(8)	3.493
C(1) · · · C(15)	3.654	C(6) · · · C(20)	3.420	O(5) · · · C(32)	3.488
C(1) · · · C(16)	3.483	C(7) · · · C(14)	3.488	O(6) · · · C(14)	3.747
C(2) · · · C(3)	2.617	C(7) · · · C(21)	3.626	O(6) · · · C(20)	3.690
C(2) · · · C(4)	2.641	C(7) · · · C(22)	3.255	O(7) · · · C(9)	3.367
C(2) · · · C(21)	3.705	C(8) · · · C(15)	3.540	O(7) · · · C(22)	3.441
C(2) · · · C(26)	3.490	C(8) · · · C(20)	3.179	O(8) · · · C(20)	3.364
C(2) · · · C(27)	3.675	C(8) · · · C(28)	3.502	O(8) · · · C(27)	3.212
C(2) · · · C(28)	3.538	C(8) · · · C(32)	3.577	O(8) · · · C(28)	3.311
C(3) · · · C(9)	3.486	C(9) · · · C(16)	3.104	O(8) · · · C(32)	3.728
C(3) · · · C(10)	3.227	C(10) · · · C(16)	3.786		
C(3) · · · C(22)	3.616	C(14) · · · C(15)	3.183		

the lower bond order of the former bonds. The substitution of the electron-donating methyl groups on the phosphorus atom by the electron-withdrawing phenyl goups may cause a decrease of coordination ability of the phosphido-phosphorus atom to the manganese atom. The dihedral angle between the two phenyl groups attached to the phosphorus atom (77°, 82°) is close to 90°. The orientation of the phenyl groups is favorable for π-bonding between the phosphorus atom and phenyl group, and it increases the electron-withdrawing nature of diphenylphosphido group. Although the P · · · P distance and Mn–P–Mn angles are large, these expansions are probably due to steric repulsion between the phenyl groups and axial carbonyls.

As mentioned in Introduction, the title complex is a starting material in the photochemical decarbonylation to $Mn_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ which has a semi-bridging carbonyl on a distorted molecular framework [1]. The separation of manganese atoms, 3.690(1) Å, in the present complex is significantly longer than the sum of normal covalent radii by 1.2 Å and also longer than the previously reported Mn–Mn single bond distances, 2.50–3.23 Å [7]. This long Mn–Mn separation is consistent with the predicted bond order of zero; based on the 18-electron rule. The outward-bending of one carbonyl and slight distortion of the molecular framework as observed in the present complex may become the trigger in the decarbonylation reaction, because their directions, which are opposite each other, correspond to the direction of the decarbonylation and distortion.

Supplementary material

Tables of thermal parameters of non-hydrogen atoms, fractional coordinates of the hydrogen atoms and the structure factors are available from the authors.

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