Crystal structure of tricarbonyl($\eta^{2:2:1}$-1,2,3,11-tetramethyl-9-(2'-buten-2'-yl)tricyclo[5.3.1.$0^{4,10}$]undeca-2,5-dien-11-yl)manganese, $C_{22}H_{27}MnO_3$

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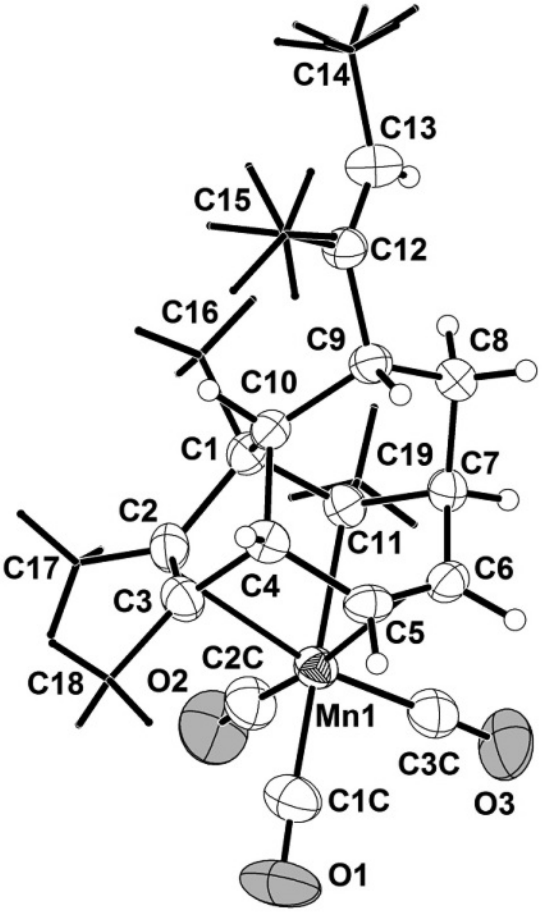

Abstract

$C_{22}H_{27}MnO_3$, monoclinic, $P2_1/n$ (no. 14), a = 7.690(2) Å, b = 25.610(5) Å, c = 10.390(2) Å, β = 101.00(3)°, V = 2008.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0369, $wR_{ref}(F^2)$ = 0.0877, T = 290 K.

Source of material

The synthesis and the spectroscopy (^{1}H, ^{13}C, IR) of the title compound have been reported in detail as part of the thesis project of one of us [1].

Experimental details

All hydrogen atoms are placed geometrically. U_{iso} values were set to 1.2 (CH_2) and 1.5 (CH_3) times of the U_{eq} of the carbon atom they are attached to. The U_{iso} values of all other hydrogen atoms were refined freely. The hydrogen atoms of the two methyl groups in the side chain (C14 and C15) appear disordered. A crystal to detector distance of 80 mm on a STOE IPDS diffractometer limited the 2theta value to 48°.

Table 1. Data collection and handling.

Crystal:	yellow isometric, size 0.1×0.15×0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.75 cm^{-1}
Diffractometer, scan mode:	IPDS I, φ
$2\theta_{max}$:	48.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22146, 3137
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2915
$N(param)_{refined}$:	251
Programs:	SHELX [2], DIAMOND [3], IPDS-Expose, Cell, Integrate [4]

Discussion

The photochemical reactions of transition metal complexes with olefinic ligands have been extensively studied [5-8]. The exact understanding of the bonding schemes of olefinic ligands in transition metal complexes is still in the focus of our interest [9-14]. The asymmetric unit of the title structure consists of one complete complex (Fig.; methyl groups are drawn in a wire frame style; ellipsoids are drawn at the 40 % probability level). The manganese metal center shows a distorted octahedral coordination sphere caused by the $\eta^{2:2:1}$ coordination of the tricyclic organic ligand and the three carbonyl ligands (see, the figure). All bond lengths and angles in the title complex are generally in the expected ranges. The aforementioned $\eta^{2:2:1}$ coordination is well known for diolefinic manganese complexes [15-18]. The C–C distances of the π coordinating olefinic carbon atoms are in agreement with the values found in the corresponding complexes (C2–C3 = 1.365(3) Å; C5–C6 = 1.346(3) Å). The Mn–C distances for these olefinic units range from 2.323(2) to 2.391(2) whereas the η^1 coordinated carbon atom C11 has a typically short Mn–C distance of 2.144(2) Å. Consequently, the Mn–C bond of the carbonyl ligand located in a *trans*-position to the η^1 coordinated carbon atom C11 is weakened expressed by a slightly shortened Mn–C distance (Mn1–C1C 1.829(3) Å), whereas the two other carbonyl ligands show the usual Mn–C distances (Mn1–C2C = 1.777(3) Å; Mn1–C3C = 1.780(3) Å).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(4)	4*e*		0.4961	0.3335	0.8230	0.041(6)
H(5)	4*e*		0.4182	0.3829	0.6286	0.052(7)
H(6)	4*e*		0.2762	0.4585	0.6275	0.043(6)
H(14)	4*e*		0.0679	0.4764	0.7533	0.036(6)
H(8A)	4*e*		0.1603	0.4665	0.9836	0.053
H(8B)	4*e*		0.3057	0.4939	0.9199	0.053
H(9)	4*e*		0.4818	0.4256	0.9436	0.044(6)

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Table 2. continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(10)	4*e*		0.3518	0.3387	0.9947	0.037(6)
H(13)	4*e*		0.259(4)	0.464(1)	1.179(3)	0.057(8)
H(14A)	4*e*	0.5	0.3153	0.4618	1.3940	0.119
H(14B)	4*e*	0.5	0.5144	0.4682	1.3822	0.119
H(14C)	4*e*	0.5	0.4344	0.4123	1.3912	0.119
H(14D)	4*e*	0.5	0.5274	0.4331	1.3842	0.119
H(14E)	4*e*	0.5	0.3283	0.4267	1.3961	0.119
H(14F)	4*e*	0.5	0.4083	0.4826	1.3871	0.119
H(15A)	4*e*	0.5	0.6641	0.3821	1.1062	0.108
H(15B)	4*e*	0.5	0.5671	0.3532	1.2053	0.108
H(15C)	4*e*	0.5	0.6742	0.4044	1.2480	0.108
H(15D)	4*e*	0.5	0.6061	0.3777	1.2668	0.108
H(15E)	4*e*	0.5	0.7031	0.4066	1.1677	0.108

Table 2. continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(15F)	4*e*	0.5	0.5960	0.3554	1.1250	0.108
H(16A)	4*e*		0.0848	0.3209	1.0630	0.087
H(16B)	4*e*		–0.0990	0.3402	0.9854	0.087
H(16C)	4*e*		0.0363	0.3804	1.0621	0.087
H(17A)	4*e*		–0.0501	0.2455	0.7200	0.096
H(17B)	4*e*		–0.1568	0.2827	0.7960	0.096
H(17C)	4*e*		–0.0137	0.2450	0.8737	0.096
H(18A)	4*e*		0.3648	0.2324	0.7439	0.097
H(18B)	4*e*		0.3852	0.2677	0.6244	0.097
H(18C)	4*e*		0.2043	0.2399	0.6273	0.097
H(19A)	4*e*		–0.1691	0.4315	0.8818	0.088
H(19B)	4*e*		–0.2401	0.3832	0.7946	0.088
H(19C)	4*e*		–0.2165	0.4372	0.7289	0.088

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4*e*	0.06417(4)	0.36422(2)	0.61247(3)	0.0377(2)	0.0390(2)	0.0381(2)	–0.0018(1)	0.0019(2)	–0.0039(1)
O(1)	4*e*	0.1734(4)	0.3171(1)	0.3780(2)	0.112(2)	0.121(2)	0.061(1)	0.019(2)	0.018(1)	–0.037(1)
C(1C)	4*e*	0.1373(4)	0.3346(1)	0.4717(3)	0.061(2)	0.063(2)	0.051(2)	0.004(1)	0.000(1)	–0.013(1)
O(2)	4*e*	–0.2922(3)	0.3188(1)	0.5426(3)	0.054(1)	0.105(2)	0.109(2)	–0.030(1)	–0.015(1)	–0.001(2)
C(2C)	4*e*	–0.1488(4)	0.3349(1)	0.5724(3)	0.056(2)	0.056(2)	0.058(2)	–0.007(1)	–0.003(1)	–0.004(1)
O(3)	4*e*	–0.1096(3)	0.45060(9)	0.4514(2)	0.096(2)	0.066(1)	0.090(2)	0.001(1)	–0.037(1)	0.020(1)
C(3C)	4*e*	–0.0364(4)	0.4174(1)	0.5157(3)	0.057(2)	0.053(2)	0.049(2)	–0.006(1)	–0.008(1)	–0.005(1)
C(1)	4*e*	0.1054(3)	0.35684(9)	0.8882(2)	0.039(1)	0.039(1)	0.039(1)	–0.0039(9)	0.014(1)	0.002(1)
C(2)	4*e*	0.0953(3)	0.30815(9)	0.7995(2)	0.045(1)	0.033(1)	0.049(1)	–0.005(1)	0.005(1)	0.004(1)
C(3)	4*e*	0.2453(3)	0.30344(9)	0.7481(2)	0.046(1)	0.035(1)	0.046(1)	0.004(1)	0.005(1)	–0.004(1)
C(4)	4*e*	0.3744(3)	0.34671(9)	0.8013(2)	0.031(1)	0.042(1)	0.041(1)	0.0030(9)	0.0074(9)	–0.004(1)
C(5)	4*e*	0.3559(3)	0.38808(9)	0.6959(2)	0.035(1)	0.053(1)	0.033(1)	–0.007(1)	0.0099(9)	–0.005(1)
C(6)	4*e*	0.2573(3)	0.43173(9)	0.6907(2)	0.044(1)	0.043(1)	0.033(1)	–0.010(1)	0.005(1)	0.003(1)
C(7)	4*e*	0.1414(3)	0.44653(8)	0.7888(2)	0.045(1)	0.032(1)	0.038(1)	0.0028(9)	0.005(1)	0.0016(9)
C(8)	4*e*	0.2431(3)	0.46132(9)	0.9251(2)	0.057(2)	0.035(1)	0.039(1)	–0.003(1)	0.007(1)	–0.003(1)
C(9)	4*e*	0.3755(3)	0.41858(8)	0.9799(2)	0.040(1)	0.040(1)	0.034(1)	–0.005(1)	0.0086(9)	–0.0016(9)
C(10)	4*e*	0.3080(3)	0.36435(8)	0.9260(2)	0.039(1)	0.035(1)	0.033(1)	0.0013(9)	0.0076(9)	0.0026(9)
C(11)	4*e*	0.0202(3)	0.39949(8)	0.7907(2)	0.035(1)	0.037(1)	0.043(1)	0.0019(9)	0.009(1)	–0.002(1)
C(12)	4*e*	0.4366(3)	0.41859(9)	1.1287(2)	0.049(1)	0.044(1)	0.035(1)	–0.007(1)	0.004(1)	–0.001(1)
C(13)	4*e*	0.3576(4)	0.4452(1)	1.2102(3)	0.063(2)	0.068(2)	0.039(2)	–0.000(2)	0.008(1)	–0.006(1)
C(14)	4*e*	0.4102(5)	0.4471(2)	1.3579(3)	0.094(2)	0.106(3)	0.038(2)	–0.009(2)	0.014(2)	–0.013(2)
C(15)	4*e*	0.6003(4)	0.3867(1)	1.1763(3)	0.077(2)	0.080(2)	0.051(2)	0.015(2)	–0.010(2)	–0.007(2)
C(16)	4*e*	0.0242(4)	0.3488(1)	1.0113(3)	0.059(2)	0.069(2)	0.054(2)	–0.010(1)	0.028(1)	0.007(1)
C(17)	4*e*	–0.0440(4)	0.2666(1)	0.7971(3)	0.065(2)	0.046(2)	0.079(2)	–0.018(1)	0.008(2)	0.006(1)
C(18)	4*e*	0.3054(4)	0.2566(1)	0.6797(3)	0.074(2)	0.048(2)	0.069(2)	0.012(1)	0.006(2)	–0.016(1)
C(19)	4*e*	–0.1689(3)	0.4142(1)	0.7999(3)	0.043(1)	0.064(2)	0.072(2)	0.009(1)	0.016(1)	–0.005(1)

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