Crystal structure of bis(η^5 -pentamethylcyclopentadienyl)[μ_3 -(η^2 -3-trimethyl-propynylcarboxylato)-bis(tricarbonylcobalt)-titan], $C_{33}H_{39}Co_2O_8Ti$

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Received January 30, 2002, accepted and available on-line April 12, 2002; CCDC-No. 1267795

Abstract

$C_{33}H_{39}Co_2O_8Ti$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.651(2)$ Å, $b = 19.184(4)$ Å, $c = 20.632(4)$ Å, $\beta = 90.50(3)^\circ$, $V = 3424.0$ Å³, $Z = 4$, $R_g(F) = 0.046$, $wR_{ref}(F^2) = 0.112$, $T = 200$ K.

Source of material

$[Cp^*_2TiO_2CC\equiv C^tBu]$ (124 mg, 0.28 mmol) and $Co_2(CO)_8$ (96 mg, 0.28 mmol) were dissolved in 5 ml hexane. The colour changed immediately from dark green to dark red. At 243 K, dark red crystals of the title compound (98%) were obtained.

Discussion

Cobalt complexes are used to mediate a host of many organic reactions [1]. These include e.g. the Diels-Alder reactions, π -cation mediated cyclizations, the Pauson-Khand reaction, different [2+2+2] and related higher mediated cyclizations, the Nicholas reaction, cobalt mediated oxidations and reductions as well as many other examples. Often μ -acetylene-dicobalt complexes act as stoichiometric reagents or catalysts in these reactions. A lot of such complexes were structurally characterized by X-ray crystallography and represent a classical type of alkyne complexes. We came to such complexes in investigations of the reaction behaviour of very rare monomeric titanocene-mono- σ -alkynyl complexes $Cp^*_2TiC\equiv CR$. One compound of this type $Cp^*_2TiC\equiv C^tBu$ reacts with carbon dioxide to give by an insertion reaction the corresponding carboxylate $Cp^*_2TiO_2CC\equiv C^tBu$ [2]. The reaction of the last compound with dicobaltoctacarbonyl gave the title compound.

The titanium atom in the title compound is tetracoordinated by the pentamethylcyclopentadienyl ligands and the two carboxylate oxygens. The Ti—O bond lengths are comparable with those found in the starting material $[Cp^*_2TiO_2CC\equiv C^tBu]$ [2]. Compared to this carboxylate, the triple bond in the title compound

($d(C22—C23) = 1.321(6)$ Å) is elongated due to coordination by the Co units. The structure shows the typical connectivity of μ -acetylene dicobalt complexes [3].

Table 1. Data collection and handling.

Crystal:	dark red prism, size $0.2 \times 0.2 \times 0.5$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	12.32 cm^{-1}
Diffraction, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2^\circ$
$2\theta_{\text{max}}$:	48.78°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	10232, 5275
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2912
$N(\text{param})_{\text{refined}}$:	397
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(11A)	4e	−0.1161	0.8022	0.2296	0.120
H(11B)	4e	−0.2690	0.7769	0.2658	0.120
H(11C)	4e	−0.2452	0.7590	0.1908	0.120
H(12A)	4e	0.2668	0.7245	0.2759	0.112
H(12B)	4e	0.1397	0.7793	0.2995	0.112
H(12C)	4e	0.1686	0.7680	0.2237	0.112
H(13A)	4e	0.3015	0.6241	0.3040	0.111
H(13B)	4e	0.2462	0.5475	0.2835	0.111
H(13C)	4e	0.2091	0.5766	0.3544	0.111
H(14A)	4e	−0.2172	0.5031	0.3080	0.108
H(14B)	4e	−0.0911	0.5209	0.3627	0.108
H(14C)	4e	−0.0411	0.4799	0.2987	0.108
H(15A)	4e	−0.3854	0.5743	0.2650	0.121
H(15B)	4e	−0.3984	0.6371	0.2142	0.121
H(15C)	4e	−0.4098	0.6523	0.2903	0.121
H(16A)	4e	0.3200	0.5568	0.0696	0.135
H(16B)	4e	0.3225	0.4788	0.0971	0.135
H(16C)	4e	0.3329	0.5434	0.1461	0.135
H(17A)	4e	0.1634	0.6067	0.0051	0.117
H(17B)	4e	0.0055	0.6497	0.0102	0.117
H(17C)	4e	0.0094	0.5779	−0.0292	0.117
H(18A)	4e	−0.2602	0.6074	0.0232	0.127
H(18B)	4e	−0.3465	0.6013	0.0913	0.127
H(18C)	4e	−0.3468	0.5366	0.0423	0.127
H(19A)	4e	0.2071	0.4357	0.1981	0.147
H(19B)	4e	0.0612	0.3872	0.1820	0.147
H(19C)	4e	0.0564	0.4395	0.2423	0.147
H(20A)	4e	−0.3611	0.4822	0.1528	0.134
H(20B)	4e	−0.2622	0.4656	0.2168	0.134
H(20C)	4e	−0.2568	0.4134	0.1564	0.134
H(25A)	4e	0.5160	0.8207	−0.0798	0.105

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(25B)	4e	0.4841	0.8635	-0.0147	0.105
H(25C)	4e	0.3663	0.8694	-0.0746	0.105
H(26A)	4e	0.5338	0.7113	-0.0167	0.108
H(26B)	4e	0.3947	0.6873	0.0288	0.108

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(26C)	4e	0.5000	0.7524	0.0491	0.108
H(27A)	4e	0.3531	0.7227	-0.1115	0.109
H(27B)	4e	0.2023	0.7705	-0.1061	0.109
H(27C)	4e	0.2116	0.6983	-0.0675	0.109

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	4e	0.00908(9)	0.84287(3)	0.00940(3)	0.0456(5)	0.0401(4)	0.0425(4)	-0.0012(3)	-0.0030(3)	0.0060(3)
Co(2)	4e	0.20950(8)	0.86933(3)	0.09165(3)	0.0419(5)	0.0353(4)	0.0406(4)	-0.0035(3)	0.0011(3)	0.0004(3)
Ti	4e	-0.0128(1)	0.61432(4)	0.17302(4)	0.0376(6)	0.0308(5)	0.0352(5)	-0.0014(4)	0.0031(4)	0.0033(4)
C(1)	4e	-0.1130(7)	0.6976(3)	0.2513(2)	0.064(5)	0.043(3)	0.034(3)	0.016(3)	0.004(3)	-0.004(2)
C(11)	4e	-0.1928(9)	0.7648(3)	0.2328(3)	0.120(6)	0.064(4)	0.056(4)	0.040(4)	0.015(4)	0.003(3)
C(2)	4e	0.0457(7)	0.6888(3)	0.2649(2)	0.056(4)	0.045(3)	0.030(3)	-0.004(3)	0.003(2)	0.000(2)
C(12)	4e	0.1655(8)	0.7450(3)	0.2661(3)	0.106(6)	0.067(4)	0.050(4)	-0.033(4)	0.001(3)	0.000(3)
C(3)	4e	0.0705(6)	0.6185(3)	0.2840(2)	0.039(4)	0.056(4)	0.032(3)	0.007(3)	0.005(2)	0.005(2)
C(13)	4e	0.2196(7)	0.5892(3)	0.3086(3)	0.060(5)	0.088(5)	0.074(5)	0.015(4)	-0.008(3)	0.009(4)
C(4)	4e	-0.0756(7)	0.5845(3)	0.2829(2)	0.051(4)	0.047(3)	0.037(3)	-0.001(3)	0.008(2)	0.006(2)
C(14)	4e	-0.1092(8)	0.5161(3)	0.3160(3)	0.112(6)	0.050(4)	0.054(4)	-0.015(3)	0.024(4)	0.009(3)
C(5)	4e	-0.1894(6)	0.6332(3)	0.2607(2)	0.036(4)	0.062(4)	0.038(3)	0.001(3)	0.012(2)	-0.005(3)
C(15)	4e	-0.3604(7)	0.6234(4)	0.2573(3)	0.049(5)	0.115(6)	0.079(5)	0.005(4)	0.009(3)	-0.013(4)
C(6)	4e	0.1166(7)	0.5276(3)	0.1099(3)	0.048(5)	0.048(3)	0.060(4)	0.006(3)	0.004(3)	-0.018(3)
C(16)	4e	0.2874(8)	0.5266(4)	0.1053(4)	0.061(6)	0.100(5)	0.109(6)	0.014(4)	0.018(4)	-0.032(4)
C(7)	4e	0.0112(7)	0.5641(3)	0.0690(2)	0.060(4)	0.040(3)	0.042(3)	-0.009(3)	0.006(3)	-0.003(2)
C(17)	4e	0.0508(9)	0.6029(3)	0.0086(3)	0.141(7)	0.048(4)	0.045(4)	-0.024(4)	0.028(4)	-0.008(3)
C(8)	4e	-0.1406(7)	0.5493(3)	0.0897(3)	0.055(4)	0.042(3)	0.046(3)	-0.007(3)	-0.004(3)	-0.009(3)
C(18)	4e	-0.2860(8)	0.5759(3)	0.0590(3)	0.082(6)	0.080(5)	0.092(5)	0.007(4)	-0.034(4)	-0.020(4)
C(9)	4e	0.0280(8)	0.4894(3)	0.1547(3)	0.073(5)	0.036(3)	0.052(4)	0.007(3)	0.002(3)	0.003(3)
C(19)	4e	0.094(1)	0.4330(3)	0.1981(3)	0.150(8)	0.068(5)	0.075(5)	0.050(5)	-0.003(5)	0.008(4)
C(10)	4e	-0.1296(8)	0.5024(3)	0.1422(3)	0.072(5)	0.040(3)	0.050(4)	-0.014(3)	0.010(3)	-0.004(3)
C(20)	4e	-0.2642(8)	0.4624(3)	0.1694(3)	0.091(6)	0.077(5)	0.101(6)	-0.043(4)	0.030(4)	-0.013(4)
O(1)	4e	0.1725(4)	0.6812(2)	0.1352(1)	0.042(2)	0.037(2)	0.037(2)	0.002(2)	0.003(2)	0.004(2)
O(2)	4e	-0.0698(4)	0.7038(2)	0.1124(2)	0.033(3)	0.045(2)	0.041(2)	-0.003(2)	0.002(2)	-0.001(2)
C(21)	4e	0.0707(7)	0.7191(2)	0.1064(2)	0.044(4)	0.030(3)	0.031(3)	0.000(2)	0.003(2)	-0.003(2)
C(22)	4e	0.1197(6)	0.7798(2)	0.0663(2)	0.043(4)	0.035(3)	0.031(3)	-0.001(2)	0.005(2)	0.000(2)
C(23)	4e	0.2155(6)	0.8015(2)	0.0210(2)	0.045(4)	0.036(3)	0.037(3)	-0.005(2)	0.005(2)	0.008(2)
C(24)	4e	0.3430(7)	0.7764(3)	-0.0241(2)	0.053(4)	0.046(3)	0.041(3)	-0.002(3)	0.015(3)	0.006(3)
C(25)	4e	0.4357(7)	0.8380(3)	-0.0507(3)	0.070(5)	0.069(4)	0.073(4)	-0.001(3)	0.034(3)	0.016(3)
C(26)	4e	0.4527(7)	0.7275(3)	0.0126(3)	0.057(5)	0.069(4)	0.090(5)	0.020(3)	0.026(3)	0.012(4)
C(27)	4e	0.2710(8)	0.7385(3)	-0.0826(3)	0.094(6)	0.075(4)	0.050(4)	-0.005(4)	0.017(3)	-0.014(3)
C(28)	4e	0.2848(7)	0.9462(3)	0.0554(3)	0.066(5)	0.038(3)	0.058(4)	-0.004(3)	0.004(3)	0.003(3)
O(3)	4e	0.3313(5)	0.9967(2)	0.0325(2)	0.099(4)	0.053(3)	0.091(3)	-0.027(3)	0.018(3)	0.011(2)
C(29)	4e	0.3689(7)	0.8402(3)	0.1403(3)	0.052(5)	0.051(4)	0.058(4)	-0.004(3)	0.000(3)	-0.002(3)
O(4)	4e	0.4670(5)	0.8205(3)	0.1716(2)	0.052(3)	0.111(4)	0.079(3)	0.006(3)	-0.018(2)	0.008(3)
C(30)	4e	0.0908(7)	0.9040(3)	0.1544(3)	0.058(4)	0.034(3)	0.054(4)	0.000(3)	0.004(3)	0.000(3)
O(5)	4e	0.0168(5)	0.9278(2)	0.1947(2)	0.086(4)	0.068(3)	0.067(3)	0.010(2)	0.022(2)	-0.016(2)
C(31)	4e	-0.0847(8)	0.7835(3)	-0.0423(3)	0.072(5)	0.058(4)	0.063(4)	0.002(3)	-0.024(4)	0.001(3)
O(6)	4e	-0.1479(6)	0.7438(3)	-0.0749(3)	0.117(5)	0.086(4)	0.105(4)	-0.006(3)	-0.052(3)	-0.014(3)
C(32)	4e	0.0359(7)	0.9133(3)	-0.0452(3)	0.056(4)	0.050(4)	0.049(4)	0.007(3)	0.000(3)	0.009(3)
O(7)	4e	0.0558(6)	0.9593(2)	-0.0805(2)	0.101(4)	0.067(3)	0.073(3)	0.011(3)	0.010(3)	0.030(3)
C(33)	4e	-0.1570(7)	0.8660(3)	0.0567(3)	0.041(4)	0.062(4)	0.062(4)	-0.003(3)	0.000(3)	0.010(3)
O(8)	4e	-0.2618(6)	0.8811(2)	0.0870(2)	0.054(4)	0.107(4)	0.095(4)	0.010(3)	0.018(3)	0.002(3)

Acknowledgments. We thank the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie.

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