Crystal structure of bis(η^5-pentamethylcyclopentadienyl)(μ_3-(oxymethylidin)-cyclo-(tricarbonylcobalt)(monocarbonylcobalt)-(μ_2-η^2-3-trimethylpropinyl)titan, $C_{31}H_{39}Co_2O_5Ti$

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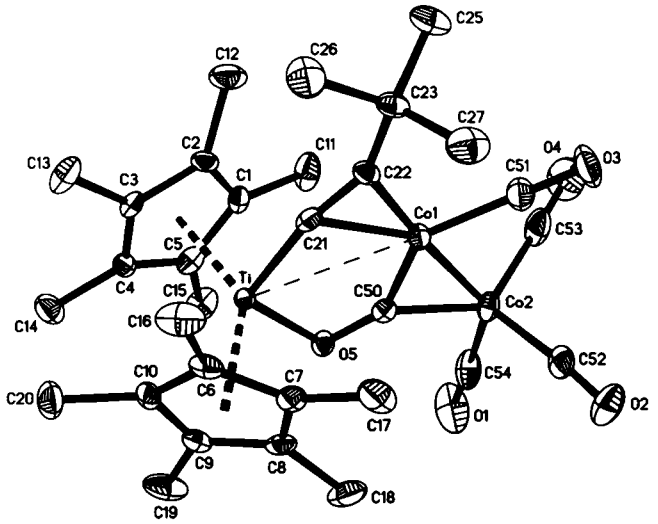

Abstract

$C_{31}H_{39}Co_2O_5Ti$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 12.714(3)$ Å, $b = 15.495(3)$ Å, $c = 15.596(3)$ Å, $V = 3072.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.090$, $T = 200$ K.

Source of material

[Cp*$_2$Ti(C≡C^{t}Bu)] (76 mg, 0.19 mmol) and $Co_2(CO)_8$ (65 mg, 0.19 mmol) were dissolved in 5 ml hexane. After 2 days at room temperature the black-orange solution was kept at 195 K. Black crystals appeared which were filtrated and dried in vacuo to afford 123 mg (98%) of the title compound.

Discussion

Early-late heterobimetallics are able to act selectively with different reaction centers of a bifunctional molecule or substrate and to cooperate in selective reactions [1, 2]. This is the reason why they are considered as important reagents and catalysts to study synergistic effects. Some years ago we came to the question of heterobimetallics by investigating the C—C single bond cleavage reactions of 1,3-butadiynes as the basic for their C—C single bond metathesis. We could show that in some cases such a reaction is only possible by combinations like Ti–Ni or Zr–Ni [3, 4]. Later we described Ti-Co compounds, obtained by N–N cleavage reaction of 2,3-diazadienes [5]. Now we came also to Ti–Co combination investigating the reaction behaviour of very rare monomeric titanocene-mono-σ-alkynyl complexes Cp_2Ti-C≡CR which are assumed to be the key compounds in the above mentioned C—C single bond metathesis of 1,3-butadiynes. We found in a series of investigations that compounds with unsubstituted cyclopentadienyl Cp are less stable compared to the corresponding pentamethyl-cyclopentadienyl complexes. One compound of this type Cp*$_2$Ti-C≡C^{t}Bu was the first structurally characterized example [6]. In this work we describe the reaction behaviuor of this compound towards dicobalt-octacarbonyl giving a heterodimetallic compound. The complex differs in respect to the Ti–Co interaction to unbridged examples like (^{t}BuO)$_3$Ti-Co(CO)$_4$ (2.565(2) Å [7]) and is more similar to the bridged compound Cp(Co$_3$(CO)$_9$(μ-CO)TiCo(CO)$_4$ (2.614 Å [8]).

Table 1. Data collection and handling.

Crystal:	black prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.57 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2°$.
$2\theta_{max}$:	48.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9248, 4910
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4193
$N(param)_{refined}$:	352
Programs:	SHELXS-97 [9], SHELXL-97 [10]

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

Atom	Site	x	y	z	U_{iso}
H(11A)	4a	–0.1274	0.1411	–0.0946	0.091
H(11B)	4a	–0.1212	0.1360	–0.1970	0.091
H(11C)	4a	–0.0154	0.1390	–0.1415	0.091
H(12A)	4a	–0.2247	0.0653	–0.0139	0.089
H(12B)	4a	–0.2201	–0.0242	0.0372	0.089
H(12C)	4a	–0.3001	–0.0127	–0.0412	0.089
H(13A)	4a	–0.1692	–0.2456	–0.0886	0.075
H(13B)	4a	–0.2677	–0.1827	–0.0750	0.075
H(13C)	4a	–0.1807	–0.1918	–0.0014	0.075
H(14A)	4a	–0.0804	–0.2488	–0.2076	0.073
H(14B)	4a	0.0204	–0.2036	–0.2495	0.073
H(14C)	4a	–0.0941	–0.1860	–0.2883	0.073
H(15A)	4a	0.0331	0.0541	–0.2730	0.084
H(15B)	4a	–0.0155	–0.0248	–0.3260	0.084
H(15C)	4a	0.0916	–0.0374	–0.2735	0.084
H(16A)	4a	–0.0200	–0.2636	0.0840	0.086
H(16B)	4a	–0.0139	–0.1743	0.1353	0.086
H(16C)	4a	0.0741	–0.2466	0.1500	0.086
H(17A)	4a	0.1517	–0.0908	0.1753	0.080
H(17B)	4a	0.2038	–0.0125	0.1235	0.080
H(17C)	4a	0.2723	–0.0961	0.1462	0.080

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(18A)	4a	0.3406	-0.0589	-0.1063	0.085
H(18B)	4a	0.3750	-0.0722	-0.0085	0.085
H(18C)	4a	0.3012	0.0073	-0.0344	0.085
H(19A)	4a	0.1778	-0.2227	-0.2085	0.092
H(19B)	4a	0.2937	-0.2041	-0.1728	0.092
H(19C)	4a	0.2241	-0.1266	-0.2099	0.092
H(20A)	4a	0.0005	-0.3178	-0.0357	0.087
H(20B)	4a	0.1112	-0.3409	-0.0787	0.087
H(20C)	4a	0.0231	-0.2917	-0.1332	0.087

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(25A)	4a	-0.2104	0.0979	0.2699	0.076
H(25B)	4a	-0.2279	0.0919	0.1684	0.076
H(25C)	4a	-0.1359	0.1511	0.2064	0.076
H(26A)	4a	-0.2010	-0.0586	0.2770	0.088
H(26B)	4a	-0.1152	-0.1109	0.2228	0.088
H(26C)	4a	-0.2136	-0.0678	0.1753	0.088
H(27A)	4a	-0.0593	0.0317	0.3390	0.082
H(27B)	4a	0.0223	0.0800	0.2774	0.082
H(27C)	4a	0.0244	-0.0230	0.2851	0.082

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}
Co(1)	4a	0.05349(4)	0.08941(3)	0.05580(3)	0.0301(3)	0.0241(3)	0.0263(3)	-0.0025(3)	0.0010(3)	-0.0025(2)
Co(2)	4a	0.17873(5)	0.18420(4)	-0.01762(4)	0.0385(3)	0.0252(3)	0.0339(3)	-0.0107(3)	-0.0055(3)	0.0031(3)
Ti	4a	0.03752(5)	-0.06532(4)	-0.05656(4)	0.0195(3)	0.0176(3)	0.0210(3)	-0.0003(3)	0.0001(3)	0.0004(3)
C(1)	4a	-0.0875(3)	0.0201(3)	-0.1386(3)	0.032(2)	0.020(2)	0.035(2)	-0.001(2)	-0.015(2)	0.003(2)
C(11)	4a	-0.0879(5)	0.1176(3)	-0.1433(4)	0.065(4)	0.027(3)	0.089(4)	0.000(3)	-0.040(3)	0.005(3)
C(2)	4a	-0.1468(3)	-0.0302(3)	-0.0805(3)	0.023(2)	0.039(3)	0.035(2)	0.013(2)	-0.006(2)	-0.008(2)
C(12)	4a	-0.2303(4)	0.0024(4)	-0.0192(4)	0.031(3)	0.089(4)	0.058(3)	0.019(3)	-0.009(3)	-0.026(3)
C(3)	4a	-0.1318(3)	-0.1182(3)	-0.1024(3)	0.022(2)	0.027(2)	0.028(2)	-0.007(2)	-0.006(2)	0.007(2)
C(13)	4a	-0.1926(4)	-0.1908(3)	-0.0635(4)	0.037(3)	0.051(3)	0.063(3)	-0.017(3)	-0.013(3)	0.014(3)
C(4)	4a	-0.0672(3)	-0.1209(3)	-0.1760(2)	0.027(2)	0.028(2)	0.024(2)	0.003(2)	-0.008(2)	-0.005(2)
C(14)	4a	-0.0542(4)	-0.1964(3)	-0.2355(3)	0.052(3)	0.046(3)	0.048(3)	0.012(3)	-0.011(3)	-0.016(2)
C(5)	4a	-0.0392(4)	-0.0358(3)	-0.1962(2)	0.031(2)	0.043(3)	0.020(2)	-0.005(2)	-0.007(2)	0.010(2)
C(15)	4a	0.0229(4)	-0.0086(4)	-0.2740(3)	0.055(3)	0.082(4)	0.032(3)	-0.019(3)	0.000(2)	0.011(3)
C(6)	4a	0.0917(3)	-0.1819(3)	0.0373(3)	0.033(2)	0.024(2)	0.033(3)	0.012(2)	0.004(2)	0.015(2)
C(16)	4a	0.0275(4)	-0.2199(4)	0.1077(4)	0.050(3)	0.053(3)	0.069(4)	0.012(3)	0.022(3)	0.035(3)
C(7)	4a	0.1692(3)	-0.1165(3)	0.0468(3)	0.030(2)	0.033(2)	0.030(2)	0.008(2)	-0.008(2)	0.003(2)
C(17)	4a	0.2021(4)	-0.0754(4)	0.1303(3)	0.060(3)	0.059(4)	0.041(3)	0.028(3)	-0.023(3)	-0.012(3)
C(8)	4a	0.2220(3)	-0.1083(3)	-0.0314(3)	0.020(2)	0.031(2)	0.045(3)	0.007(2)	-0.002(2)	0.009(2)
C(18)	4a	0.3181(4)	-0.0532(3)	-0.0465(4)	0.025(2)	0.052(3)	0.093(4)	0.001(2)	0.002(3)	0.015(3)
C(9)	4a	0.1778(4)	-0.1654(3)	-0.0904(3)	0.031(2)	0.034(2)	0.029(2)	0.011(2)	0.003(2)	-0.002(2)
C(19)	4a	0.2222(4)	-0.1811(4)	-0.1780(3)	0.054(3)	0.089(4)	0.041(3)	0.034(4)	0.010(2)	-0.007(3)
C(10)	4a	0.0978(3)	-0.2133(3)	-0.0470(3)	0.035(2)	0.018(2)	0.041(3)	0.006(2)	-0.012(2)	0.002(2)
C(20)	4a	0.0544(5)	-0.2983(3)	-0.0762(4)	0.057(3)	0.026(3)	0.090(4)	-0.001(3)	-0.028(3)	-0.005(2)
O(1)	4a	0.3019(4)	0.1860(3)	-0.1747(3)	0.133(4)	0.076(3)	0.054(2)	-0.045(3)	0.041(3)	-0.006(2)
O(2)	4a	0.3438(3)	0.1820(3)	0.1143(2)	0.058(2)	0.072(3)	0.060(2)	-0.012(2)	-0.028(2)	0.006(2)
O(3)	4a	0.0575(4)	0.2289(2)	0.1820(2)	0.085(3)	0.052(2)	0.059(2)	-0.010(2)	0.010(2)	-0.032(2)
O(4)	4a	0.0660(4)	0.3503(3)	-0.0143(4)	0.094(3)	0.036(2)	0.140(4)	0.011(2)	-0.031(3)	0.009(3)
O(5)	4a	0.1354(2)	0.0295(2)	-0.1131(2)	0.030(2)	0.027(2)	0.029(2)	-0.006(1)	0.004(1)	0.001(1)
C(21)	4a	-0.0203(3)	-0.0228(3)	0.0576(3)	0.018(2)	0.027(2)	0.037(2)	-0.002(2)	-0.004(2)	0.006(2)
C(22)	4a	-0.0430(3)	0.0174(3)	0.1266(2)	0.027(2)	0.031(2)	0.021(2)	0.006(2)	0.000(2)	-0.005(2)
C(23)	4a	-0.1000(4)	0.0214(3)	0.2098(3)	0.031(2)	0.041(3)	0.028(2)	0.002(2)	0.013(2)	-0.004(2)
C(25)	4a	-0.1752(4)	0.0973(4)	0.2140(3)	0.050(3)	0.061(3)	0.040(3)	0.018(3)	0.014(2)	-0.005(2)
C(26)	4a	-0.1631(5)	-0.0614(4)	0.2223(3)	0.069(4)	0.060(4)	0.047(3)	-0.019(3)	0.032(3)	-0.007(3)
C(27)	4a	-0.0209(4)	0.0281(4)	0.2847(3)	0.051(3)	0.081(4)	0.032(3)	0.008(3)	0.003(2)	-0.001(3)
C(50)	4a	0.1265(3)	0.0806(3)	-0.0518(3)	0.026(2)	0.025(2)	0.026(2)	0.001(2)	-0.004(2)	0.007(2)
C(51)	4a	0.0555(4)	0.1749(3)	0.1309(3)	0.045(3)	0.042(3)	0.040(3)	-0.007(3)	0.002(2)	-0.006(2)
C(52)	4a	0.2767(4)	0.1857(3)	0.0640(3)	0.044(3)	0.032(2)	0.051(3)	-0.016(2)	0.007(3)	-0.003(3)
C(53)	4a	0.1095(5)	0.2852(4)	-0.0127(4)	0.059(3)	0.034(3)	0.072(4)	-0.013(3)	-0.022(3)	0.004(3)
C(54)	4a	0.2545(5)	0.1884(3)	-0.1125(4)	0.074(4)	0.036(3)	0.049(3)	-0.027(3)	0.000(3)	0.005(3)

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