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Carbonyl adducts of open titanocenes – syntheses and structures

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Abstract

Carbonyl adducts of open titanocenes, Ti[2,4-$(CH_3)_2C_5H_5]_2CO$, Ti[2,3-$(CH_3)_2C_5H_5]_2CO$, Ti[3-$CH_3C_5H_6]_2CO$, Ti[2-$CH_3C_5H_6]_2CO$ and Ti$[C_5H_7]_2CO$ have been synthesized. Ti[3-$CH_3C_5H_6]_2CO$ has been characterized by X-ray diffraction. The crystal of Ti[3-$CH_3C_5H_6]_2CO$ is orthorhombic with the space group *Pbca*, $a = 11.224(3)$, $b = 14.038(5)$, $c = 16.009(7)$ Å, $z = 8$. The structure was refined by the block-matrix least-squares method. The final R value was 0.045. NMR was used to characterize the conformations of carbonyl adducts of open titanocenes.

1. Introduction

Organometallic derivatives of low-valent titanium containing Ti with a formal oxidation state of below 4 are of considerable interest as reagents or catalysts in organic synthesis [1]. Cyclopentadienyl as well as open pentadienyl ligands have provided a wide range of low-valent titanium compounds [2–5].

2. Experimental details

All operations involving organometallics were carried out under a nitrogen atmosphere in Schlenk apparatus or in a glovebox. Non-aqueous solvents were thoroughly dried and deoxygenated and were distilled immediately before use. The ^{1}H NMR spectrum was recorded in benzene-d_6 on a Varian UNIT-400 spectrometer. Chemical shifts are given relative to C_6D_5H (internal standard $\delta = 7.23$). The IR spectrum was obtained on a Nicolet-7199 spectrometer.

K[2,4-$(CH_3)_2C_5H_5$], K[2,3-$(CH_3)_2C_5H_5$], K[3-$CH_3C_5H_6$], K[2-CH_3-C_5H_6] and K[C_5H_7] have been prepared analogously to methods described in the literature [6,7]. $P(CH_3)_3$ and CO were obtained commercially, without further purification.

2.1. *Preparation of Ti[2,3-$(CH_3)_2C_5H_5]_2CO$, Ti[2,4-$(CH_3)C_5H_5]_2CO$ and Ti[2-$CH_3C_5H_6]_2CO$*

A 100 ml three-necked flask equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel (charged with 1.0 g (7.5 mmol) of K[2,3-$(CH_3)_2C_5H_5$] in 30 ml of THF) was charged with 0.15 g (6 mmol) of magnesium metal and 40 ml of anhydrous THF. $TiCl_4$ (0.5 ml) was slowly added by syringe and the mixture was stirred for 10 min at room temperature. The flask containing the Ti^{II} species was then cooled to −25°C, and K[2,3-$(CH_3)C_5H_5$] was added dropwise to the stirred solution over a period of 5 min. Upon completion of the addition, the reaction flask was allowed to warm to room temperature and then stirred for an additional 15 min. THF was removed under reduced pressure to give a black–green residue. This residue was extracted with 100 ml petroleum ether. Bubbling CO through the deep-green solution led to the formation of a light-green solution. The resulting solution was filtered and concentrated to 30 ml *in vacuo* and cooled to −70°C for 2 days. Green crystals were isolated. Anal. Found: C, 66.88; H, 8.59. $C_{15}H_{22}OTi$ calc.: C, 67.68; H, 8.33%. ^{1}H NMR (C_6D_6): δ 1.404 (s, CH_3, 3H), 1.774 (s, CH_3, 3H), 0.734 (d, H_{n1}, 1H), 1.168 (d of d, H_{n2}, 1H), 3.026 (d, H_{x1}, 1H), 2.520 (d of d, H_{x2}, 1H), 4.172 (t, H_b, 1H). Ti[2,3-$(CH_3)_2$-$C_5H_5]_2CO$ possesses an IR stretching frequency at 1946 cm^{-1} (ν(CO)).

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$Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ and $Ti[2\text{-}CH_3C_5H_6]_2CO$ were synthesized in a manner strictly analogous to that of $Ti[2,3\text{-}(CH_3)_2C_5H_5]_2CO$. Anal. for $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$: Found: C, 67.52; H, 8.62. $C_{15}H_{22}OTi$ calc.: C, 67.68; H, 8.33%. ^1H NMR (C_6D_6): δ 0.929 (d, H_n, 2H), 2.840 (d, H_x, 2H), 1.554 (s, CH_3, 3H), 4.744 (s, H_c, 1H). $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ possesses an IR stretching frequency at 1942 cm^{-1} (ν(CO)). The synthesis of $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ has been reported in the literature [2]. Anal. for $Ti[2\text{-}CH_3C_5H_6]_2CO$: Found: C, 65.87; H, 8.00. $C_{13}H_{18}OTi$ calc.: C, 65.56; H, 7.62%. ^1H NMR (C_6D_6): δ 0.517 (d, H_{n1}, 1H), 1.000 (d of d, H_{n2}, 1H), 1.418 (s, CH_3, 3H), 2.614 (d of d, H_{x2}, 1H), 3.029 (t, H_{x1}, 1H), 3.992 (d of d of d, H_b, 1H), 4.621 (d, H_c, 1H), 0.741 (d, H_{n1}, 1H), 1.109 (d of d, H_{n2}, 1H), 1.429 (s, CH_3, 3H), 2.897 (d of d, H_{x1}, 1H), 3.172 (d of d of d, H_{x2}, 1H), 4.377 (d of d of d, H_b, 1H), 4.931 (d of d, H_c, 1H). $Ti[2\text{-}CH_3C_5H_6]_2CO$ possesses an IR stretching frequency at 1950 cm^{-1} (ν(CO)).

2.2. Preparation of $Ti[3\text{-}CH_3C_5H_6]_2CO$ and $Ti[C_5H_7]_2CO$

$TiCl_2$ is synthesized with $TiCl_4$ and Mg in a manner analogous to that described above. A 100 ml three-necked flask was equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel (charged with 1.09 (8 mmol) of $K[3\text{-}CH_3C_5H_6]$ dissolved in 20 ml THF) was charged with 4 mmol $TiCl_2$ in 30 ml THF. The flask was cooled to −25°C, and 0.3 g (4 mmol) $P(CH_3)_3$ was added to the stirred solution. $[3\text{-}CH_3C_5H_6]K$ was then added dropwise over a period of 10 min. Upon completion of the addition the reaction mixture was allowed to warm to room temperature and then stirred for an additional 4 h. The THF was removed under reduced pressure to give a black–red residue. This residue was extracted with 100 ml petroleum ether, and the resulting mixture was then filtered to yield a gold–red solution. Bubbling CO through the gold-red solution led to the formation of a light-green solution. The light-green solution was filtered and concentrated to 30 ml *in vacuo* and cooled to −70°C for 2 days. Green crystals were isolated. The elemental analysis suggested a formula of $C_{13}H_{18}OTi$ for the product, which had an IR stretching frequency at 1953 cm^{-1} (ν(CO)). Anal. Found: C, 65.64; H, 7.71. $C_{13}H_{18}OTi$ calc.: C, 65.56; H, 7.62%. ^1H NMR (C_6D_6): δ 1.777 (s, CH_3, 3H), 0.880 (d of d, H_n, 2H), 2.794 (d of d, H_x, 2H), 4.237 (t, H_b, 2H).

$Ti[C_5H_7]_2CO$ was synthesized in a manner strictly analogous to that of $Ti[3\text{-}CH_3C_5H_6]_2CO$. Anal. Found: C, 62.44; H, 6.83. $C_{11}H_{14}OTi$ calc.: C, 62.80; H, 6.72%. ^1H NMR (C_6D_6): δ 0.792 (d of d, H_n, 2H), 2.853 (d of d of d, H_x, 2H), 4.406 (t of d, H_b, 2H); 4.655 (t, H_c, 1H). $Ti[C_5H_7]CO$ possesses an IR stretching frequency at 1960 cm^{-1} (ν(CO)).

2.3. X-Ray diffraction study of $Ti[3\text{-}CH_3C_5H_6]CO$

A suitable crystal of $[3\text{-}CH_3C_5H_6]_2TiCO$ was wedged in a thin-walled glass capillary and sealed under nitrogen. It was mounted on a Nicolet XRD R3 four-circle diffractometer and the intensity data were collected at room temperature. Graphite-monochromated Mo $K\alpha$ (0.71069) X-ray radiation in the θ–2θ mode was employed and a total of 2193 reflections were collected within the range of $3 \leqslant 2\theta \leqslant 50°$ of which 1673 reflections with $I > 3\sigma(I)$ were considered to be observed. The intensity data were corrected for absorption factors. The coordinates of the heavy atom Ti were obtained by using the Patterson function within the SHELXTL program. Subsequent Fourier syntheses provided the coordinates of all non-hydrogen atoms, and all hydrogen coordinates were added theoretically. After several cycles of block matrix least-squares refinement, R converged to a final value of 0.045. All calculations were performed on an ECLIPSES/250 microcomputer.

3. Results and discussion

The potassium salts of the 2,4-dimethylpentadienyl, 2,3-dimethylpentadienyl and 2-methylpentadienyl anions can react directly with $TiCl_2$ in THF to form $Ti[2,4\text{-}(CH_3)C_5H_6]_2$ [2], $Ti[2,3\text{-}(CH_3)_2C_5H_5]_2$ and $Ti[2\text{-}CH_3C_5H_6]_2$, respectively. The above three compounds can react with CO to form the adducts, $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$, $Ti[2,3\text{-}(CH_3)_2C_5H_5]_2CO$ and $Ti[2\text{-}CH_3C_5H_6]_2CO$. However, the reaction between the potassium salt of 3-methylpentadienyl and pentadienyl anions with $TiCl_2$ in THF should occur while $Ti[3\text{-}CH_3C_5H_6]_2$ and $Ti[C_5H_7]_2$ were not obtained. When $P(CH_3)_3$ was present in the reaction flask, $K[3\text{-}CH_3C_5H_6]$ and $K[C_5H_7]$ can react with "$TiCl_2 + P(CH_3)_3$" leading to $Ti[3\text{-}CH_3C_5H_6]_2P(CH_3)_3$ and $Ti[C_5H_7]_2P(CH_3)_3$. Then $P(CH_3)_3$ can be easily exchanged by CO to form $Ti[3\text{-}CH_3C_5H_6]_2CO$ and $Ti[C_5H_7]_2CO$.

$$2K[2,4\text{-}(CH_3)_2C_5H_5] + TiCl_2 \xrightarrow[-25°C]{THF} Ti[2,4\text{-}(CH_3)_2C_5H_5]_2 \xrightarrow{CO} Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO \qquad (1)$$

$$2K[3\text{-}CH_3C_5H_6] + TiCl_2 + P(CH_3)_3 \xrightarrow[-25°C]{THF} Ti[3 - CH_3C_5H_6]_2P(CH_3)_3 \xrightarrow{CO} Ti[3\text{-}CH_3C_5H_6]_2CO \qquad (2)$$

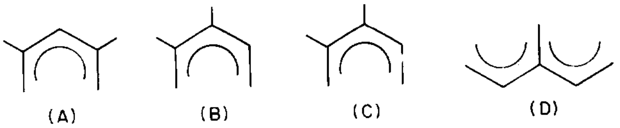


Fig. 1. The configurations of the pentadienyl anions.

Unlike K[2,4-$(CH_3)_2C_5H_5$], K[2,3-$(CH_3)_2C_5H_5$] and K[2-$CH_3C_5H_6$] ligands, the reaction of K[3-$CH_3C_5H_6$] and K[C_5H_7] with $TiCl_2$ cannot form Ti[3-$CH_3C_5H_6$]$_2$ and Ti[C_5H_7]$_2$. The reasons for the different results may be the different configurations of the ligand anions in THF (Fig. 1) [8,9].

When $P(CH_3)_3$ is present in the reaction flask, "Ti$P(CH_3)_3Cl_2$" can be formed, which can then react with [3-$CH_3C_5H_6$]$^-$ to lead to the formation of the more stable compound Ti[3-$CH_3C_5H_6$]$_2$$P(CH_3)_3$ (a 16-electron compound) compared with Ti[3-$CH_3C_5H_6$]$_2$ (a 14-electron compound). The formation of the thermodynamically more stable Ti[3-$CH_3C_5H_6$]$_2$$P(CH_3)_3$ could offset the rotational barrier which the configuration transformation must overcome.

The crystallographic data are given in Table 1, the atomic coordinates and isotropic thermal temperature factors for the non-hydrogen atoms are given in Table 2, and the bond distances and angles are given in Tables 3 and 4, respectively. The numbering scheme of the molecule in the crystal is illustrated in Fig. 2.

The single crystal result for Ti[3-$CH_3C_5H_6$]$_2$CO is presented in Fig. 2. The structural result clearly confirms the eclipsed open sandwich configuration expected for the complex. The data for the least-square planes are given in Table 5. Planes I and II are defined by the C(1), C(2), C(3), C(4), C(5), and C(7), C(8), C(9), C(10), C(11) positions, respectively, while III and IV are defined by positions C(1)–C(6) and C(7)–C(12), respectively. Furthermore, the dihedral angles between planes I–II and planes III–IV are 0.8° and 1.6°, respectively. Therefore, it can be reasonably recognized that the pentadienyl ligand lies almost in a plane. In addition, the dihedral angle of I–III is 2.8° and that of I–IV is 1.6°. Two methyl groups are bent out of the ligand planes in a direction away from the titanium

TABLE 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U
Ti	698(2)	7066(1)	6265(1)	42(1)
O	1211(10)	4925(6)	5847(5)	115(5)
C	1009(11)	5703(9)	5999(7)	64(6)
C(1)	−1210(9)	6521(7)	5980(6)	60(5)
C(2)	−1246(10)	7508(8)	6098(6)	63(5)
C(3)	−529(11)	8189(7)	5677(6)	56(5)
C(4)	383(10)	7966(10)	5111(6)	64(5)
C(5)	720(11)	7074(8)	4817(6)	70(5)
C(6)	−791(13)	9222(8)	5890(8)	98(6)
C(7)	829(14)	5406(7)	7586(6)	62(5)
C(8)	726(14)	7402(8)	7651(8)	50(5)
C(9)	1459(11)	8090(9)	7259(7)	50(5)
C(10)	2337(11)	7857(10)	6658(7)	63(5)
C(11)	2770(10)	6968(9)	6404(7)	68(5)
C(12)	1257(12)	9113(8)	7468(9)	90(7)

TABLE 3. Bond lengths (Å)

Ti–C	1.991(12)	Ti-C(1)	2.319(10)
Ti-C(2)	2.284(12)	Ti-C(3)	2.295(11)
Ti-C(4)	2.265(11)	Ti-C(5)	2.318(9)
Ti-C(7)	2.314(10)	Ti-C(8)	2.270(12)
Ti-C(9)	2.309(12)	Ti-C(10)	2.240(13)
Ti-C(11)	2.341(11)	O-C	1.142(15)
C(1)-C(2)	1.400(11)	C(2)-C(3)	1.419(16)
C(3)-C(4)	1.402(16)	C(3)-C(6)	1.519(15)
C(4)-C(5)	1.390(17)	C(7)-C(8)	1.406(15)
C(8)-C(9)	1.417(18)	C(9)-C(10)	1.414(17)
C(9)-C(12)	1.493(17)	C(10)-C(11)	1.400(19)
C(1)-C(5) [a]	2.961	C(7)-C(11) [a]	2.991
PD-Ti [b]	1.701		

[a] Non-bonding distance. [b] PD–Ti: perpendicular distance from Ti to the ligand plane.

TABLE 1. Crystallographic parameters

Chemical formula	Ti[3-$CH_3C_5H_6$]$_2$CO
Molecular weight	238.16
Crystal system	Orthorhombic
Space group	*Pbca*
Absorption factor (cm^{-1})	μ(Mo Kα) = 7.11
$F(000)$	1008
Crystal cell parameters	
a (Å)	11.224(3)
b (Å)	14.038(5)
c (Å)	16.009(7)
V ($Å^3$)	2522.51(1.59)
E	8

TABLE 4. Bond angles (°)

C–Ti–C(1)	78.6(0.4)	C(1)-Ti-C(2)	35.4(0.4)
C-Ti-C(5)	77.8(0.4)	C(4)-Ti-C(5)	35.3(0.4)
C(2)-Ti-C(3)	36.1(0.4)	C(3)-Ti-C(4)	35.8(0.4)
C(1)-Ti-C(5)	79.4(0.4)	C-Ti-C(7)	78.4(0.4)
C(7)-Ti-C(8)	35.7(0.4)	C(8)-Ti-C(9)	36.0(0.4)
C(9)-Ti-C(10)	36.2(0.4)	C-Ti-C(11)	77.9(0.5)
C(7)-Ti-C(11)	80.0(0.5)	C(10)-Ti-C(11)	35.5(0.5)
Ti-C-O	178.6(1.2)	C(1)-C(2)-C(3)	125.9(1.0)
C(2)-C(3)-C(4)	124.7(10)	C(3)-C(4)-C(5)	128.3(1.1)
C(2)-C(3)-C(6)	115.3(1.0)	C(4)-C(3)-C(6)	120.0(1.1)
C(7)-C(8)-C(9)	126.7(1.2)	C(8)-C(9)-C(10)	123.3(1.1)
C(9)-C(10)-C(11)	130.2(1.2)	C(8)-C(9)-C(12)	117.9(1.1)
C(10)-C(9)-C(12)	118.7(1.1)		

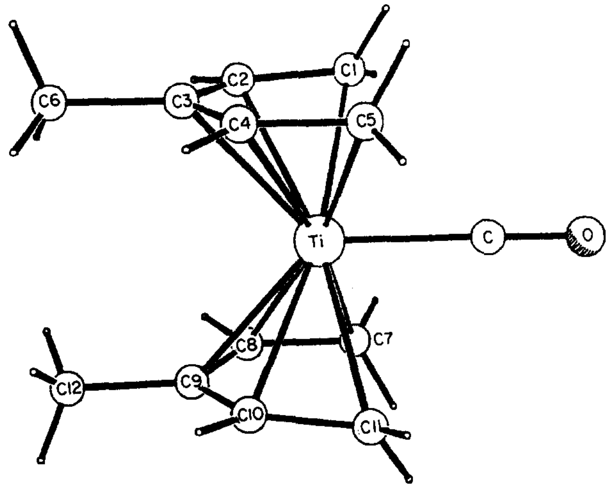
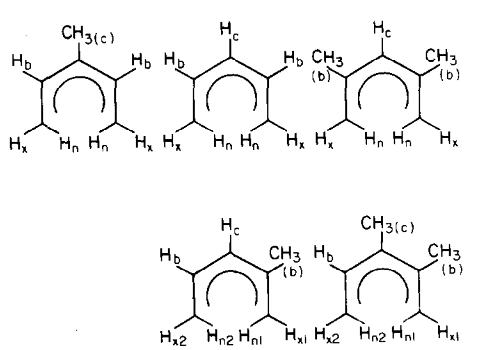


Fig. 2. Perspective view.

atom. The carbonyl ligand is situated on the open edges of the 3-methylpentadienyl ligands.

The average Ti–C(*n*) bond distances can be seen to be Ti–C(1,5,7,11) = 2.323(10) Å, Ti–C(2,4,8,10) = 2.265(12) Å, Ti–C(3,9) = 2.302(11) Å. The distance between Ti and the $[3\text{-}CH_3C_5H_6]^-$ ligand planes is 1.701 Å. The average of the non-bonded C(1) ··· C(5) and C(6) ··· C(11) distances is 2.976 Å.



The interior C–C–C bond angles are observed to fall in three sets, 124.0° (1.0) around the C(3,9) atoms, 126.0° (1.0) around the C(2,8) atoms, and 129.2° (1.0) around the C(4,10) atoms. On average, those positions with an attached methyl group clearly have the smaller interior C–C–C bond angles. This result was also observed in the structure of $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ [10]. It was clear that significant bending of each of the C–H bonds (in CH_2 groups) occurred which brought the two *endo* hydrogen atoms above the ligand planes (away from the titanium atom) and (to a lesser extent) the two *exo* hydrogen atoms below the ligand plane. While a small amount of bending might be expected in order to increase the overlap between the P orbits of the CH_2 groups and the titanium atom, the larger magnitude of bending experienced by the *endo* hydrogen atoms might come about from an attempt to relieve $H_{endo} \cdots H_{endo}$ repulsions which would be substantial in a planar arrangement.

TABLE 5. Deviations of atoms from the least-square plane

	I	II		III	IV
C(1)	−0.0051 [a]	−0.0147 [a]	C(7)	0.0048 [a]	0.0231 [a]
C(2)	0.0135 [a]	0.0231 [a]	C(8)	−0.0205 [a]	−0.0379 [a]
C(3)	−0.0167 [a]	0.0017 [a]	C(9)	0.0335 [a]	−0.0011 [a]
C(4)	0.0112 [a]	0.0204 [a]	C(10)	−0.0292 [a]	−0.0467 [a]
C(5)	−0.0028 [a]	−0.0126 [a]	C(11)	0.0115 [a]	0.0291 [a]
C(6)	−0.0572 [a]	−0.0178 [a]	C(12)	0.1064	0.0336 [a]

[a] Atoms used to define a given plane. Equation of planes: (I) $7.463x - 0.953y + 11.908z = 5.602$; (II) $7.438x - 0.766y + 11.957z = 5.766$; (III) $7.423x - 0.274y + 12.004z = 9.642$; (IV) $7.472x - 0.622y + 11.925z = 9.245$.

The Ti–C and C–O bond distances are 2.341(11) Å and 1.142(15) Å respectively. Since the Ti–C–O angle is 179° (1), it approaches a straight line. The crystals of $Ti[3\text{-}CH_2C_5H_6]_2CO$ and $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ are all orthorhombic, but there are eight molecules in the unit cell of $Ti[3\text{-}CH_3C_5H_6]_2CO$, while there are four molecules in the unit cell of $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ [10].

Only four resonances are observed in the ^1H NMR spectrum of $Ti[3\text{-}CH_3C_5H_6]_2CO$. It is therefore apparent that the two $[3\text{-}CH_3C_5H_6]^-$ ligands in $Ti[3\text{-}CH_3C_5H_6]_2CO$ are equivalent, and they are not only in mirror-symmetry parallel to the two idealized ligand planes but also in mirror-symmetry perpendicular to the two idealized ligand planes. The molecular conformation of $Ti[3\text{-}CH_3C_5H_6]_2CO$ in solution is identical to that of $Ti[3\text{-}CH_3C_5H_6]_2CO$ in the solid state.

Similarly, the ^1H NMR spectra of $Ti[C_5H_7]_2CO$ and $Ti[2,4\text{-}(CH_3)_2C_5H_5]_2CO$ each also display four resonances. The results show that in the liquid state $Ti[3\text{-}CH_3C_5H_6]_2CO$, $Ti[C_5H_7]CO$ and $Ti[2,4\text{-}(CH_3)_2\text{-}C_5H_5]_2CO$ adopt the eclipsed form (conformation angle 0°).

A more complex situation is found in $Ti[2\text{-}CH_3C_5H_6]_2CO$ and $Ti[2,3\text{-}(CH_3)_2C_5H_5]_2CO$. The presence of the methyl substituents in positions 2 and 3

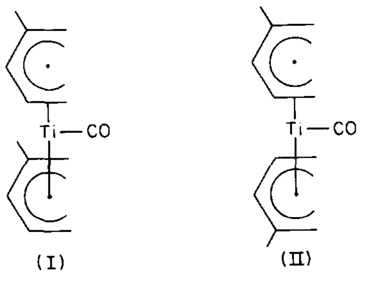


Fig. 3. The two isomers of $Ti[2\text{-}CH_3C_5H_6]_2CO$.

means that pentadienyl ligands no longer have an element of perpendicular symmetry.

The ^{1}H NMR spectrum of Ti[2-$CH_3C_5H_6$]CO shows that two isomers are present in the ratio 1:1. Under these conditions, each of these isomers yields a set of seven signals with the expected multiplicity. Similar results were not observed in the ^{1}H NMR spectra of Ti[2,3-$(CH_3)_2C_5H_5]_2$CO and Ti[2,3-$(CH_3)_2C_5H_5]_2$CO where only seven resonances were displayed. According to the ^{1}H NMR spectrum, Ti[2,3-$(CH_3)_2C_5H_5]_2$CO has only one isomer.

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