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THE FORMATION, CRYSTAL AND MOLECULAR STRUCTURES OF BIS(η^5-INDENYL)DICARBONYLTITANIUM AND BIS(η^5-INDENYL)DICARBONYLZIRCONIUM

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Summary

Bis(η^5-indenyl)dicarbonyltitanium has been produced in 47% yield by reduction of bis(η^5-indenyl)dichlorotitanium with activated aluminum in THF solution under a carbon monoxide atmosphere. Bis(η^5-indenyl)dicarbonylzirconium can similarly be prepared in 45% yield by the reductive carbonylation of bis(η^5-indenyl)dichlorozirconium using activated magnesium turnings. IR spectral evidence has been obtained for the corresponding hafnium analog, although it could not be isolated. Detailed syntheses for the precursors (η^5-indenyl)$_2$MCl$_2$ (M = Ti, Zr, Hf) have been developed. Bis(η^5-indenyl)dicarbonyltitanium crystallizes in the monoclinic space group $C2/c$ with unit cell parameters a 30.435(8), b 7.357(5), c 28.279(8) Å and β 90.93(5)°. Refinement of 3530 observed reflections lead to final agreement indices of $R = 0.052$ and $R_w = 0.049$. Bis(η^5-indenyl)dicarbonylzirconium crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters of a 7.288(5), b 14.398(8), c 15.273(7) Å and β 89.84(5)°. Refinement of 2253 observed reflections lead to final agreement indices of $R = 0.049$ and $R_w = 0.055$.

Introduction

The formation, structural features and chemical reactivities of the Group 4 metallocene dicarbonyls, (η^5-C$_5$H$_5$)$_2$M(CO)$_2$ (M = Ti, Zr, Hf) as well as their ring-methylated analogs represent a very rapidly growing area of organometallic chemistry [1]. The development [2–5] of facile synthetic routes to these compounds

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has greatly facilitated studies of their reactivities, and until our recent syntheses and studies of the much more reactive compounds $(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)_2$ [6–8], the metallocene dicarbonyls have represented the most useful organometallic forms of low-valent Group 4 metals available.

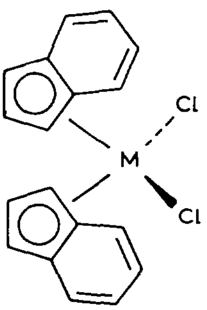
In contrast, very little is known at present concerning the analogous series of compounds $(\eta^5\text{-indenyl})_2M(CO)_2$, where M is a Group 4 metal [1]. In this paper, we report on the formation and spectral characterization of bis(η^5-indenyl)-dicarbonyltitanium (**4**) and bis(η^5-indenyl)dicarbonylzirconium (**5**). Attempts to obtain bis(η^5-indenyl)dicarbonylhafnium (**6**) are discussed, and detailed procedures for the syntheses of the precursors $(\eta^5\text{-indenyl})_2TiCl_2$ (**1**), $(\eta^5\text{-indenyl})_2ZrCl_2$ (**2**), and $(\eta^5\text{-indenyl})_2HfCl_2$ (**3**) are also given. Single crystal X-ray diffraction studies on **4** and **5** are also described.

Results and dicussion

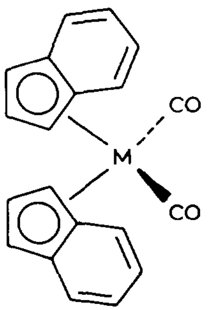
Synthetic and spectral studies

Bis(η^5-indenyl)dichlorotitanium (**1**) was first described in the chemical literature in 1962 [9]. It was reported to be formed in unspecific yield from a reaction between indenyllithium and $TiCl_4$ in ethyl ether solution, and was stated to exist as dark green crystals of m.p. 312–313 °C (dec). In 1965, Samuel and Setton [10] briefly reported the formation of **1** from a reaction between indenylsodium and $TiCl_4$ in THF solution. Their product was described as a dark brown crystalline solid of m.p. 210 °C. The zirconium analog **2** could be made in a similar manner, starting with indenylsodium and $ZrCl_4$ [10]. IR spectra of **1** and **2** were recorded, and were remarkably similar. The corresponding hafnium analog **3** has only been briefly described. Samuel and Rausch reported it as an intermediate in the formation of bis(η^5-indenyl)dimethylhafnium [11].

Compounds **1**–**3** offer potential utility as starting materials for the formatioin and stabilization of new low-valent organotitanium, -zirconium, and -hafnium derivatives. We decided to develop improved syntheses for these compounds, since attempts to prepare them on the basis of existing literature information were often



(**1**, M = Ti ;
2, M = Zr ;
3, M = Hf)



(**4**, M = Ti ;
5, M = Zr ;
6, M = Hf)

not reproducible. In the Experimental section of this paper, detailed procedures for the formation of **1**–**3** are given, and represent modifications of the original method of Samuel and Setton [10].

As noted earlier [10], the titanium compound **1** cannot be recrystallized or vacuum-sublimed without decomposition. However, we have found that the insoluble reaction product after rapid washing and drying is of sufficiently high purity that it can be utilized in further reactions. We were unable to obtain a ^1H NMR spectrum of **1**, owing to its very low solubility in most organic solvents and its apparent instability in solution. In contrast, it was reported earlier that the zirconium analog **2** could be further purified by vacuum sublimation [10], and we have utilized this technique in the purification of both **2** and **3**.

Although **2** and **3**, like **1**, could not be successfully recrystallized, we have been able to record their ^1H NMR spectra in CD_2Cl_2 solution. The ^1H NMR spectrum of **2** exhibited a doublet at δ 6.02, a triplet at δ 6.33, and an A_2B_2 multiplet centered at δ 7.22, whereas **3** displayed a doublet at δ 6.08, a triplet at δ 6.51, and an A_2B_2 multiplet centered at δ 7.49. These data are consistent with the proposed structures for **1**–**3**. Furthermore, **1**–**3** have been previously converted into dimethyl analogs whose structures have been confirmed by X-ray diffraction techniques [12]. Elemental analyses of **1**–**3** are likewise within acceptable limits.

The reduction of **1** with activated aluminum turnings in THF solution under a carbon monoxide atmosphere produced bis(η^5-indenyl)dicarbonyltitanium (**4**) in 47% yield. Complex **4** has previously been prepared in 50% yield by the photolysis of (η^5-indenyl)$_2$Ti(CH$_3$)$_2$ in the presence of carbon monoxide [14], however, the present procedure represents the most reliable and efficient route to **4** [13]. Demerseman and coworkers have also briefly mentioned that **4** could be obtained from a reaction of (η^5-indenyl)$_2$Ti(CH$_2$Ph)$_2$ and $AlEt_3$ in the presence of carbon monoxide, and by reduction of **1** in the presence of carbon monoxide [2,15]. In neither case, however, were reaction details or yield data given, and in the latter method, it was stated that **4** could not be isolated.

Compound **4** is a dark-green, air-sensitive solid which is very soluble in both aromatic and aliphatic solvents. The ^1H NMR spectrum of **4** (acetone-d_6) prepared in this study exhibits a triplet at δ 4.83, a doublet at δ 5.05, and an A_2B_2 multiplet centered at δ 6.80. The IR spectrum of **4** in pentane displays a high energy carbonyl band at 1987 cm^{-1}, and a low energy carbonyl band which is split into a doublet at 1913/1906 cm^{-1}. These spectral results are generally consistent with those reported earlier for **4** [14].

Bis(η^5-indenyl)dichlorozirconium (**2**) proved totally resistant to reduction when activated aluminum turnings or aluminum powder were used. The reductive carbonylation of **2** did occur, however, when the reaction was carried out in the presence of activated magnesium turnings, producing bis(η^5-indenyl)dicarbonylzirconium (**5**) in 45% yield. The use of 60 mesh magnesium also produced **5**, however, the yield was only 20%.

Complex **5** is a dark-green, highly air-sensitive solid which is soluble in both aromatic and aliphatic solvents. The ^1H NMR spectrum of **5** in acetone-d_6 exhibits a doublet at δ 5.31, a triplet at δ 5.54, and an A_2B_2 multiplet centered at δ 7.00. The IR spectrum in pentane displays two carbonyl stretching frequencies at 1985 and 1899 cm^{-1}, with no evidence for the lower energy band splitting observed for **4**.

Attempts to prepare bis(η^5-indenyl)dicarbonylhafnium (**6**) were for the most part

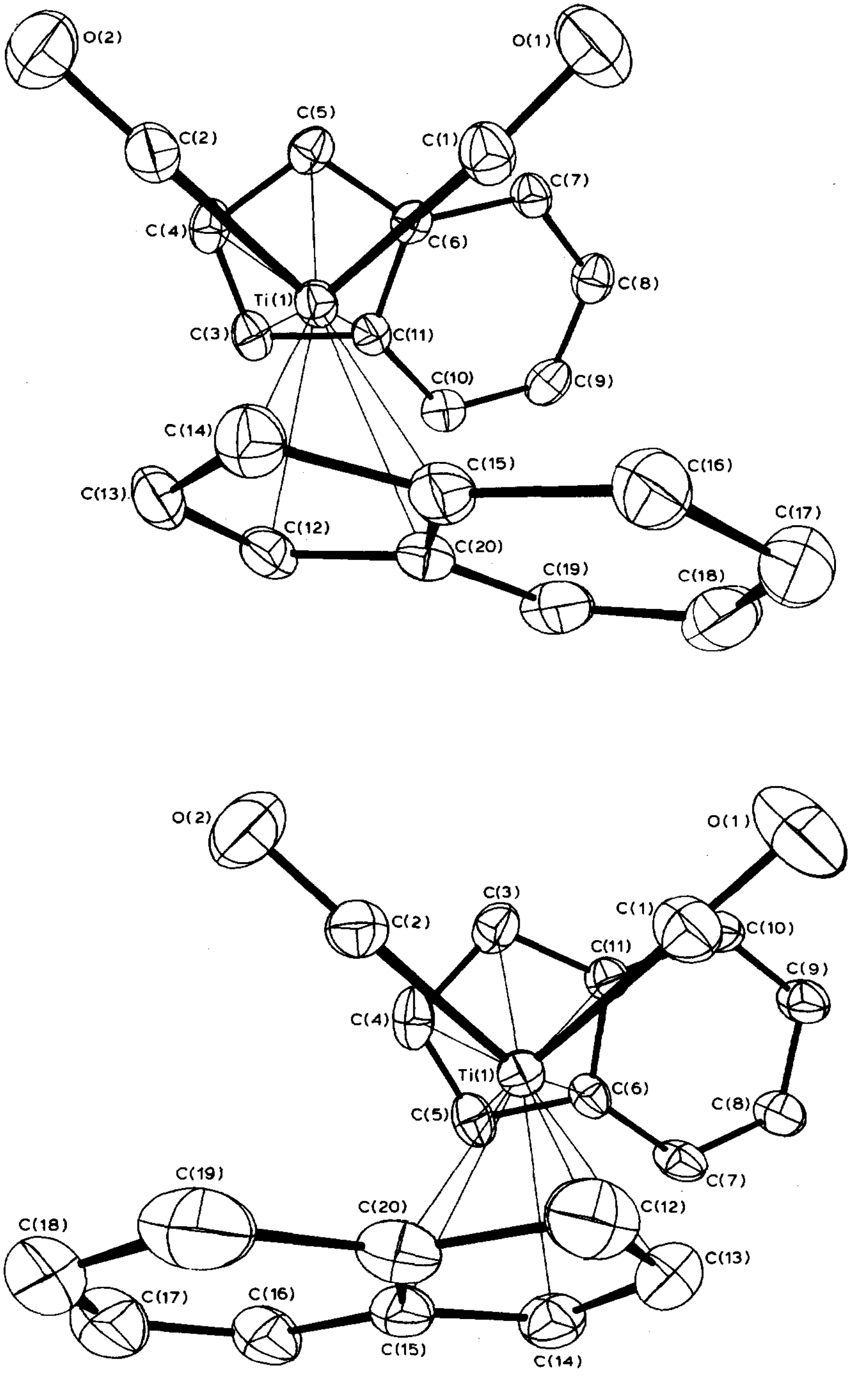


Fig. 1. (a) Molecular structure and numbering scheme for molecule A of $(C_9H_7)_2Ti(CO)_2$. (b) Molecular structure and numbering scheme for molecule B of $(C_9H_7)_2Ti(CO)_2$.

unsuccessful. Magnesium powder, both 60 and 200–300 mesh activated with $HgCl_2$, failed to induce the reductive carbonylation of **3**. Use of Rieke magnesium [5,16], a highly activated form of magnesium prepared from anhydrous $MgCl_2$ and potassium metal in refluxing THF, did yield the highly air-sensitive dicarbonyl complex **6** on several occasions. However, the yields of **6** were always extremely low and not reproducible. The IR spectrum of **6** recorded in pentane displays two metal carbonyl stretching frequencies at 1979 and 1892 cm^{-1}, however, further characterization was not possible.

Crystallographic studies

One could envision two extremes with regard to the orientation of the two indenyl groups in **4**, either *syn* or *anti*. Indeed, as is shown in Fig. 1, both are found in equal population. Just as there is a gross configurational difference between the two isomers, so also are there significant metrical differences between related parameters. The two Ti–C(carbonyl) lengths in the *anti* isomer (molecule B) are equal at 2.032(5) and 2.035(5) Å (Table 3). The values are close to the 2.030(1) Å found in $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ [17] and the 2.01(1) Å in $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$ [4]. However, the *syn* isomer (molecule A) exhibits Ti–C(carbonyl) lengths of 2.027(4) and 2.071(4) Å. The former is near the expected value, but the latter is significantly longer. Important comparisons also relate to the Ti–C(π) lengths. For each of the two isomers the range is similar, 2.30–2.49 Å, with the long distances being associated with the carbon atoms in common to both the five- and six-membered rings. The range as expressed by $\Delta = (M\text{–}C_{max}) - (M\text{–}C_{min})$ compares well with that for $(\eta^5\text{-}C_9H_7)_2TiMe_2$ [12], but the distances themselves are substantially different. This result has been noted previously for Ti^{2+} versus Ti^{4+} cyclopentadienyl com-

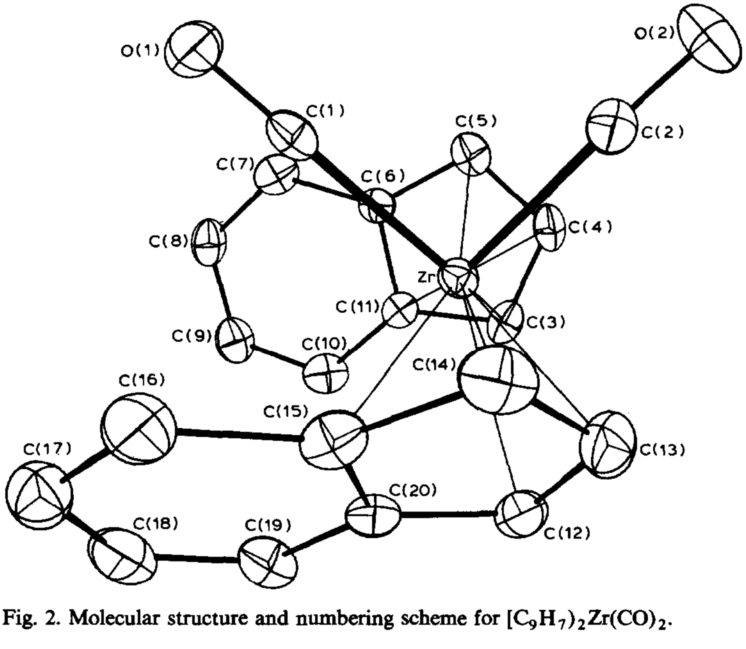


Fig. 2. Molecular structure and numbering scheme for $[C_9H_7)_2Zr(CO)_2$.

plexes [17]. For $(\eta^5\text{-}C_9H_7)_2Ti(CO)_2$, the Ti–C($\pi$) separation is 2.38 Å on the average, whereas the related parameter for $(\eta^5\text{-}C_9H_7)_2TiMe_2$ is 2.44 Å.

The same trend holds for the Zr–C(π) lengths. The Zr–C(π) average is 2.51 Å in $(\eta^5\text{-}C_9H_7)_2Zr(CO)_2$ compared to 2.55 Å in $(\eta^5\text{-}C_9H_7)_2ZrMe_2$ [12]. The configuration of the molecule is *gauche* (Fig. 2), and the Δ is 0.12 Å for the Zr–C(π) distances. The Zr–C(carbonyl) distances, 2.186(7) and 2.221(7) Å, are near the 2.187(4) Å found in $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ [18].

Experimental

General

All operations were carried out under argon using standard Schlenk or vacuum-line techniques unless otherwise specified. Dry argon was obtained by passing it through magnesium perchlorate, phosphorus pentoxide and molecular sieves. Trace oxygen was removed by means of a heated BTS catalyst column. Pentane, hexane and benzene were dried over CaH_2 and distilled under argon. Tetrahydrofuran (THF) was predried over KOH followed by sodium wire and then distilled under argon from sodium/benzophenone. Alumina (CAMAG, neutral grade) was predried in an oven overnight, then heated with a heatgun while mixing on a rotary evaporator attached to a vacuum pump for 2 h. The alumina was subsequently deactivated with argon-saturated water (5% by weight) and stored under argon until use.

^1H NMR spectra were recorded on a Varian A-60 spectrometer, whereas IR spectra were obtained on a Perkin–Elmer 237B spectrometer in pentane solution. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA. $TiCl_4$ was obtained from Fisher Scientific Co., whereas $ZrCl_4$ and $HfCl_4$ (both 99.9% pure on a metal-metal basis) were obtained from Research Organic/Inorganic Chemicals Co. The latter compounds were further purified (75–88% recovery) by sublimation at 270–290 °C/10^{-4} mmHg and were stored under argon until used. Indene was purchased from Aldrich Chemical Co.

Bis(η^5-indenyl)dichlorotitanium (1)

Pentane-washed sodium sand (1.98 g, 0.086 mol) was added to a 250-ml, single-neck round-bottom flask with sidearm stopcock and magnetic stirrer bar. Freshly distilled THF (ca. 150 ml) and indene (10.0 g, 0.086 mol) were added at room temperature. A reflux condenser was attached to the flask and the mixture was heated at reflux for 72 h, after which time it was allowed to cool to room temperature. Into another 250-ml, single-neck round-bottom flask with sidearm stopcock was added $TiCl_4$ (8.78 g, 0.043 mol) and dry benzene (ca. 50 ml). The solution was cooled to ca. 0 °C and THF (20–30 ml) was slowly added, producing a yellow precipitate. The indenylsodium solution was then slowly added to the $TiCl_4$ solution via a cannula, maintaining the temperature of the reaction at 0 °C. On addition, the solution turned from yellow to red-brown and remained this color throughout the reaction. Following the addition, the solution was stirred for 1 h at 0 °C and then filtered through a Buchner funnel in air. The filtration proceeded slowly due to the thickness of the solution, however, a black-violet solid was obtained on completion of the filtration. This solid was ground into a fine powder and dried under vacuum. After drying, the solid was slowly added to a vigorously stirred 10% aqueous hydrochloric acid solution at 0 °C. After the addition, 10–20 ml of diethyl ether was added and the slurry was filtered through a Buchner funnel. The solid was washed rapidly with 95% ethanol followed by diethyl ether. The resulting material was dried under reduced pressure and the washing procedure was repeated. The brown-black solid was subsequently dried under high vacuum, affording 5.2 g (35%) of **1**. Found: C, 61.52; H, 4.04. $C_{18}H_{14}Cl_2Ti$ calc: C, 61.92; H, 4.04%.

Bis(η^5-indenyl)dichlorozirconium (2)

A reaction procedure analogous to that described above was used, employing 2.25 g (0.098 mol) of sodium sand, 150 ml of THF, and 11.37 g (0.098 mol) of indene in one flask, and 11.30 g (0.049 mol) of sublimed $ZrCl_4$ and ca. 50 ml of dry benzene in the second flask. The latter solution was cooled to 0 °C and THF (20–30 ml) was added, forming a yellow precipitate. The indenylsodium solution was then slowly added via a cannula at 0 °C, giving a canary yellow suspension. Following the addition, the reaction mixture was stirred for 1 h at 0 °C and then filtered in air through a Buchner funnel. The resulting solid was ground into a fine powder, dried under high vacuum, and transferred to a sublimer. The solid was heated to 50 °C/10^{-4} mmHg for 6 h and subsequently at 185–190 °C/10^{-4} mmHg, producing a sublimate of bis(η^5-indenyl)dichlorozirconium in the form of yellow needles (9.6 g, 50%). Found: C, 55.35; H, 3.65. $C_{18}H_{14}Cl_2Zr$ calc: C, 55.09; H, 3.60%.

TABLE 1

CRYSTAL DATA FOR $(C_9H_7)_2M(CO)_2$ (M = Ti, Zr)

	M = Ti	M = Zr
Molecular weight	334.21	377.53
Space group	$C2/c$	$P2_1/n$
Cell constants:		
a (Å)	30.435(8)	7.288(5)
b (Å)	7.357(5)	14.398(8)
c (Å)	28.279(8)	15.273(7)
β (°)	90.93(5)	89.84(5)
V (Å^3)	6331.1	1602.6
Molecules/unit cell	16	4
Calcd. density (g cm^{-3})	1.49	1.56
Lin. abs. coeff. (cm^{-1})	5.70	6.83
Radiation	Mo-K_α	Mo-K_α
Crystal dim. (max, mm)	0.3 × 0.3 × 0.35	0.25 × 0.25 × 0.35
Scan width (°)	0.8 + 0.2tan(th)	0.8 + 0.2tan(th)
Standard reflections	1000, 020, 0012	400, 040, 008
Decay of standards	< 2%	< 3%
Reflections measured	6119	3303
θ-range (°)	1–25	1–25
Observed reflections	3530	2253
Parameters varied	415	208
Goodness of fit	2.78	1.87
R	0.052	0.049
R_w	0.049	0.055

Bis(η^5-indenyl)dichlorohafnium (3)

The procedure was identical to that described for the preparation of **2**, except that 15.70 g (0.049 mol) of sublimed $HfCl_4$ was used. Vacuum sublimation of the

TABLE 2

ATOMIC POSITIONS IN FRACTIONAL COORDINATES AND THERMAL PARAMETERS FOR $(C_9H_7)_2Ti(CO)_2$

TABLE 2A

Atom	x/a	y/b	z/c	U_{eq}
Ti(1)A	0.18784(2)	0.38869(9)	0.82855(2)	0.037
C(1)A	0.2035(1)	0.1160(6)	0.8220(1)	0.049
O(1)A	0.2145(1)	−0.0300(4)	0.8175(1)	0.077
C(2)A	0.2524(1)	0.4308(5)	0.8156(1)	0.047
O(2)A	0.2885(1)	0.4553(5)	0.8080(1)	0.069
C(3)A	0.1481(1)	0.6013(6)	0.7819(1)	0.053
C(4)A	0.1872(1)	0.5609(6)	0.7591(1)	0.054
C(5)A	0.1865(1)	0.3740(6)	0.7462(1)	0.050
C(6)A	0.1445(1)	0.3033(5)	0.7589(1)	0.043
C(7)A	0.1241(1)	0.1301(5)	0.7523(1)	0.048
C(8)A	0.0824(1)	0.1074(6)	0.7668(2)	0.059
C(9)A	0.0587(1)	0.2481(7)	0.7889(2)	0.061
C(10)A	0.0774(1)	0.4146(6)	0.7967(1)	0.053
C(11)A	0.1207(1)	0.4447(5)	0.7814(1)	0.045
C(12)A	0.1593(1)	0.5538(5)	0.8901(1)	0.051
C(13)A	0.2051(1)	0.5664(5)	0.8928(1)	0.051
C(14)A	0.2226(1)	0.3938(6)	0.9036(1)	0.049
C(15)A	0.1869(1)	0.2740(5)	0.9113(1)	0.046
C(16)A	0.1848(2)	0.0909(6)	0.9278(1)	0.064
C(17)A	0.1449(2)	0.0169(7)	0.9353(2)	0.076
C(18)A	0.1062(2)	0.1117(8)	0.9259(2)	0.078
C(19)A	0.1061(1)	0.2850(7)	0.9089(1)	0.065
C(20)A	0.1470(1)	0.3720(6)	0.9020(1)	0.047
Ti(1)B	0.41775(2)	−0.0632(1)	0.41597(2)	0.044
C(1)B	0.4457(2)	−0.2674(7)	0.4545(2)	0.067
O(1)B	0.4607(1)	−0.3831(6)	0.4769(1)	0.105
C(2)B	0.4145(1)	0.0758(7)	0.4779(2)	0.060
O(2)B	0.4142(1)	0.1587(6)	0.5121(1)	0.097
C(3)B	0.4867(1)	0.0791(70	0.4196(2)	0.064
C(4)B	0.4570(2)	0.1986(7)	0.3970(2)	0.073
C(5)B	0.4425(2)	0.1187(6)	0.3542(2)	0.065
C(6)B	0.4656(1)	−0.0479(6)	0.3484(1)	0.052
C(7)B	0.4649(1)	−0.1816(7)	0.3126(1)	0.067
C(8)B	0.4916(2)	−0.3259(7)	0.3170(2)	0.073
C(9)B	0.5204(1)	−0.3493(7)	0.3559(2)	0.067
C(10)B	0.5212(1)	−0.2258(6)	0.3915(2)	0.059
C(11)B	0.4935(1)	−0.0711(6)	0.3890(1)	0.051
C(12)B	0.3572(2)	−0.2489(8)	0.4367(2)	0.078
C(13)B	0.3700(2)	−0.2885(8)	0.3903(2)	0.080
C(14)B	0.3627(1)	−0.1359(7)	0.3623(2)	0.067
C(15)B	0.3435(1)	0.0000(6)	0.3911(1)	0.052
C(16)B	0.3304(1)	0.1803(7)	0.3819(2)	0.069
C(17)B	0.3120(2)	0.2783(8)	0.4162(2)	0.086
C(18)B	0.3051(2)	0.205(1)	0.4609(2)	0.093
C(19)B	0.3184(2)	0.035(1)	0.4729(2)	0.082
C(20)B	0.3390(1)	−0.0727(7)	0.4377(1)	0.057

TABLE 2B

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)A	0.0441(4)	0.0302(3)	0.0353(4)	−0.0040(3)	−0.0004(3)	0.0013(3)
C(1)A	0.067(3)	0.041(2)	0.040(2)	−0.006(2)	−0.001(2)	−0.001(2)
O(1)A	0.114(3)	0.043(2)	0.074(2)	0.014(2)	0.004(2)	−0.005(2)
C(2)A	0.052(2)	0.043(2)	0.045(2)	−0.007(2)	0.002(2)	−0.002(2)
O(2)A	0.051(2)	0.084(2)	0.072(2)	−0.012(2)	0.008(1)	0.001(2)
C(3)A	0.070(3)	0.036(2)	0.053(2)	−0.000(2)	−0.012(2)	0.011(2)
C(4)A	0.065(3)	0.053(3)	0.045(2)	−0.016(2)	−0.005(2)	0.016(2)
C(5)A	0.053(2)	0.064(3)	0.033(2)	−0.008(2)	0.001(2)	0.006(2)
C(6)A	0.048(2)	0.051(2)	0.032(2)	−0.003(2)	−0.003(2)	0.005(2)
C(7)A	0.054(2)	0.043(2)	0.046(2)	−0.007(2)	−0.006(2)	−0.005(2)
C(8)A	0.058(3)	0.060(3)	0.059(3)	−0.018(2)	−0.009(2)	0.002(2)
C(9)A	0.043(2)	0.081(4)	0.060(3)	−0.008(2)	−0.002(2)	0.012(3)
C(10)A	0.050(2)	0.058(3)	0.050(2)	0.009(2)	−0.004(2)	0.004(2)
C(11)A	0.053(2)	0.041(2)	0.040(2)	0.001(2)	−0.007(2)	0.007(2)
C(12)A	0.071(3)	0.038(2)	0.045(2)	0.005(2)	−0.001(2)	−0.007(2)
C(13)A	0.071(3)	0.038(2)	0.045(2)	−0.013(2)	−0.003(2)	−0.008(2)
C(14)A	0.051(2)	0.051(2)	0.044(2)	−0.003(2)	−0.005(2)	0.000(2)
C(15)A	0.063(3)	0.044(2)	0.030(2)	−0.003(2)	0.000(2)	−0.001(2)
C(16)A	0.105(4)	0.044(3)	0.042(2)	0.003(3)	0.008(2)	0.006(2)
C(17)A	0.128(5)	0.052(3)	0.048(3)	−0.025(3)	0.012(3)	0.004(2)
C(18)A	0.099(4)	0.093(4)	0.043(3)	−0.050(4)	0.014(3)	−0.007(3)
C(19)A	0.057(3)	0.092(4)	0.044(2)	−0.009(3)	0.009(2)	−0.010(3)
C(20)A	0.055(2)	0.050(2)	0.035(2)	−0.003(2)	0.003(2)	−0.007(2)
Ti(1)B	0.0478(4)	0.0451(4)	0.0381(4)	0.0051(3)	−0.0037(3)	−0.0036(3)
C(1)B	0.070(3)	0.075(3)	0.056(3)	0.016(3)	0.004(2)	0.003(3)
O(1)B	0.117(3)	0.107(3)	0.091(3)	0.047(3)	0.009(2)	0.042(3)
C(2)B	0.051(2)	0.075(3)	0.054(3)	0.007(2)	−0.005(2)	−0.012(3)
O(2)B	0.085(2)	0.131(4)	0.074(2)	0.012(2)	−0.008(2)	−0.055(2)
C(3)B	0.053(2)	0.068(3)	0.071(3)	−0.002(2)	0.005(2)	−0.021(3)
C(4)B	0.076(3)	0.044(3)	0.099(4)	0.011(3)	0.024(3)	−0.005(3)
C(5)B	0.071(3)	0.055(3)	0.069(3)	0.012(3)	0.011(2)	0.016(3)
C(6)B	0.053(2)	0.057(3)	0.047(2)	0.012(2)	0.004(2)	0.008(2)
C(7)B	0.066(3)	0.099(4)	0.036(2)	0.024(3)	−0.006(2)	−0.005(2)
C(8)B	0.078(3)	0.087(4)	0.054(3)	0.033(3)	−0.008(2)	−0.024(3)
C(9)B	0.064(3)	0.080(3)	0.057(3)	0.027(3)	−0.006(2)	−0.012(3)
C(10)B	0.052(2)	0.073(3)	0.052(2)	0.014(2)	−0.008(2)	−0.008(2)
C(11)B	0.043(2)	0.059(3)	0.051(2)	0.003(2)	0.002(2)	−0.006(2)
C(12)B	0.071(3)	0.073(4)	0.090(4)	−0.016(3)	−0.011(3)	0.026(3)
C(13)B	0.076(3)	0.062(3)	0.102(4)	−0.004(3)	−0.016(3)	−0.021(3)
C(14)B	0.065(3)	0.087(4)	0.050(3)	0.002(3)	−0.014(2)	−0.016(3)
C(15)B	0.046(2)	0.064(3)	0.046(2)	0.001(2)	−0.010(2)	0.001(2)
C(16)B	0.059(3)	0.078(4)	0.071(3)	0.015(3)	−0.014(2)	0.012(3)
C(17)B	0.061(3)	0.085(4)	0.113(5)	0.022(3)	−0.014(3)	−0.009(4)
C(18)B	0.046(3)	0.133(6)	0.101(5)	0.021(3)	−0.002(3)	−0.049(4)
C(19)B	0.052(3)	0.147(6)	0.049(3)	−0.002(3)	0.004(2)	−0.001(3)
C(20)B	0.047(2)	0.073(3)	0.051(2)	−0.003(2)	−0.006(2)	0.011(2)

crude product at 50 °C/10^{-4} mmHg for 6 h and subsequently at 185–190 °C/10^{-4} mmHg resulted in a sublimate of bis(η^5-indenyl)dichlorohafnium as yellow needles; 6.11 g (26%). Found: C, 45.41; H, 2.92. $C_{18}H_{14}Cl_2Hf$ calc: C, 45.07; H, 2.94%.

TABLE 2C

Atom	x/a	y/b	z/c
H(1)A	0.1402(1)	0.7209(6)	0.7962(1)
H(2)A	0.2215(1)	0.6489(6)	0.7531(1)
H(3)A	0.2105(1)	0.3040(6)	0.7309(1)
H(4)A	0.1406(1)	0.0288(5)	0.7370(1)
H(5)A	0.0681(1)	−0.0136(6)	0.7619(2)
H(6)A	0.0278(1)	0.2248(7)	0.7987(2)
H(7)A	0.0607(1)	0.5134(6)	0.8128(1)
H(8)A	0.1385(1)	0.6542(5)	0.8813(1)
H(9)A	0.2226(1)	0.6797(5)	0.8878(1)
H(10)A	0.2544(1)	0.3604(6)	0.9057(1)
H(11)A	0.2123(2)	0.0191(6)	0.9333(1)
H(12)A	0.1433(2)	−0.1083(7)	0.9489(2)
H(13)A	0.0776(2)	0.0488(8)	0.9316(2)
H(14)A	0.0779(1)	0.3491(7)	0.9013(1)
H(1)B	0.5006(1)	0.0962(7)	0.4516(2)
H(2)B	0.4474(2)	0.3196(7)	0.4092(2)
H(3)B	0.4200(2)	0.1691(6)	0.3315(2)
H(4)B	0.4450(1)	−0.1666(7)	0.2844(1)
H(5)B	0.4909(2)	−0.4215(7)	0.2919(2)
H(6)B	0.5406(1)	−0.4565(70	0.3574(2)
H(7)B	0.5407(1)	−0.2449(6)	0.4198(2)
H(8)B	0.3606(2)	−0.3307(8)	0.4648(2)
H(9)B	0.3823(2)	−0.4072(8)	0.3795(2)
H(10)B	0.3699(1)	−0.1224(7)	0.3281(2)
H(11)B	0.3346(1)	0.2313(7)	0.3495(2)
H(12)B	0.3039(2)	0.4077(8)	0.4096(2)
H(13)B	0.2894(2)	0.280(1)	0.4850(2)
H(14)B	0.3139(2)	−0.014(1)	0.5055(2)

Bis(η^5-indenyl)dicarbonyltitanium (4)

Bis(η^5-indenyl)dichlorotitanium (1.00 g, 2.86 mmol), aluminium turnings (0.41 g, 15 mmol) and 50 ml of THF were placed in a 250-ml single-neck round-bottom flask with sidearm stopcock. The flask was stirred magnetically and was flushed for 10 min with carbon monoxide. Mercuric chloride (0.82 g, 3.0 mmol) was then added to the mixture and carbon monoxide was allowed to flow over the solution through the sidearm and out to a mercury overpressure valve. The reaction mixture was stirred under carbon monoxide for 24 h, during which time the solution changed from red-brown to dark green. The reaction flask was flushed with argon and the solution was poured into a fritted funnel containing a plug (3 × 10 cm) of 5% deactivated alumina covered by 1.5 cm of sea sand. The plug was eluted with hexane until the solution emerging remained colorless. The solvent was removed under reduced pressure, leaving a dark green solid. The residue was taken up in hexane and added to another plug of 5% deactivated alumina in a fritted funnel. The initial fractions emerging from the plug were discarded, and a fresh Schlenk tube was added on the appearance of a green color. The plug was then eluted with additional hexane until the solution emerging from the plug was colorless. The solvent was concentrated under reduced pressure and the solution cooled at −20 °C to produce dark green crystals. The solution was decanted into another Schlenk tube and further concentrated and cooled. The combined crystal crops after drying yielded 0.45 g (47%) of **4**. Found: C, 71.62; H, 4.36. $C_{26}H_{14}O_2Ti$ calc: C, 71.87; H, 4.22%.

Bis(η^5-indenyl)dicarbonylzirconium (5)

The reaction procedure was similar to that described above, utilizing 1.00 g (2.55 mmol) of bis(η^5-indenyl)dichlorozirconium, 0.314 g (13 mmol) of magnesium turnings, 50 ml of THF, and 0.679 g (2.5 mmol) of mercuric chloride. The reaction mixture was stirred under carbon monoxide for 24 h, during which time the solution changed from clear yellow to dark green. The reaction flask was flushed with argon and the solution was poured into a fritted funnel containing a plug (3 × 10 cm) of 5% deactivated alumina covered by sea sand. The plug was eluted with hexane until

TABLE 3A

BOND DISTANCES (Å) AND ANGLES (°) FOR $(C_9H_7)_2Ti(CO)_2$ (MOLECULE A)

Ti(1)–C(1)	2.071(4)	Ti(1)–C(2)	2.027(4)
Ti(1)–C(3)	2.367(4)	Ti(1)–C(4)	2.336(4)
Ti(1)–C(5)	2.331(4)	Ti(1)–C(6)	2.435(4)
Ti(1)–C(11)	2.455(4)	Ti(1)–C(12)	2.304(4)
Ti(1)–C(13)	2.294(4)	Ti(1)–C(14)	2.357(4)
Ti(1)–C(15)	2.487(4)	Ti(1)–C(20)	2.440(4)
Ti(1)–Cnt(1)	2.058	Ti(1)–Cnt(2)	2.049
Ti(1)–Ave(1)	2.38(5)	Ti(1)–Ave(2)	2.38(8)
C(1)–O(1)	1.133(5)	C(2)–O(2)	1.139(4)
C(3)–C(4)	1.395(6)	C(3)–C(11)	1.421(5)
C(4)–C(5)	1.422(6)	C(5)–C(6)	1.429(5)
C(6)–C(7)	1.429(5)	C(6)–C(11)	1.424(5)
C(7)–C(8)	1.349(5)	C(8)–C(9)	1.413(6)
C(9)–C(10)	1.368(6)	C(10)–C(11)	1.411(5)
C(12)–C(13)	1.400(6)	C(12)–C(20)	1.431(5)
C(13)–C(14)	1.408(6)	C(14)–C(15)	1.418(5)
C(15)–C(16)	1.428(5)	C(15)–C(20)	1.433(5)
C(16)–C(17)	1.349(7)	C(17)–C(18)	1.392(7)
C(18)–C(19)	1.363(70	C(19)–C(20)	1.417(6)
C(1)–Ti(1)–C(2)	84.7(2)	C(1)–Ti(1)–Cnt(1)	105.036
C(2)–Ti(1)–Cnt(1)	103.302	C(1)–Ti(1)–Cnt(2)	104.780
C(2)–Ti(1)–Cnt(2)	102.860	Cnt(1)–Ti(1)–Cnt(2)	141.712
Ti(1)–C(1)–O(1)	175.7(4)	Ti(1)–C(2)–O(2)	179.5(3)
C(4)–C(3)–C(11)	109.1(4)	C(3)–C(4)–C(5)	108.3(4)
C(4)–C(5)–C(6)	107.3(4)	C(5)–C(6)–C(7)	132.9(4)
C(5)–C(6)–C(11)	108.0(4)	C(7)–C(6)–C(11)	119.1(3)
C(6)–C(7)–C(8)	118.7(4)	C(7)–C(8)–C(9)	122.2(4)
C(8)–C(9)–C(10)	120.9(4)	C(9)–C(10)–C(11)	118.6(4)
C(3)–C(11)–C(6)	107.1(3)	C(3)–C(11)–C(10)	132.4(4)
C(6)–C(11)–C(10)	120.4(4)	C(13)–C(12)–C(20)	108.2(4)
C(12)–C(13)–C(14)	108.9(4)	C(13)–C(14)–C(15)	107.9(4)
C(14)–C(15)–C(16)	132.4(4)	C(14)–C(15)–C(20)	108.0(3)
C(16)–C(15)–C(20)	119.5(4)	C(15)–C(16)–C(17)	118.5(5)
C(16)–C(17)–C(18)	122.0(5)	C(17)–C(18)–C(19)	122.2(5)
C(18)–C(19)–C(20)	118.3(5)	C(12)–C(20)–C(15)	106.8(3)
C(12)–C(20)–C(19)	113.5(4)	C(15)–C(20)–C(19)	119.5(4)

TABLE 3B

BOND DISTANCES (Å) AND ANGLES (°) FOR $(C_9H_7)_2Ti(CO)_2$ (MOLECULE B)

Ti(1)–C(1)	2.035(5)	Ti(1)–C(2)	2.032(5)
Ti(1)–C(3)	2.347(4)	Ti(1)–C(4)	2.333(5)
Ti(1)–C(5)	2.335(4)	Ti(1)–C(6)	2.424(4)
Ti(1)–C(11)	2.442(4)	Ti(1)–C(12)	2.375(5)
Ti(1)–C(13)	2.313(5)	Ti(1)–C(14)	2.304(4)
Ti(1)–C(15)	2.400(4)	Ti(1)–C(20)	2.483(4)
Ti(1)–Cnt(3)	2.048	Ti(1)–Cnt(4)	2.051
Ti(1)–Ave(1)	2.38(5)	Ti(1)–Ave(2)	2.38(7)
C(1)–O(1)	1.151(5)	C(2)–O(2)	1.143(5)
C(3)–C(4)	1.408(7)	C(3)–C(11)	1.421(6)
C(4)–C(5)	1.410(7)	C(5)–C(6)	1.424(6)
C(6)–C(7)	1.411(6)	C(6)–C(11)	1.427(5)
C(7)–C(8)	1.342(6)	C(8)–C(9)	1.406(6)
C(9)–C(10)	1.355(6)	C(10)–C(11)	1.417(6)
C(12)–C(13)	1.405(7)	C(12)–C(20)	1.409(7)
C(13)–C(14)	1.390(7)	C(14)–C(15)	1.422(6)
C(15)–C(16)	1.409(6)	C(15)–C(20)	1.430(6)
C(16)–C(17)	1.339(7)	C(17)–C(18)	1.393(8)
C(18)–C(19)	1.362(8)	C(19)–C(20)	1.424(7)
C(1)–Ti(1)–C(2)	86.3(2)	C(1)–Ti(1)–Cnt(3)	104.659
C(2)–Ti(1)–Cnt(3)	104.023	C(1)–Ti(1)–Cnt(4)	104.304
C(2)–Ti(1)–Cnt(4)	104.066	Cnt(3)–Ti(1)–Cnt(4)	140.518
Ti(1)–C(1)–O(1)	178.5(4)	Ti(1)–C(2)–O(2)	176.9(4)
C(4)–C(3)–C(11)	107.9(4)	C(3)–C(4)–C(5)	108.7(4)
C(4)–C(5)–C(6)	108.0(4)	C(5)–C(6)–C(7)	132.9(4)
C(5)–C(6)–C(11)	107.4(4)	C(7)–C(6)–C(11)	119.7(4)
C(6)–C(7)–C(8)	118.8(4)	C(7)–C(8)–C(9)	122.6(4)
C(8)–C(9)–C(10)	120.1(4)	C(9)–C(10)–C(11)	119.9(4)
C(3)–C(11)–C(6)	107.9(4)	C(3)–C(11)–C(10)	133.3(4)
C(6)–C(11)–C(10)	118.8(4)	C(13)–C(12)–C(20)	108.9(5)
C(12)–C(13)–C(14)	108.7(5)	C(13)–C(14)–C(15)	107.7(4)
C(14)–C(15)–C(16)	132.4(5)	C(14)–C(15)–C(20)	108.1(4)
C(16)–C(15)–C(20)	119.4(4)	C(15)–C(16)–C(17)	119.6(5)
C(16)–C(17)–C(18)	121.4(6)	C(17)–C(18)–C(19)	122.2(5)
C(18)–C(19)–C(20)	118.0(5)	C(12)–C(20)–C(15)	106.4(4)
C(12)–C(20)–C(19)	134.5(5)	C(25)–C(20)–C(19)	119.1(5)

the solution emerging was colorless. The solvent was removed under reduced pressure, leaving a dark green solid. The residue was taken up in hexane and added to another plug of 5% deactivated alumina in a fritted funnel. The green eluate upon hexane elution was collected as above, the solution was concentrated and cooled at −20 °C to give dark green crystals. A second crop was collected by decanting, further concentration and cooling. The combined crystal crops were dried to give 0.43 g (45%) of **5**. Found: C, 63.65; H, 3.56. $C_{20}H_{14}O_2Zr$ calc: C, 63.62; H, 3.74%.

X-ray data collection, solution and refinement of $(C_9H_7)_2Ti(CO)_2$ (4)

Crystals suitable for the X-ray study were grown from hexane and sealed under nitrogen in thin-walled glass capillaries. The final lattice parameters, determined from a least-squares refinement of the angular settings of 25 accurately centered

TABLE 4

ATOMIC POSITIONS IN FRACTIONAL COORDINATES AND THERMAL PARAMETERS FOR $(C_9H_7)_2Zr(CO)_2$

Atom	x/a	y/b	z/c	U_{eq}
Zr	0.61423(7)	0.30364(4)	0.42326(4)	0.035
C(1)	0.7853(8)	0.1761(5)	0.4180(4)	0.044
O(1)	0.8730(6)	0.1117(3)	0.4156(4)	0.060
C(2)	0.871(1)	0.3817(5)	0.4236(5)	0.052
O(2)	1.0005(7)	0.4257(4)	0.4237(4)	0.079
C(3)	0.412(1)	0.3653(5)	0.5392(4)	0.051
C(4)	0.594(1)	0.3872(5)	0.5632(5)	0.057
C(5)	0.689(1)	0.3053(5)	0.5811(4)	0.051
C(6)	0.5655(9)	0.2293(5)	0.5758(4)	0.044
C(7)	0.577(1)	0.1331(5)	0.5908(4)	0.054
C(8)	0.426(1)	0.0776(5)	0.5793(4)	0.058
C(9)	0.260(1)	0.1150(5)	0.5496(5)	0.060
C(10)	0.2425(9)	0.2069(6)	0.5336(4)	0.058
C(11)	0.3896(8)	0.2667(4)	0.5471(4)	0.040
C(12)	0.4002(9)	0.3685(5)	0.3144(4)	0.049
C(13)	0.578(1)	0.3990(5)	0.2906(5)	0.061
C(14)	0.682(1)	0.3210(6)	0.2645(4)	0.057
C(15)	0.5656(9)	0.2416(5)	0.2665(4)	0.044
C(16)	0.586(1)	0.1462(5)	0.2413(5)	0.058
C(17)	0.447(1)	0.0880(6)	0.2523(5)	0.071
C(18)	0.277(1)	0.1168(6)	0.2882(5)	0.068
C(19)	0.2490(9)	0.2060(6)	0.3108(4)	0.056
C(20)	0.3907(8)	0.2715(5)	0.2990(4)	0.042

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0341(3)	0.0369(3)	0.0348(3)	−0.0030(3)	0.0008(2)	0.0014(3)
C(1)	0.038(3)	0.048(4)	0.045(4)	−0.014(3)	−0.002(3)	0.002(3)
O(1)	0.046(3)	0.042(3)	0.092(4)	0.006(2)	0.005(3)	0.003(3)
C(2)	0.055(4)	0.045(4)	0.056(4)	−0.001(3)	−0.003(3)	0.002(3)
O(2)	0.054(3)	0.081(4)	0.103(5)	−0.031(3)	0.001(3)	0.004(3)
C(3)	0.066(5)	0.043(4)	0.042(4)	0.010(3)	0.013(3)	0.002(3)
C(4)	0.078(5)	0.039(4)	0.054(4)	−0.015(4)	0.001(4)	−0.006(3)
C(5)	0.060(4)	0.057(4)	0.035(3)	−0.010(4)	−0.001(3)	−0.003(3)
C(6)	0.043(4)	0.048(4)	0.040(3)	0.003(3)	0.001(3)	−0.006(3)
C(7)	0.063(5)	0.063(5)	0.036(4)	0.006(4)	0.003(3)	0.014(3)
C(8)	0.088(6)	0.037(4)	0.047(7)	−0.008(4)	0.008(4)	0.008(3)
C(9)	0.070(5)	0.055(5)	0.056(5)	−0.016(4)	0.010(4)	0.003(4)
C(10)	0.047(4)	0.076(6)	0.051(4)	−0.003(4)	0.011(3)	0.013(4)
C(11)	0.043(3)	0.047(4)	0.031(3)	0.003(3)	0.008(3)	0.001(3)
C(12)	0.054(4)	0.049(4)	0.045(4)	0.008(3)	−0.007(3)	0.002(3)
C(13)	0.074(5)	0.051(5)	0.057(5)	−0.010(4)	−0.001(4)	0.015(4)
C(14)	0.049(4)	0.078(6)	0.043(4)	−0.008(4)	0.004(3)	0.012(4)
C(15)	0.049(4)	0.054(4)	0.030(3)	0.006(3)	0.006(3)	0.004(3)
C(16)	0.071(5)	0.060(5)	0.045(4)	0.006(4)	−0.007(3)	−0.010(4)
C(17)	0.120(8)	0.046(4)	0.047(4)	0.007(5)	−0.025(5)	−0.006(4)
C(18)	0.087(6)	0.069(6)	0.049(4)	−0.025(5)	−0.021(4)	0.002(4)
C(19)	0.050(4)	0.069(5)	0.048(4)	−0.012(4)	−0.005(3)	−0.002(4)
C(20)	0.043(3)	0.052(4)	0.032(3)	0.001(3)	−0.006(3)	0.003(3)

continued

TABLE 4 (continued)

Atom	x/a	y/b	z/c
H(1)	0.315(1)	0.4104(5)	0.5202(4)
H(2)	0.646(1)	0.4513(5)	0.5666(5)
H(3)	0.823(1)	0.3009(5)	0.5956(4)
H(4)	0.696(1)	0.1050(5)	0.6097(4)
H(5)	0.434(1)	0.0096(5)	0.5925(4)
H(6)	0.153(1)	0.0728(5)	0.5395(5)
H(7)	0.1230(9)	0.2323(6)	0.5122(4)
H(8)	0.2985(9)	0.4082(5)	0.3377(4)
H(9)	0.624(1)	0.4646(5)	0.2923(5)
H(10)	0.814(1)	0.3208(6)	0.2471(4)
H(11)	0.705(1)	0.1236(5)	0.2159(5)
H(12)	0.461(1)	0.0217(6)	0.2337(5)
H(13)	0.117(1)	0.0700(6)	0.2975(5)
H(14)	0.1285(9)	0.2258(6)	0.3363(4)

reflections, are given in Table 1. The diffracted intensities were collected on an Enraf–Nonius CAD-4 diffractometer in the usual manner [19].

One independent quadrant of data was measured out to $2\theta = 50°$. A total of 6119 reflections were measured with 3530 considered observed $[I > 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The full matrix least-squares refinement was carried out using the SHELX system [20]. The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [21] for Ti and scattering factors stored within the SHELX system were used for O, C, and H. The scattering for titanium was corrected for the real and imaginary components of anomalous dispersion with the table of Cromer and Liberman [22].

Since $Z = 16$ in the space group $C2/c$, it was necessary to locate two complete molecules. Efforts to locate the positions of the titanium atoms via Patterson techniques proved fruitless. Using the direct methods system MULTAN80 [23], we were able to locate the metal atoms and subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. The hydrogen atoms were placed at calculated positions 1.00 Å from the bonded carbon atom and allowed to ride on the bonded atom during the refinement process. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were given fixed U's of 0.08. Full-matrix least-squares refinement lead to final values of $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.052$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_0|)^2]^{1/2} = 0.049$.

X-ray data collection, solution and refinement of $(C_9H_7)_2Zr(CO)_2$ (5)

Crystal preparation, X-ray data collection and structure solution and refinement for the zirconium analog was done in a manner similar to that described above. Table 1 presents a summary of the pertinent crystal data. The final values of the positional and thermal parameters for the zirconium compound are given in Table 4. Table 5 summarizes the pertinent structural data for this compound.

TABLE 5

BOND DISTANCES (Å) AND ANGLES (°) FOR $(C_9H_7)_2Zr(CO)_2$

Zr–C(1)	2.221(7)	Zr–C(2)	2.186(7)
Zr–C(3)	2.467(6)	Zr–C(4)	2.457(7)
Zr–C(5)	2.473(6)	Zr–C(6)	2.587(7)
Zr–C(11)	2.554(6)	Zr–C(12)	2.466(6)
Zr–C(13)	2.463(7)	Zr–C(14)	2.485(6)
Zr–C(15)	2.581(6)	Zr–C(20)	2.547(6)
Zr–Cnt(1)	2.196	Zr–Cnt(2)	2.199
Zr–Ave(1)	2.51(5)	Zr–Ave(2)	2.51(5)
C(1)–O(1)	1.127(7)	C(2)–O(2)	1.133(8)
C(3)–C(4)	1.41(1)	C(3)–C(11)	1.434(9)
C(4)–C(5)	1.40(1)	C(5)–C(6)	1.421(9)
C(6)–C(7)	1.41(1)	C(6)–C(11)	1.459(9)
C(7)–C(8)	1.37(1)	C(8)–C(9)	1.40(1)
C(9)–C(10)	1.35(1)	C(10)–C(11)	1.390(9)
C(12)–C(13)	1.42(1)	C(12)–C(20)	1.417(9)
C(13)–C(14)	1.41(1)	C(14)–C(15)	1.42(1)
C(15)–C(16)	1.43(1)	C(15)–C(20)	1.433(9)
C(16)–C(17)	1.33(1)	C(17)–C(18)	1.42(1)
C(18)–C(19)	1.35(1)	C(19)–C(20)	1.410(9)
C(1)–Zr–C(2)	86.8(2)	X(1)–Zr–Cnt(1)	103.222
C(2)–Zr–Cnt(1)	102.208	C(1)–Zr–Cnt(2)	103.097
C(2)–Zr–Cnt(2)	101.913	Cnt(1)–Zr–Cnt(2)	144.994
Zr–C(1)–O(1)	179.6(4)	Zr–C(2)–O(2)	177.0(6)
C(4)–C(3)–C(11)	107.8(6)	C(3)–C(4)–C(5)	109.3(6)
C(4)–C(5)–C(6)	108.8(6)	C(5)–C(6)–C(7)	135.2(7)
C(5)–C(6)–C(11)	106.9(6)	C(7)–C(6)–C(11)	117.9(6)
C(6)–C(7)–C(8)	120.1(7)	C(7)–C(8)–C(9)	120.8(7)
C(8)–C(9)–C(10)	121.1(7)	C(9)–C(10)–C(11)	120.4(7)
C(3)–C(11)–C(6)	106.9(6)	C(3)–C(11)–C(10)	133.4(7)
C(6)–C(11)–C(10)	119.6(6)	C(13)–C(12)–C(20)	107.9(6)
C(12)–C(13)–C(14)	108.3(6)	C(13)–C(14)–C(15)	108.5(6)
C(14)–C(15)–C(16)	134.6(7)	C(14)–C(15)–C(20)	107.1(6)
C(16)–C(15)–C(20)	118.2(6)	C(15)–C(16)–C(17)	119.5(7)
C(16)–C(17)–C(18)	122.1(8)	C(17)–C(18)–C(19)	120.7(8)
C(18)–C(19)–C(20)	119.7(7)	C(12)–C(20)–C(15)	108.0(6)
C(12)–C(20)–C(19)	132.4(7)	C(15)–C(20)–C(19)	119.6(6)

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structural factors for both Ti and Zr compounds are available from J.L.A.

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