The Molecular Structure of 1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole and Its Hafnium Analogue

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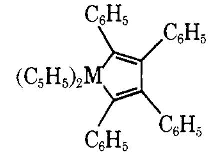
Abstract: The crystal structures of (η^5-C_5H_5)$_2$TiC_4(C_6H_5)$_4$ and its Hf analogue have been determined from three-dimensional x-ray data measured by counter methods. The compounds are isostructural and crystallize in the monoclinic space group $P2_1/n$. For 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole the cell dimensions are a = 13.758 (5) Å, b = 11.059 (5) Å, c = 18.492 (6) Å, and β = 93.76 (3)°. Full-matrix least-squares refinement led to a final R value of 0.039 based on 1790 independent observed reflections. For 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnole the cell dimensions are a = 13.822 (8) Å, b = 11.149 (8) Å, c = 18.694 (9) Å, and β = 93.18 (5)°. The refinement led to a final R value of 0.048 based on 1360 reflections. The configuration of each species is that of a metallocycle, rather than that of a metal-coordinated cyclobutadiene. Within each five-membered heterocyclic ring system, the π-electron framework is largely localized. For the titanium structure, the values of the two crystallographically independent Ti-C(σ) bond lengths are 2.172 (5) and 2.141 (5) Å, and the Ti-C(η^5) distances range from 2.338 (6) to 2.413 (6) Å. For the hafnium structure, the Hf-C(σ) bond lengths are 2.18 (2) and 2.22 (2) Å, while the Hf-C(η^5) lengths range from 2.45 (3) to 2.54 (3) Å. The contraction of the metal-carbon σ bond lengths is explained for titanium in terms of the energies of the orbitals involved in the bonds.

As part of a general study of the rich preparative chemistry of titanocene derivatives, a series of stable metallocycles has been encountered. Initially, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconole was prepared by the action of 1,4-dilithiotetraphenylbutadiene on an ethereal solution of bis(cyclopentadienyl)zirconium chloride.[2] Although several methods for the production of these substances have since been described,[3-6] the most facile synthetic route[7] involves the photolysis of dimethyl derivatives of titanocene, zirconocene, and hafnocene in the presence of diphenylacetylene:

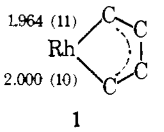
$$(C_5H_5)_2M(CH_3)_2 + 2C_6H_5C{\equiv}CC_6H_5 \xrightarrow[\text{pentane}]{h\nu}$$



M = Ti, Zr, Hf

The compounds were believed to be metallocycles, as shown above, rather than metal-coordinated cyclobutadienes because of the similarity of the electronic absorption spectra[4] to those of other metallocycles. This formulation has also been substantiated by the preparation of the titanium derivative from titanocene dichloride and the dilithium salt of 1,4-diphenylbutadiene.[6]

Several structural studies[8-12] have been carried out on metallocycles which contain two or more metal atoms, but the only previous reports of those containing one metal atom are the rhodacycles RhCl[Sb(C_6H_5)$_3$]$_2$$C_4$($CF_3$)$_4$·$CH_2Cl_2$ (**1**)[13] and RhCl(H_2O)[As(CH_3)$_3$]$_2$$C_4$($CF_3$)$_4$ (**2**).[14]



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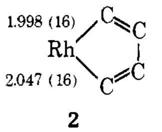

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In both of these structures an asymmetry in the two Rh-C σ bonds was noted. Although the disparity in the bond lengths is only marginally significant from a mathematical point of view, it was believed to be real, and calculations were carried out[15] with the hope of gaining insight into the origin of the effect. It was also shown that dπ-pπ bonding is important in the stability of the Rh-C bonds.[15]

In a previous study of the entire series of group 4b metal bis(indenyl)dimethyl derivatives,[16] a marked contraction of the metal-carbon (sp^3) σ bond length relative to the polyhapto values was noted. Thus the Ti-C(σ) distance[17] is found to be 2.20 (2) Å (compared to the Ti-C(η^5-) standard[18] of 2.36 Å)[19-21] while the Zr(σ) value is 2.255 (5) Å (vs. 2.50 Å[22-24] for Zr-C(η^5-)), and the Hf-C(σ) length is 2.329 (9) Å (vs. 2.48 Å[25-27] for Hf-C(η^5-)). Another interesting feature of the study is the fact that the Hf-C(σ) bond is significantly longer than the Zr-C(σ) bond, even though the opposite is true for the pentahapto linkage.

To further define the symmetry of the five-membered metallocyclic ring, and to clarify the nature of the group 4b metal-carbon σ bond, we report here the crystal structures of (C_5H_5)$_2$MC_4(C_6H_5)$_4$, where M = Ti or Hf. In addition, we develop a full discussion of the meaning of the metal-carbon σ bond lengths among the first-row transition metals.

Experimental Section

Sample Preparations. The compounds were prepared by the literature method,[7] and recrystallized from a 1:1 mixture of pentane and dichloromethane. (η^5-C_5H_5)$_2$TiC_4(C_6H_5)$_4$ and its Zr and Hf analogues are air-sensitive in solution, but seem quite stable in the solid state. So far it has not been possible to obtain diffraction-quality crystals of (η^5-C_5H_5)$_2$ZrC_4(C_6H_5)$_4$.

X-Ray Data Collection and Structure Determination for (η^5-C_5H_5)$_2$TiC_4(C_6H_5)$_4$. Single crystals of the substances were sealed in thin-walled glass capillaries prior to x-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 14 reflections ($2\theta > 20°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. The space group was uniquely determined to be $P2_1/n$ [alternate setting of $P2_1/c$; C^5_{2h}; No. 14] from the systematic absences in $h0l$ for $h + l = 2n + 1$, and in $0k0$ for $k = 2n + 1$.

Data were taken on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω-2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20°

Table I. Crystal Data

Compound	$(C_5H_5)_2TiC_4(C_6H_5)_4$	$(C_5H_5)_2HfC_4(C_6H_5)_4$
Mol wt	534.6	665.2
Linear abs coeff u̇, cm^{-1}	3.47	38.55
Calcd density, cm^{-3}	1.26 g	1.54g
Max crystal dimensions, mm	0.35 × 0.28 × 0.25	0.38 × 0.25 × 0.05
Space group	$P2_1/n$	$P2_1/n$
Molecules/unit cell	4	4
Cell constants,[a] *a*, Å	13.758 (5)	13.822 (8)
b, Å	11.059 (5)	11.149 (8)
c, Å	18.492 (6)	18.694 (9)
β, deg	93.76 (3)	93.18 (5)
Cell vol, Å^3	2807.4	2876.4

[a] Mo Kα radiation, λ 0.71069 Å. Ambient temperature of 23°.

min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.2° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 1.00°$ and $B = 0.25°$. Aperture settings were determined in a like manner with $A = 4.0$ mm and $B = 0.87$ mm. Other diffractometer parameters and the method of estimation of the standard deviations have been described previously.[28] As a check on the stability of the instrument and the crystal, three reflections, the $(0\bar{1}\bar{4})$, $(3\bar{1}\bar{1})$, and (230), were measured after every 25 reflections; the standards fluctuated within a range of ±3%.

One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 1790 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. Based on these considerations, the data set of 1790 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 3.47$ cm^{-1}).

Full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[29] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Ti and C were taken from Cromer and Waber;[30] those for H were from "International Tables for X-Ray Crystallography".[31]

The existence of four molecules per unit cell in the space group $P2_1/n$ imposed no crystallographic symmetry on the molecule. The position of the titanium atom was revealed by the inspection of a Patterson map, and the subsequent calculation of Fourier maps allowed the location (after four maps) of all 38 carbon atoms. Isotropic least-squares refinement led to a discrepancy factor of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.095$. Anisotropic refinement produced an $R_1 = 0.071$. The hydrogen atoms of the cyclopentadienyl rings and phenyl groups were then placed at calculated positions 0.98 Å from the bonded carbon atoms, and anisotropic refinement of the nonhydrogen atoms was resumed. The final R values were $R_1 = 0.039$ and $R_2 = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{1/2} = 0.041$. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.4 e/Å^3. The standard deviation of an observation of unit weight was 1.44. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Tables II and III.[32]

Data Collection and Structure Refinement for $(\eta^5\text{-}C_5H_5)_2HfC_4(C_6H_5)_4$. Difficulty was encountered in finding good quality crystals of the compound, and the data were therefore of poorer quality than for the titanium analogue. Following the data collection procedures given above, 1360 unique observed reflections in the range $2\theta < 50°$ were obtained and corrected for absorption effects[29] (the transmission factors varied from 0.55 to 0.82).

Table II. Final Fractional Coordinates for 1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole

Atom	*x/a*	*y/b*	*z/c*
Ti	0.54062 (7)	0.22672 (9)	0.27333 (5)
C1	0.5552 (3)	0.2208 (4)	0.1572 (2)
C2	0.4658 (3)	0.2228 (4)	0.1200 (2)
C3	0.3768 (3)	0.2166 (4)	0.1622 (2)
C4	0.3899 (3)	0.2234 (4)	0.2362 (2)
C5	0.5695 (5)	0.4338 (5)	0.2415 (3)
C6	0.5009 (4)	0.4327 (5)	0.2945 (3)
C7	0.5477 (5)	0.3862 (5)	0.3587 (3)
C8	0.6448 (5)	0.3583 (5)	0.3453 (3)
C9	0.6587 (4)	0.3874 (5)	0.2730 (4)
C10	0.6500 (4)	0.0752 (5)	0.3131 (3)
C11	0.5949 (5)	0.1009 (6)	0.3730 (3)
C12	0.4990 (5)	0.0680 (6)	0.3553 (4)
C13	0.4919 (5)	0.0193 (5)	0.2846 (4)
C14	0.5872 (4)	0.0220 (5)	0.2581 (3)
C15	0.6475 (3)	0.2433 (4)	0.1236 (2)
C16	0.7293 (4)	0.1703 (5)	0.1394 (3)
C17	0.8186 (4)	0.1962 (6)	0.1132 (4)
C18	0.8305 (4)	0.2965 (6)	0.0703 (3)
C19	0.7516 (4)	0.3694 (5)	0.0535 (3)
C20	0.6610 (4)	0.3440 (5)	0.0798 (3)
C21	0.4528 (3)	0.2338 (3)	0.0393 (2)
C22	0.3922 (4)	0.3215 (5)	0.0059 (3)
C23	0.3760 (4)	0.3269 (5)	−0.0687 (3)
C24	0.4193 (4)	0.2444 (6)	−0.1114 (3)
C25	0.4814 (4)	0.1568 (5)	−0.0805 (3)
C26	0.4985 (4)	0.1527 (4)	−0.0056 (4)
C27	0.2797 (4)	0.1927 (4)	0.1234 (3)
C28	0.1988 (4)	0.2643 (5)	0.1365 (3)
C29	0.1077 (4)	0.2380 (6)	0.1045 (3)
C30	0.0946 (4)	0.1394 (6)	0.0590 (3)
C31	0.1734 (4)	0.0689 (5)	0.0443 (3)
C32	0.2660 (4)	0.0954 (5)	0.0764 (3)
C33	0.3086 (4)	0.1999 (4)	0.2836 (3)
C34	0.2872 (4)	0.2799 (5)	0.3396 (3)
C35	0.2157 (4)	0.2538 (5)	0.3861 (3)
C36	0.1644 (4)	0.1465 (6)	0.3802 (3)
C37	0.1837 (4)	0.0649 (5)	0.3264 (3)
C38	0.2551 (4)	0.0920 (5)	0.2786 (3)
H1	0.558	0.462	0.191
H2	0.433	0.459	0.288
H3	0.518	0.375	0.405
H4	0.694	0.325	0.380
H5	0.719	0.377	0.248
H6	0.710	0.092	0.310
H7	0.620	0.136	0.419
H8	0.455	0.077	0.387
H9	0.433	−0.011	0.258
H10	0.606	−0.008	0.211
H11	0.723	0.099	0.170
H12	0.874	0.142	0.125
H13	0.894	0.315	0.052
H14	0.606	0.398	0.067
H15	0.759	0.441	0.023
H16	0.360	0.381	0.036
H17	0.333	0.390	−0.091
H18	0.407	0.247	−0.164
H19	0.513	0.098	−0.111
H20	0.544	0.092	0.016
H21	0.324	0.356	0.346
H22	0.201	0.312	0.424
H23	0.114	0.128	0.414
H24	−0.148	−0.011	0.322
H25	0.268	0.034	0.240
H26	0.207	0.334	0.169
H27	0.052	0.290	0.114
H28	0.030	0.120	0.037
H29	0.165	−0.000	0.011
H30	0.322	0.045	0.066

In view of the limited quality of the reflection data, four different refinement procedures were carried out. Completely isotropic refinement without hydrogen atom contribution gave R values of $R_1 = 0.065$ and $R_2 = 0.074$. Addition of anisotropic treatment of the hafnium atom gave $R_1 = 0.054$ and $R_2 = 0.063$. Completely

Table III. Anisotropic Thermal Parameters[a, b] for Nonhydrogen Atoms of 1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\langle U \rangle$[c]		
Ti	0.00367 (6)	0.00658 (9)	0.00221 (3)	0.00023 (7)	−0.00045 (3)	−0.00020 (5)	0.169	0.199	0.216
C1	0.0040 (3)	0.0052 (4)	0.0026 (2)	0.0006 (4)	0.0003 (2)	0.0001 (3)	0.172	0.202	0.214
C2	0.0039 (3)	0.0051 (4)	0.0021 (2)	0.0012 (3)	−0.0003 (2)	0.0001 (2)	0.155	0.190	0.216
C3	0.0036 (3)	0.0054 (5)	0.0022 (2)	0.0008 (3)	−0.0004 (2)	−0.0003 (3)	0.166	0.181	0.218
C4	0.0046 (3)	0.0055 (4)	0.0021 (2)	0.0001 (4)	0.0000 (2)	−0.0005 (2)	0.171	0.199	0.213
C5	0.0068 (4)	0.0058 (5)	0.0038 (2)	−0.0005 (4)	0.0001 (3)	−0.0005 (3)	0.186	0.252	0.261
C6	0.0057 (4)	0.0078 (6)	0.0031 (2)	0.0005 (4)	−0.0004 (2)	−0.0014 (3)	0.189	0.223	0.267
C7	0.0070 (5)	0.0105 (7)	0.0027 (2)	−0.0006 (5)	−0.0009 (3)	−0.0012 (3)	0.181	0.266	0.277
C8	0.0068 (5)	0.0084 (7)	0.0041 (3)	−0.0000 (5)	−0.0019 (3)	−0.0015 (4)	0.184	0.236	0.319
C9	0.0061 (5)	0.0081 (7)	0.0047 (3)	−0.0020 (5)	0.0004 (3)	−0.0020 (4)	0.182	0.254	0.305
C10	0.0059 (4)	0.0090 (6)	0.0033 (2)	0.0010 (4)	−0.0012 (3)	0.0004 (3)	0.190	0.242	0.278
C11	0.0088 (5)	0.0123 (8)	0.0030 (2)	0.0017 (5)	−0.0007 (3)	0.0008 (3)	0.208	0.274	0.308
C12	0.0086 (5)	0.0104 (8)	0.0038 (3)	0.0015 (6)	0.0008 (3)	0.0027 (4)	0.191	0.272	0.316
C13	0.0066 (5)	0.0070 (6)	0.0046 (3)	0.0002 (5)	0.0003 (3)	0.0013 (3)	0.198	0.252	0.290
C14	0.0066 (5)	0.0071 (6)	0.0035 (2)	0.0014 (5)	−0.0009 (3)	−0.0001 (3)	0.194	0.226	0.285
C15	0.0032 (3)	0.0066 (5)	0.0024 (2)	0.0001 (3)	0.0000 (2)	−0.0005 (2)	0.174	0.191	0.215
C16	0.0049 (4)	0.0085 (6)	0.0036 (2)	0.0010 (4)	0.0001 (2)	0.0008 (3)	0.199	0.235	0.258
C17	0.0045 (4)	0.0130 (8)	0.0049 (3)	0.0022 (5)	0.0007 (3)	−0.0000 (4)	0.190	0.291	0.296
C18	0.0042 (4)	0.0144 (9)	0.0042 (4)	0.0001 (5)	0.0006 (2)	0.0001 (4)	0.197	0.270	0.299
C19	0.0039 (3)	0.0100 (4)	0.0032 (2)	−0.0006 (4)	−0.0000 (2)	−0.0001 (3)	0.190	0.234	0.251
C20	0.0040 (4)	0.0085 (7)	0.0031 (2)	−0.0006 (4)	−0.0000 (2)	−0.0003 (3)	0.190	0.229	0.239
C21	0.0036 (3)	0.0063 (5)	0.0022 (2)	−0.0011 (3)	−0.0001 (2)	−0.0002 (2)	0.164	0.202	0.214
C22	0.0043 (3)	0.0066 (5)	0.0030 (2)	−0.0001 (3)	−0.0007 (2)	0.0006 (3)	0.182	0.202	0.247
C23	0.0064 (4)	0.0086 (6)	0.0026 (2)	−0.0001 (4)	−0.0006 (2)	0.0013 (3)	0.182	0.237	0.267
C24	0.0063 (4)	0.0126 (8)	0.0025 (2)	−0.0006 (5)	−0.0003 (2)	0.0005 (3)	0.201	0.246	0.284
C25	0.0065 (4)	0.0102 (7)	0.0023 (2)	0.0002 (4)	0.0003 (2)	−0.0006 (3)	0.196	0.248	0.256
C26	0.0052 (3)	0.0062 (5)	0.0023 (2)	−0.0010 (4)	0.0004 (2)	−0.0005 (2)	0.180	0.202	0.234
C27	0.0040 (3)	0.0066 (5)	0.0023 (2)	−0.0012 (3)	−0.0003 (2)	0.0004 (2)	0.173	0.192	0.232
C28	0.0042 (4)	0.0093 (6)	0.0034 (2)	0.0008 (5)	−0.0002 (2)	−0.0007 (2)	0.194	0.236	0.263
C29	0.0034 (4)	0.0153 (6)	0.0049 (2)	0.0005 (6)	−0.0008 (2)	−0.0008 (3)	0.171	0.267	0.313
C30	0.0051 (4)	0.0141 (8)	0.0033 (2)	−0.0013 (5)	−0.0011 (2)	0.0001 (3)	0.185	0.263	0.301
C31	0.0063 (4)	0.0092 (6)	0.0026 (2)	−0.0019 (4)	−0.0001 (2)	−0.0004 (3)	0.199	0.224	0.271
C32	0.0045 (3)	0.0079 (6)	0.0026 (2)	−0.0011 (4)	−0.0001 (2)	−0.0001 (3)	0.190	0.215	0.236
C33	0.0043 (3)	0.0064 (5)	0.0028 (2)	−0.0003 (3)	−0.0002 (2)	0.0002 (2)	0.196	0.200	0.229
C34	0.0051 (3)	0.0087 (5)	0.0030 (2)	−0.0005 (4)	0.0004 (2)	−0.0005 (3)	0.215	0.220	0.243
C35	0.0062 (4)	0.0103 (7)	0.0035 (2)	−0.0007 (4)	0.0017 (2)	−0.0003 (3)	0.200	0.249	0.281
C36	0.0048 (4)	0.0112 (7)	0.0037 (2)	−0.0008 (4)	0.0007 (2)	0.0002 (3)	0.205	0.255	0.267
C37	0.0056 (4)	0.0099 (7)	0.0028 (2)	−0.0012 (4)	0.0006 (2)	−0.0004 (3)	0.212	0.222	0.262
C38	0.0047 (4)	0.0086 (6)	0.0028 (2)	−0.0004 (4)	−0.0000 (2)	−0.0004 (3)	0.204	0.224	0.235

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters of 5.0 Å^2 were assumed for all hydrogen atoms. [c] These values are the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major) of its vibration ellipsoid.

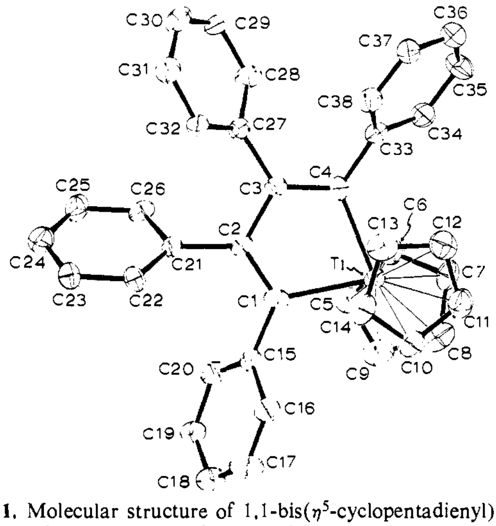


Figure 1. Molecular structure of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole and its hafnium analogue.

anisotropic least squares yielded R_1 = 0.048 and R_2 = 0.056. However, this introduced 352 total variable parameters; it is believed that the best procedure consisted of anisotropic refinement of the hafnium atom, isotropic refinement of the carbon atoms, and a geometry-fixed contribution from the hydrogen atoms (isotropic B's set at 5.0 Å^2). This led to discrepancy indices of R_1 = 0.048 and R_2 = 0.057 and corresponds to the parameters shown in Table IV. The largest parameter shifts in the final cycle were less than 0.03 of their estimated standard deviations. The standard deviation of an observation of unit weight was 1.53.

Description of the Structures

An examination of the crystal data given in Table I affords the observation that $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$ and its hafnium analogue are isostructural. The molecular structure of the titanium derivative and atom numbering scheme are shown in Figure 1, while the important bond distances and angles are listed in Table V. The configuration is clearly that of a metallocycle, rather than that of a metal-coordinated cyclobutadiene.

The two cyclopentadienyl rings exhibit the staggered configuration commonly found for $(C_5H_5)_2MX_2$ compounds[33] with the exception of those for which the rings are bridged together.[21,24,26] The Ti-C(η^5) bond lengths, which range from 2.338 (6) to 2.413 (6) Å, are quite similar to those found in other well-determed structures.[19-21] The distances from the titanium atom to the ring centers are 2.06 and 2.07 Å; these values may be compared with 2.08 Å in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$,[20] 2.06 Å in $(CH_2)_3\text{-}(C_5H_4)_2TiCl_2$,[21] and 2.06 Å in $(C_5H_5)_2TiCl_2$.[34] The titanium-ring center distance is, in fact, nearly constant for titanium(IV) structures but is significantly shorter (2.02 Å) in the only reported titanium(II) structure, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$.[35]

Although the Hf-C(η^5-) bond lengths are known with less precision than for the Ti case, their range, 2.45 (3) →

Table IV. Final Fractional Coordinates and Thermal Parameters for 1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnole

Atom	x/a	y/b	z/c	B
Hf	0.53840 (8)	0.22483 (8)	0.27292 (6)	a
C1	0.5508 (15)	0.2204 (18)	0.1551 (11)	4.0 (4)
C2	0.4618 (15)	0.2222 (18)	0.1157 (10)	3.8 (4)
C3	0.3751 (15)	0.2140 (18)	0.1609 (11)	3.7 (5)
C4	0.3863 (14)	0.2191 (18)	0.2334 (11)	3.7 (4)
C5	0.5736 (22)	0.4396 (23)	0.2412 (16)	6.8 (7)
C6	0.5068 (19)	0.4408 (20)	0.2939 (14)	5.2 (6)
C7	0.5507 (18)	0.3899 (18)	0.3585 (13)	4.7 (5)
C8	0.6468 (21)	0.3651 (22)	0.3440 (16)	6.7 (7)
C9	0.6623 (18)	0.3902 (20)	0.2759 (13)	5.6 (6)
C10	0.6430 (20)	0.0602 (22)	0.3175 (16)	6.7 (7)
C11	0.5878 (23)	0.0909 (24)	0.3754 (16)	7.8 (8)
C12	0.4996 (20)	0.0543 (21)	0.3543 (14)	5.8 (6)
C13	0.4906 (23)	0.0063 (24)	0.2860 (16)	7.0 (7)
C14	0.5862 (19)	0.0089 (20)	0.2644 (13)	4.7 (5)
C15	0.6436 (15)	0.2427 (18)	0.1186 (11)	4.0 (5)
C16	0.7238 (18)	0.1680 (19)	0.1364 (13)	5.0 (5)
C17	0.8133 (19)	0.1926 (21)	0.1083 (14)	6.0 (6)
C18	0.8274 (18)	0.2910 (22)	0.0685 (13)	6.0 (6)
C19	0.7506 (18)	0.3646 (19)	0.0481 (13)	5.0 (5)
C20	0.6592 (16)	0.3406 (18)	0.0753 (12)	4.2 (5)
C21	0.4476 (13)	0.2354 (16)	0.0368 (10)	3.0 (4)
C22	0.3884 (15)	0.3246 (17)	0.0091 (12)	3.6 (5)
C23	0.3743 (17)	0.3297 (19)	−0.0658 (14)	5.0 (5)
C24	0.4149 (16)	0.2525 (19)	−0.1093 (12)	5.0 (5)
C25	0.4748 (16)	0.1590 (19)	−0.0801 (13)	4.5 (5)
C26	0.4935 (15)	0.1532 (17)	−0.0061 (12)	3.6 (5)
C27	0.2786 (14)	0.1902 (15)	0.1226 (10)	3.2 (4)
C28	0.1999 (16)	0.2654 (20)	0.1351 (12)	5.1 (5)
C29	0.1062 (17)	0.2368 (21)	0.1004 (12)	5.7 (6)
C30	0.0970 (18)	0.1371 (21)	0.0583 (13)	5.6 (6)
C31	0.1735 (18)	0.0629 (19)	0.0448 (13)	5.0 (5)
C32	0.2665 (15)	0.0924 (16)	0.0773 (11)	3.4 (4)
C33	0.3016 (14)	0.1996 (16)	0.2804 (11)	3.5 (4)
C34	0.2798 (16)	0.2766 (20)	0.3357 (12)	4.7 (5)
C35	0.2062 (18)	0.2505 (20)	0.3821 (12)	5.5 (6)
C36	0.1575 (18)	0.1445 (20)	0.3748 (13)	5.2 (6)
C37	0.1778 (17)	0.0632 (19)	0.3236 (13)	4.5 (5)
C38	0.2483 (19)	0.0892 (20)	0.2748 (13)	5.4 (6)

[a] The hafnium atom was refined with anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$: $\beta_{11} = 0.0038$ (1), $\beta_{22} = 0.0086$ (1), $\beta_{33} = 0.0029$ (1), $\beta_{12} = 0.0000$ (1), $\beta_{13} = -0.0001$ (1), $\beta_{23} = -0.0002$ (1).

Table V. Comparison of Structural Parameters for 1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole and Its Hafnium Analogue

Bond	Bond Length (Å) Titanium	Hafnium
M–C1	2.172 (5)	2.22 (2)
M–C4	2.141 (5)	2.18 (2)
M–C5	2.404 (6)	2.52 (3)
M–C6	2.380 (6)	2.48 (2)
M–C7	2.364 (6)	2.44 (2)
M–C8	2.384 (5)	2.49 (3)
M–C9	2.408 (6)	2.51 (2)
M–C10	2.338 (6)	2.45 (3)
M–C11	2.389 (6)	2.49 (3)
M–C12	2.413 (6)	2.51 (2)
M–C13	2.402 (6)	2.54 (3)
M–C14	2.374 (6)	2.50 (2)
M–C (cyclopentadienyl) av	2.386 (22)	2.49 (3)
C1–C2	1.369 (6)	1.39 (3)
C2–C3	1.495 (6)	1.51 (3)
C3–C4	1.370 (6)	1.36 (2)
	Bond Angle (deg)	
C1–M–C4	80.3 (2)	78.7 (8)
M–C1–C2	111.0 (3)	114.1 (8)
M–C4–C3	112.5 (3)	113.1 (8)
C1–C2–C3	118.5 (4)	114 (2)
C2–C3–C4	117.4 (4)	120 (2)
Cent.–M–Cent.	134.8 (3)	134 (1)
Cent.–M–C1	104.1 (3)	103 (1)
Cent.–M–C4	111.0 (3)	113 (1)
Cent. –M–C1	109.6 (3)	111 (1)
Cent. –M–C4	103.7 (3)	103 (1)

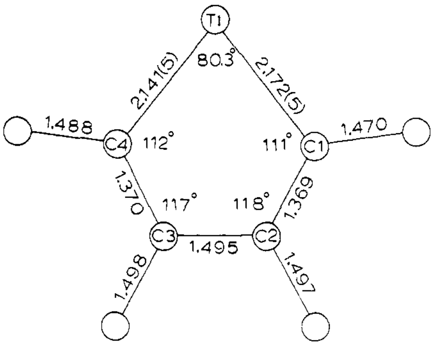


Figure 2. Geometry of the five-membered heterocyclic ring system in $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$.

2.54 (3) Å, and average,[36] 2.49(3) Å, fall easily within the boundaries of previously reported structures.[25-27] The distances of the hafnium atom to the ring centers are 2.19 and 2.22 Å; the only comparison yet available is the 2.18 Å value given for $(CH_2)_3(C_5H_4)_2HfCl_2$.[26]

The centroid-metal-centroid angles present an interesting comparison between the $(\eta^5\text{-}C_5H_5)_2MC_4(C_6H_5)_4$ structures. In the three group 4b series for which data are currently available, $(CH_2)_3(C_5H_4)_2MCl_2$, $(C_5H_5)_2MCl_2$, and $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$, the prescribed angles are approximately 3° larger for M = titanium than for hafnium. However, these angles in the present study are almost exactly equal (134.5°). In fact, scrutiny of Table V reveals that all angles involving the C_5H_5 ring centroids are remarkably similar. This may be a manifestation of the abnormally short Hf-C(σ) bonds (which could conceivably force open the centroid-hafnium-centroid angle).

The metal-carbon σ bond lengths are particularly noteworthy. For titanium, the values of 2.172 (5) and 2.141 (5) Å (Figure 2) represent the first accurate determination of the Ti-C(sp^2) bond distance.[37] In $(\eta^5\text{-}C_9H_7)_2Ti(CH_3)_2$, the Ti-C($sp^3$) length of 2.20 Å agrees well with the present study after a correction of 0.03 Å because of the change of carbon atom hybridization.[38] In both determinations the lengths are quite significantly shorter than for the σ-bonded cyclopentadienyl ligand in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$, 2.324 (6) Å.[20] For the hafnium analogue, the comparison is not so clear-cut. The Hf-C(sp^3) bond length was determined as 2.329 (9) Å in $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$,[16] surprisingly close to the 2.34 Å value given for the Hf-C σ bonds in $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$. However, the Hf-C($sp^2$) bond lengths presented in this study, 2.22 (2) and 2.18 (2) Å, are significantly shorter than might be expected from a simple change in hybridization for the carbon atom. The radius[39] of Hf^{4+} is 0.07 Å larger than that of Ti^{4+}. If one accepts the Ti-C(sp^2) average[40] bond length of 2.156 (22) Å as the standard, then a Hf-C(sp^3) length of ~2.23 Å would be expected. This is quite close to the 2.20 (3) Å average from the present study. It would thus appear that the Hf-C(sp^3) length (2.329 (9) Å) is anomalously long.

The five-membered heterocyclic ring systems show two principal features (Figure 2). Within each molecule a difference (Δ) between the metal-carbon bond lengths is noted, just as reported by Mague[13,14] for the rhodacycles. The discrepancies are again of marginal mathematical significance[41] for the hafnium compound (Δ = 0.040 (28) Å = 1.4σ) but are quite likely real for the titanium compound (Δ

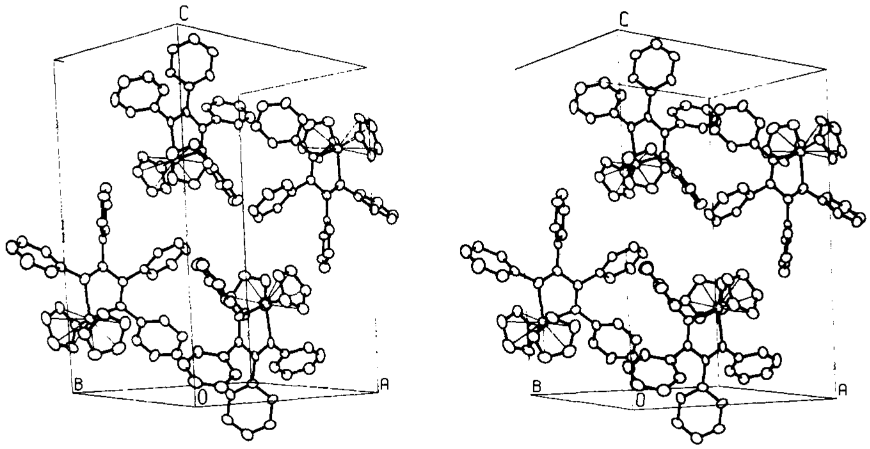


Figure 3. Stereoscopic view of the crystal packing of four molecules of $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$.

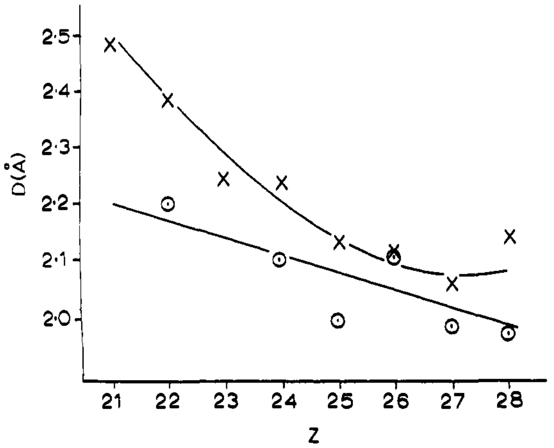


Figure 4. Representative metal-carbon bond distances for first-row transition metal complexes: X = M-C(cyclopentadienyl) and O = M-C (σ) bond lengths.

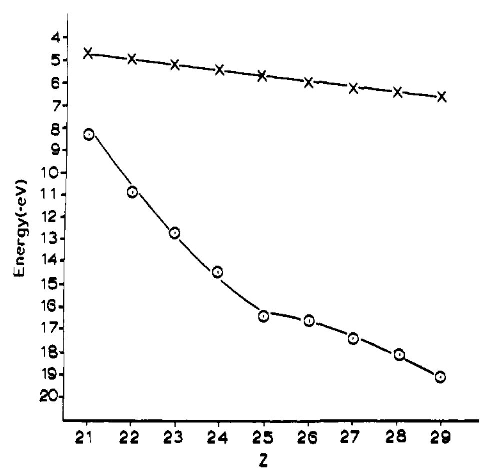
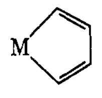


Figure 5. Orbital energies for first-row transition metals. The slope of the 4p orbital energy curve is quite similar to that of the 4s levels (see ref 53). X = 4s orbital energy; O = 3d orbital energy.

= 0.031 (7) Å = 4.4σ). In both structures the π-electron framework is largely localized between C1-C2 and C3-C4.



For titanium the "double" bond lengths average 1.370 (6) Å (compared to the C=C standard of 1.334 Å[42]), and the "single" bond length is 1.495 (6) Å (compared to the 1.54 Å standard[43] for alkanes). Additionally, the five-membered ring is planar to within 0.03 Å for Ti and 0.04 Å for Hf.[32]

Within the organic portion of the titanium structure the bond distances and angles seem particularly consistent. The range for the 24 independent C-C(phenyl) distances is only 1.368 → 1.408 Å (the average is 1.389 (10) Å), and the four rings are each planar to better than 0.01 Å. In compounds which contain cyclopentadienyl rings bound in a pentahapto fashion to the metal atom, it is not uncommon[19,33] to witness a large librational motion of the ring which has the effect of shortening the C-C (cyclopentadienyl) bond lengths below the expected 1.43 Å value.[44,45] In such cases a value of 1.39 Å may be expected;[19,33] it is thus possible to correlate librational motion to both the range and the average C-C(cyclopentadienyl) bond length. For $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$, the range is 1.387 → 1.428 Å, and the average, 1.410 (11) Å. The moderate thermal motion in this compound is also illustrated in the shapes of the thermal ellipsoids given in Figure 1.

The unit cell packing, shown in Figure 3, is typical of a molecular compound of this type.

Discussion

The principal feature of the $(\eta^5\text{-}C_5H_5)_2MC_4(C_6H_5)_4$ structures is the contracted metal-carbon σ bond length compared to the metal-carbon polyhapto distances. For titanium, the σ bond is 0.23 Å shorter, while for hafnium it is 0.29 Å shorter. This observation has also recently been made for several non-transition metal compounds,[46-48] but it is only with the first-row transition metals that a suitably large number of structures have been determined so that worthwhile comparisons can be made.

A compilation of first-row transition metal-carbon distances is presented in Table VI and in Figure 4. The dominant feature, brought out in Figure 4, is that the contraction of the metal-carbon σ bond lengths is most pronounced for the early transition metals. For iron, the many structural determinations of cyclopentadienyl complexes present Fe-C lengths largely falling between 2.04 Å, found in $Fe(C_5H_5)_2$,[49] and 2.12 Å, found in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$,[45] while the σ bond distances[50] range from 1.95 Å in $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$[10] to 2.12 Å in $(CO)_2FeC_5H_4CH_2Fe(CO)_4$.[51] Thus, for iron there is little difference between the typical Fe-C(η^5-) length and the Fe-C(σ) distance.

The major cause of the apparent metal-carbon σ bond length contraction may be seen with reference to Figure 5. The d-orbital energy is all-important in the formation of strong bonds to cyclopentadienyl ring systems, and, for the early transition metals, the d orbitals are too high in energy to be used as effectively as with the later transition metals.

Table VI. Metal–Carbon Bond Distances[a] in First-Row Transition Metal Complexes

	M–C (η^5-)			M–C (σ)		
Metal	Range	Value[a]	Ref	Range	Value[a]	Ref
Sc	2.44 → 2.52	2.48	28, *b*		—	
Ti	2.34 → 2.50	2.38	19–21	2.11 → 2.32	2.20	16
V	2.22 → 2.28	2.24	*c*		—	
Cr	2.20 → 2.26	2.23	*d, e*	2.01 → 2.20	2.10	*f*
Mn	2.12 → 2.18	2.13	*g*	1.99	1.99	*h*
Fe	2.04 → 2.13	2.11	*i*	1.94 → 2.13	2.10	*i*
Co	2.02 → 2.10	2.05	*j*	1.98	1.98	*k*
Ni	2.06 → 2.20	2.13	*l*	1.85 → 1.98	1.96	*m*

[a] Where many determinations have been carried out, the *value* given is that of a typical well-determined structure or the average of several well-determined structures for which the reference(s) are given. [b] J. L. Atwood and K. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2487 (1973). [c] F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Am. Chem. Soc.*, 95, 951 (1973). [d] M. H. Bush, G. A. Sim, G. R. Knox, M. Ahmad, and C. G. Robertson, *J. Chem. Soc. D*, 74 (1969). [e] O. L. Carter, A. T. McPhail, and G. A. Sim, *Chem. Commun.*, 49 (1966). [f] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *J. Chem. Soc. D*, 243 (1971). [g] R. M. Kirchner, T. J. Marks, J. S. Kristoff, and J. A. Ibers, *J. Am. Chem. Soc.*, 95, 6602 (1973). [h] S. Z. Goldberg, E. N. Enesler, and K. N. Raymond, *J. Chem. Soc. D*, 826 (1971). [i] M. R. Churchill and S. W. Y. N. Chang, *J. Am. Chem. Soc.*, 95, 5931 (1973). [j] M. D. Rausch, I. Bernal, B. R. Davis, A. Siegel, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, 3, 149 (1973). [k] W. W. Adams and P. G. Lenhert, *Acta Crystallogr., Sect. B*, 29, 2412 (1973). [l] M. R. Churchill, B. G. DeBoer, and J. J. Hackbarth, *Inorg. Chem.*, 13, 2098 (1974). [m] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 713 (1963).

On the other hand, pure σ bonding relies largely on the s and p orbitals, for which the energy slope through the first-row transition metals is not so steep.[52,53] Thus, the apparent contraction of metal-carbon σ bond lengths among the early transition metals may equally well be viewed as a polyhapto bond elongation.

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Supplementary Material Available: a listing of structure factor amplitudes, complete least-squares plane results, and additional bond length and angle data for both structures (18 pages). Ordering information is given on any current masthead page.

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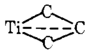
(37) In the structure of $[\eta^5\text{-}CH_3C_5H_4)_2Ti]_2C_4(C_6H_5)_2$, the Ti–C($sp^2$) distances are 2.083 (2) and 2.153 (2) Å, but the bonding picture is clouded by the presence of a third carbon atom at 2.325 (2) Å:



D. G. Sekutowski and G. D. Stucky, personal communication.

(38) See, for example, M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).

(39) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Wiley-Interscience, New York, N.Y., 1966, pp 749, 913.

(40) The standard deviation of the mean of two values is calculated by $\sigma(\text{AV}) = (\text{difference})/2^{1/2}$.

(41) The standard deviation of the difference is given as $\sigma(\text{difference}) = (\sigma_1^2 + \sigma_2^2)^{1/2}$.

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(50) In this discussion, no reference is made to bond distances involving the carbonyl ligand. It should also be noted that subtle changes in oxidation state, fluorination of the carbon atoms, and steric effects may influence the metal–carbon bond lengths. However, these factors should not obscure the general trend referred to in this section.

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