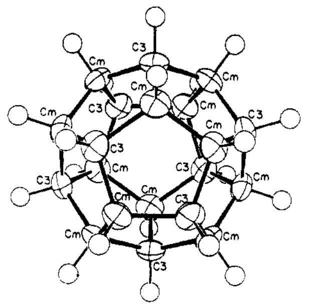
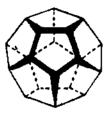
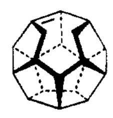


Figure 1. Carbon atoms are drawn at the 50% probability level and hydrogen atoms are drawn on an arbitrary scale. C(3) designates the atom on the threefold axis and C(m) is the atom on the mirror plane.

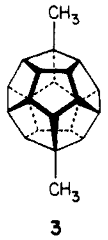
The diffraction pattern was interpreted in terms of a crystal composed of two twins distributed unequally. The unit cell is face-centered cubic with $m3$ Laue symmetry and the systematic absences restrict the space group possibilities to $F23$ or $Fm3$. At room temperature, the cell constant is a = 10.610 (3) Å with Z = 4 and ρ_{calcd} = 1.448 g/cm^3. This structure is therefore isomorphous with that earlier reported for disordered secododecahedrene **2**.[13] Noteworthily, the calculated density of **1** is higher than that of **3** (1.412 g/cm^3).[12]



1



2



3

The twinning was recognized as a result of collecting data in the triply primitive hexagonal cell representation.[14] The not uncommon mode of twinning is such that the h,k,l and k,h,l reflections are interchanged in position.[15] Exact superposition occurs when $l = 3n$, and no overlap occurs otherwise. The intensities were corrected for twinning by using the following relationships:[16]

$$I(hkl) = (1 - \alpha)J(hkl) + \alpha J(khl)$$

$$I(khl) = (1 - \alpha)J(khl) + \alpha J(hkl)$$

A comparison of the intensities of the nonoverlapping reflections resulted in a value for the twin fraction, α, of 0.246. So approximately 25% of the crystal used for data collection is in twin orientation. The standard deviations in the intensities were also corrected for twinning.[16b]

The structure was solved and successfully refined in the centrosymmetric space group $Fm3$. The final R value (on F) was 0.049 based on 118 intensities with $F_o^2 > 3\sigma F_o^2$. T_h symmetry is crystallographically imposed on the molecule, with the asymmetric unit containing two carbon atoms and two hydrogen atoms.[17] This result conforms to the prediction that gaseous dodecahedrane will have I_h symmetry since T_h is the subgroup of I_h with the highest possible crystallographically allowed symmetry.

The geometry of the molecule obtained here does not deviate significantly from I_h symmetry as can be seen in Figure 1. The framework bonds, at C(3)–C(m) = 1.541 (2) Å and C(m)–C(m) = 1.535 (5) Å, are somewhat shorter than the 1.546-Å value determined for cyclopentane.[18] The exterior C–C–C bond angles [C(m)–C(3)–C(m) = 108.1 (1)°; C(3)–C(m)–C(3) = 107.7 (2)°; C(3)–C(m)–C(m) = 107.9 (4)°] conform nicely to the value expected for perfect dodecahedral symmetry (108°).

Intracavity distances across the center of the molecule are 4.310 (3) Å for C(3)---C(3) and 4.317 (5) Å for C(m)---C(m). Taking account of the generally accepted number for the van der Waals radius of carbon,[19] the transcavity diameter is only 0.91–0.93 Å, too small for encapsulation of any but the smallest ions. Since the structure is face-centered cubic and the centers of the dodecahedrane molecules occupy the corners and the centers of the faces of the unit cell, the packing is cubic closest packing. The shortest intermolecular contacts are 3.98 Å for C---C and 2.33 Å for H---H.

Now that the three-dimensional structure of **1** has become known, the effect of substitution on dodecahedral distortion can now begin to be assessed. We hope to report on these matters at a later date.

Acknowledgment. We gratefully acknowledge the National Institutes of Health for their financial support via Grant AI-11490.

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[13] Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 251.

[14] The triply primitive hexagonal cell is related to the face-centered cubic cell like so: $a_{hexagonal} = 2^{1/2}/2(a_{cubic})$ and $c_{hexagonal} = 3^{1/2}(a_{cubic})$. In the obverse setting for the triply primitive hexagonal cell, the extinction condition is $-h+k+l = 3n$. In this case many reflections satisfying $h-k+l = 3n$ were also observed and were such that the ratios $I(hkl\text{: } h-k+l = 3n)/I(khl)$ were constant for $l \neq 3n$. An awareness of this phenomenon for several crystals along with other observations led to the deduction of the twinning problem. A full description of the structure and the twinning analysis will be forthcoming.

[15] This mode of twinning can be described in real space in the hexagonal system by either a rotation about the c axis or by reflection across the (100) plane. Other examples of this type of twinning have been reported by: Jameson, G. B.; Schneider, R.; Dubler, E.; Oswald, H. R. *Acta Crystallogr., Sect. B* **1982**, *B38*, 3016. Zalkin, A.; Forrester, J. D.; Templeton, D. H. *Acta Crystallogr.* **1964**, *17*, 1408.

[16] I is the observed intensity, J is the corrected intensity based on an untwinned crystal of the same total volume, and α is the twin fraction as defined in: (a) Britton, D. *Acta Crystallogr., Sect. A* **1972**, *A28*, 296. (b) Grainger, C. T. *Acta Crystallogr., Sect. A* **1969**, *A25*, 427.

[17] Prior to recognition of the twinning problem, the structure could be solved in $Fm3$ but could not be successfully refined to a reasonable R index in either $Fm3$ or $F23$. The final results after correction for twinning and expressed in the cubic unit cell: Mo Kα radiation, $2\theta_{max}$ = 55°, R_w = 0.051, weight = $1/\sigma^2(F_o)$, carbon atoms refined anisotropically, hydrogen atoms isotropically. One C–H unit lies on a threefold axis and the other C–H unit lies on a mirror plane: C(3)$x = y = z$ = 0.1173 (2), $U_{11} = U_{22} = U_{33}$ = 0.037 (1), $U_{12} = U_{13} = U_{23}$ = –0.009 (1), and C(m), x = 0, y = 0.1902 (2), z = 0.0723 (2), U_{11} = 0.045 (2), U_{22} = 0.023 (1), U_{33} = 0.043 (2), $U_{12} = U_{13}$ = 0, and U_{23} = –0.008 (1).

[18] Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013.

[19] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Highly Reduced Organometallics. 18.[1] Tetracarbonylcyclopentadienylmetalates(1–) of Titanium and Zirconium. Structural Characterization of $[(C_6H_5)_4As][C_5H_5Ti(CO)_4]$

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Anionic metal carbonyls are important materials in many areas of chemistry, particularly as reagents in chemical synthesis, and have been reported for all d-block transition elements except those of the group 3, 4, and 11 triads.[2] Our recent development of a facile, atmospheric pressure synthesis of the hexacarbonylmetalates(1–) of niobium and tantalum[3] prompted attempts to prepare carbonyl anions of titanium, zirconium, and hafnium by this method. We now report on the synthesis, characterization, and some reactions of the anionic carbonyls of titanium and zirconium, $C_5H_5M(CO)_4^-$. These substances are the first cyclopentadienyl derivatives of the hypothetical heptacarbonyls, $M(CO)_7$, and are the most thermally stable zero-valent carbonyls now known for Ti and Zr.[4] The only previously reported com-

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[1] Part 17: Warnock, G. F. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5016.

[2] (a) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221. (b) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (c) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. (d) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

[3] Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics* **1983**, *2*, 388.

0002-7863/86/1508-1344$01.50/0

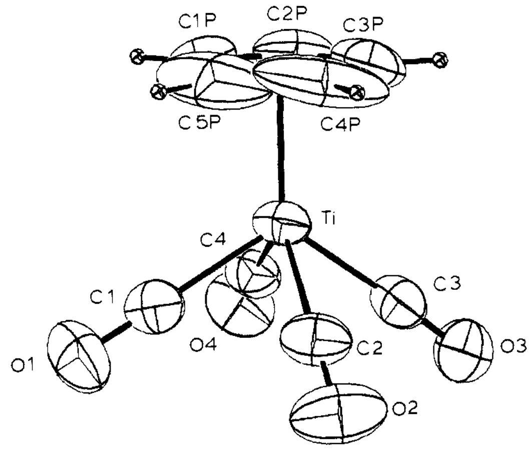

Figure 1. ORTEP drawing of $C_5H_5Ti(CO)_4^-$ showing the labeling scheme. Thermal ellipsoids are drawn with 50% probability boundaries.

pounds of this type are $Ti(CO)_6$, which is unstable above −200 °C,[5] $Ti(CO)_2(PF_3)(Me_2PC_2H_4PMe_2)_2$ (Me = CH_3),[6] $Ti(CO)_3(R_2PC_2H_4PR_2)_2$ (R = CH_3, C_2H_5),[7] and $Zr(C_4H_6)_2(Me_2PC_2H_4PMe_2)(CO)$, which survives for only *brief* periods at 25 °C under CO.[8]

Addition of cold (−65 to −70 °C) solutions of $C_5H_5MCl_3$ in tetrahydrofuran (THF) for Ti or 1,2-dimethoxyethane (DME) for Zr by cannula to cold (−78 °C) mechanically stirred slurries of sodium naphthalenide (4 equiv) in the same solvent under an argon atmosphere provided the presently uncharacterized and thermally unstable deep red brown (Ti) or bright purple (Zr) reactive intermediates, which function as *weakly solvated* monocyclopentadienylmetalates. Within 5–10 min after the addition of $C_5H_5MCl_3$, the argon was replaced by carbon monoxide, causing the solutions to change rapidly to bright red (Ti) or deep brown-red (Zr). The reaction mixtures were then slowly warmed to room temperature over a period of 12 h under a CO atmosphere with efficient stirring. After cation exchange and purification, dark red (Ti) or deep brown-red (Zr) air-sensitive crystals of the composition $[(C_2H_5)_4N][C_5H_5M(CO)_4]$ (M = Ti, **1**; Zr, **2**) were isolated in moderate (45–60% for **1**) or low yields (15–25% for **2**). Analogous pentamethylcyclopentadienide complexes have also been synthesized by the same procedure.[9] These compounds are quite thermally stable in solution and decompose as solids only above 175 °C. Analytical, IR, and ^1H and ^{13}C NMR spectral data are fully consistent with these formulations.[10] The X-ray structure of the anion (Figure 1) in $[(C_6H_5)_4As][C_5H_5Ti(CO)_4]$[11] is very similar to that found for $C_5H_5V(CO)_4$[12] and shows no surprising features. Selected mean interatomic distances are Ti–C(CO) (1.994 (6) Å), C–O (1.146 (6) Å), Ti–C(Cp) (2.356 (15) Å), and Ti–Cp centroid (2.049 (1) Å). The mean carbonyl C–Ti distance is shorter than that found in $(C_5H_5)_2Ti(CO)_2$ (2.03 (1) Å)[13] and very similar to that observed in $Ti(CO)_3(Me_2PC_2H_4PMe_2)_2$ (1.986 (4) Å),[7] while the C–O distances are within the range of usual values observed for mononuclear carbonyl monoanions. The Ti–carbonyl units are essentially linear, the mean Ti–C–O angle being 178 (3)°. Tetraphenylarsonium cations are well separated from the anions in the crystalline lattice and show no unusual features.[11]

Reactions of **1** and **2** with Ph_3SnCl and Ph_3PAuCl (Ph = C_6H_5) in CH_2Cl_2 at −78 °C have been examined. The only product isolated as a pure and thermally stable crystalline product at room temperature was purple $C_5H_5Ti(CO)_4AuPPh_3$ (**3**). Red-violet $C_5H_5Ti(CO)_4SnPh_3$ (**4**) decomposes in solution at room temperature, while the corresponding zirconium derivatives, $C_5H_5Zr(CO)_4E$, (E = $AuPPh_3$, **5**, deep green; E = $SnPh_3$, **6**, deep red) are much less stable and could only be handled below −40 °C in solution. On the basis of their carbonyl stretching frequencies and ^{13}C NMR chemical shifts,[14] these heterobimetallic compounds are formulated to contain metal–metal bonds and formally eight-coordinate titanium and zirconium.

Clearly, further studies on the chemistry of these novel anions will be desirable and should add new facets to the already rich organometallic chemistry of titanium and zirconium. Extensions of our low-temperature alkali metal–naphthalenide reduction method to other group 4 halides and halide complexes of other metals are also under way in this laboratory to assess its general utility in the synthesis of new classes of highly reduced organometallics.[15]

Acknowledgment. Financial support for this work was generously provided by National Science Foundation Grants CHE 82-10496 and CHE 85-06710 and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of crystal structure data for $[Ph_4As][C_5H_5Ti(CO)_4]$, details of the X-ray structural analysis, a drawing of the anion viewed down its pseudo 4-fold axis, and a drawing of the cation (34 pages). Ordering information is given on any current masthead page.

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(4) In 1962, R. D. Gorsich (U.S. Patent 3069445) reported on several main-group metal derivatives of $CpM(CO)_4^-$ (Cp = substituted and unsubstituted cyclopentadienyl groups, M = Ti, Zr and Hf) as well as alkali metal salts of the anions. However, no supporting data were presented for any of these substances in this or other patents. Gorsich states that the anions were obtained from "the reaction of the appropriate *inorganic* metal carbonyl (emphasis added) with the cyclopentadienyl alkali metal compound" in refluxing THF. In view of the known great thermal instability of $Ti(CO)_6$[5] and present nonexistence of "inorganic carbonyls" of Zr and Hf, these claims are interesting to say the least.

(5) Busby, R.; Klotzbucher, W.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 822.

(6) Wreford, S. S.; Fischer, M. B.; Lee, J-S.; James, E. J.; Nyburg, S. C. *J. Chem. Soc., Chem. Commun.* **1981**, 458.

(7) Domaille, P. J.; Harlow, R. L.; Wreford, S. S. *Organometallics* **1982**, **1**, 935.

(8) Beatty, R. P.; Datta, S.; Wreford, S. S. *Inorg. Chem.* 1979, *18*, 3139.

(9) Kelsey, B. A.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.*, in press.

(10) **1**. Anal. Calcd for $C_{17}H_{25}NO_4Ti$: C, 57.47; H, 7.09; N, 3.94. Found: C, 57.29; H, 7.13; N, 4.01. IR (THF) ν(CO) 1921 (m), 1779 (s) cm^{-1}. $^{13}C\{^1H\}$ NMR* δ 288.9 (CO), 92.6 (C_5H_5). ^1H NMR* δ 5.05 (s, C_5H_5). **2.** Anal. Calcd for $C_{17}H_{25}NO_4Zr$: C, 51.22;% H, 6.32; N, 3.51. Found: C, 51.16; H, 6.29; N, 3.49. IR (DME) ν(CO) 1923 (m), 1781 (s) cm^{-1}. $^{13}C\{^1H\}$ NMR* δ 291.7 (CO), 97.7 (C_5H_5). ^1H NMR* δ 5.55 (s, C_5H_5). *NMR solvent is dimethyl-d_6 sulfoxide; cation resonance positions are not shown. Interestingly, the IR-active ν(CO) values of $C_5H_5Ti(CO)_4^-$ are largely solvent independent and shifted to higher values than those of the neutral $Ti(CO)_3(Me_2PC_2H_4PMe_2)_2$[7] in THF (1848 s, 1757 sh, 1747 s cm^{-1}: Chi, K. M.; Ellis, J. E., unpublished results). A similar trend is observed for the related vanadium compounds $C_5H_5V(CO)_4$ (CS_2; 1982 m, 1890 s cm^{-1}: *Organomet. Synth.* **1965**, *1*, 108) and $V(CO)_3(o\text{-}C_6H_4(AsMe_2)_2)_2^+$ (CH_2Cl_2; 1958 s, 1881 s cm^{-1}; Ellis, J. E.; Faltynek, R. A. *J. Organomet. Chem.* **1975**, *93*, 205).

(11) Attempts to obtain suitable single crystals of the tetraethylammonium salt were unsuccessful. The tetraphenylarsonium salt $[Ph_4As][C_5H_5Ti(CO)_4]$ was obtained by exactly the same procedure used to synthesize **1**, except Ph_4AsCl was substituted in the metathesis step. The spectroscopic properties of the anion in $[Ph_4As][C_5H_5Ti(CO)_4]$ are identical with those for **1** in solution. Single crystals of the Ph_4As^+ salt were grown from tetrahydrofuran–diethyl ether at 0 °C. Data collection was carried out at 23 °C, on an Enraf-Nonius CAD-4 automated diffractometer, Mo Kα radiation. The space group is $P\bar{1}$ with a = 11.578 (2) Å, b = 14.130 (7) Å, c = 9.086 (2) Å, α = 101.43 (3)°, β = 92.14 (2)°, γ = 103.37 (3)°. Intensity data were collected for 4950 reflections of which 3394 were unique and measured $F_o^2 > 1.0\sigma F_o^2$ and were used for structure solution and refinement by using Enraf-Nonius CAD 4-SDP programs. The last cycle of least-squares refinement gave residuals of $R = 0.037$ and $R_w = 0.040$ and a goodness of fit indicator of 1.26 for a fit of 353 variables to 3394 observations. Complete details of the refinement along with tables are available as supplementary material.

(12) Wilford, J. B.; Whittla, A.; Powell, H. M. *J. Organomet. Chem.* **1967**, *8*, 495.

(13) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367.

(14) **3**. Anal. Calcd for $C_{27}H_{20}AuO_4PTi$: C, 47.39; H, 2.95; P, 4.53. Found: C, 47.38; H, 3.19; P, 4.66. IR (CH_2Cl_2) ν(CO) 1884 (s, br) cm^{-1}. $^{13}C\{^1H\}$ NMR* (−25 °C) (toluene-d_8) δ 269.1 (CO), 92.6 (C_5H_5). **4**. IR (toluene) ν(CO) 2020 (w), 1960 (s) cm^{-1}. $^{13}C\{^1H\}$ NMR* (−70 °C) (CD_2Cl_2) δ 245.7 (CO), 92.2 (C_5H_5). **5**. IR (CH_2Cl_2) ν(CO) 1887 (s, br) cm^{-1}. $^{13}C\{^1H\}$ NMR* (−60 °C) (CD_2Cl_2) δ 272.5 (CO), 94.8 (C_5H_5). **6**. IR (CH_2Cl_2) ν(CO) 1972 (s, br) cm^{-1}. $^{13}C\{^1H\}$ NMR* (CD_2Cl_2) (−70 °C) δ 241.2 (CO), 91.8 (C_5H_5). *Phenyl resonance positions are not shown.

(15) Recently we have also observed that reduction of $(C_5H_5)_2Ti(CO)_2$ by 2 equiv of Na–$C_{10}H_8$ in THF at −78 °C under a CO atmosphere provides approximately 20% yields of $C_5H_5Ti(CO)_4^-$. Interestingly, $(C_5H_5)_2Ti(CO)_2$ appears to be inert to reduction by lithium dispersion under the same conditions from −78 °C to room temperature.