

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$,¹⁰ 87.9 (6)°, but the centroid-metal-centroid angles are nearly equivalent, 138 (1)° in the former vs. 138.6° in the latter.

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Supplementary Material Available: A listing of structure factor amplitudes for both compounds and least-squares plane results for dicarbonyldicyclopentadienylzirconium(II) (26 pages). Ordering information is given on any current masthead page.

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Formation and Molecular Structure of a Novel Organometallic Titanoxane Derived from the Reaction of Dicarbonyltitanocene and Hexafluoro-2-butyne

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The reaction between dicarbonyltitanocene (**1**) and hexafluoro-2-butyne in benzene solution in a sealed system at 55 °C has produced an orange air-stable titanoxane, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3)]_2\text{O}$, in 30–35% yield. The product has been characterized by ¹H NMR, ¹⁹F NMR, IR, and mass spectrometric techniques, and its crystal structure has been determined from three-dimensional X-ray data as measured by counter techniques. The compound crystallizes in the triclinic space group *P*1 with *a* = 11.522 (5) Å, *b* = 15.015 (6) Å, *c* = 17.959 (6) Å, α = 77.52 (4)°, β = 77.93 (4)°, γ = 70.27 (4)°, and $\rho_{\text{calcd}} = 1.64 \text{ g cm}^{-3}$ for *Z* = 4. Full-matrix least-squares refinement led to a final *R* value of 0.041 based on 4888 reflections. The two independent molecules in the asymmetric unit display similar bond distances and angles but exist in different rotational conformations about the Ti–O–Ti bond: the C(σ)–Ti···Ti–C(σ) torsional angles are +54.1 and –53.7°. The Ti–O–Ti linkage is nearly linear (170°), and the Ti–O bond distance, 1.856 (6) Å, is larger than normal. This is attributed to steric effects, as are the elongated Ti–C(sp²) distance, 2.239 (3) Å, and the Ti–C(η⁵) distance, 2.421 (23) Å.

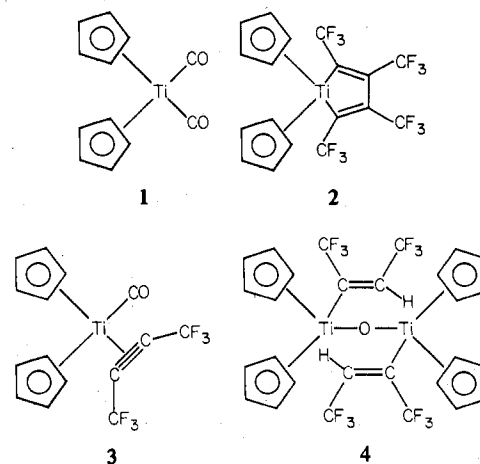
Although dicarbonyltitanocene [bis(η⁵-cyclopentadienyl)-dicarbonyltitanium] (**1**) was first obtained by Murray in 1958,² the chemistry of this unique metal carbonyl has been slow to develop, due primarily to the considerable experimental difficulties and low yields incurred in its preparation by the original literature method. Recently, however, several greatly improved methods for the synthesis of **1** have been reported,^{3,4} and a variety of reactions involving displacements of the carbonyl ligands by diphenylketene, trimethylphosphine, TCNE, 2,2'-bipyridine, alkyl halides, acyl halides, 9,10-phenanthroquinone, etc. have been described.^{3,5} An X-ray structural determination of **1** has also recently been completed in our laboratories.⁶

In contrast to the rich and varied chemistry resulting from reactions of the metal carbonyls and acetylenes,⁷ however, at the present time there exist only two reports^{8,9} on the interaction of **1** with acetylenes. As part of our continuing joint program on the formation and structure of organometallic

products derived from metal carbonyls and acetylenes, we report herein on the reaction of **1** and hexafluoro-2-butyne, as well as on the results of a single-crystal X-ray crystallographic study which together with spectral measurements fully characterize the organometallic product produced as a novel titanoxane (**4**).

Results and Discussion

Formation of 4. It was our original expectation that the interaction of dicarbonyltitanocene (**1**) with hexafluoro-2-



butyne would lead either to a titanole (**2**) or to an η²-acetylene complex (**3**),¹⁰ in analogy with earlier reported reactions of **1** with diphenylacetylene.^{8,9} Accordingly, **1** was allowed to react with an excess of hexafluoro-2-butyne in benzene solution at 55 °C in a sealed system for 16 h. Chromatography of the dark orange reaction mixture on silica gel under argon produced an orange solid, which upon crystallization from tolu-

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- (10) Formation of a product such as **3** would be less likely under our reaction conditions, since the analogous diphenylacetylene complex was produced only under conditions in which carbon monoxide was removed as it formed.

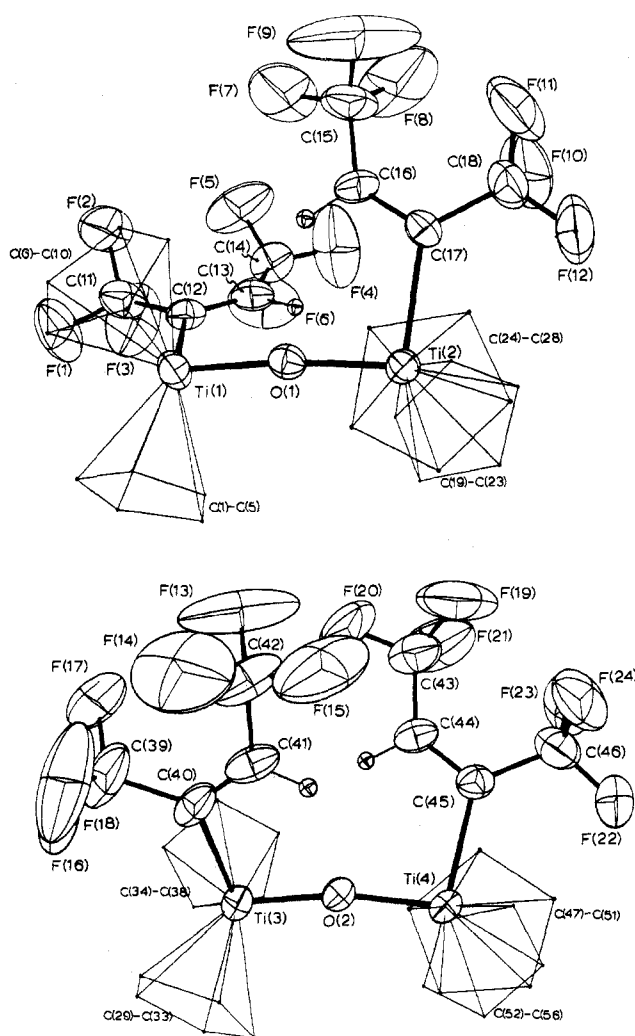


Figure 1. Molecular structure and atom numbering scheme for the two crystallographically independent molecules of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3)]_2\text{O}$.

ene-hexane afforded bright-orange, air-stable crystals, mp 222–225 °C. Elemental analyses and spectroscopic studies were not in agreement with either **2** or **3**, however, and a definitive structure assignment could not be made on the basis of the data available at that time. We then decided to undertake a single-crystal X-ray structural investigation of the product, which revealed it to have a novel titanoxane structure (**4**) as is described below.

Crystallographic Structure of 4. The molecular structure and atom numbering schemes are shown in Figure 1, while the bond distances and angles are listed in Table III. There are two independent molecules in the asymmetric unit, and they differ in rotational conformation about the Ti–O–Ti bond. This is shown most clearly in Figure 1, where the right halves of both molecules are plotted in an equivalent orientation. The C(12)–Ti(1)–Ti(2)–C(17) torsional angle is +54.1°, while that of C(40)–Ti(3)–Ti(4)–C(45) is –53.7°. However, individual bond distances and angles do compare favorably between molecules and between halves. A comparison of the aspects of the Ti–O–Ti bridge with related structures^{11–17} is

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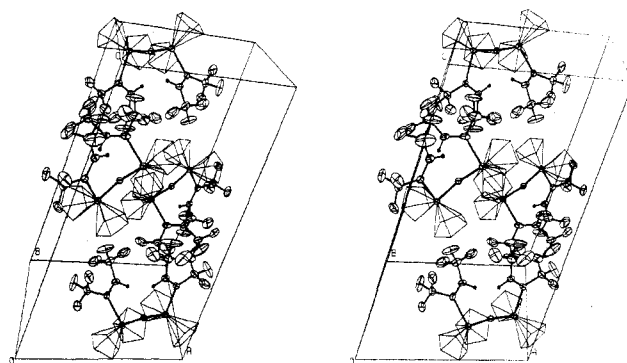


Figure 2. Stereoscopic view of the unit cell packing.

Table I. Crystal Data

molecular formula	Ti ₂ F ₁₂ OC ₂₉ H ₂₂
molecular wt	698.2
cell constants ^a <i>a</i> , Å	11.522 (5)
<i>b</i> , Å	15.015 (6)
<i>c</i> , Å	17.959 (6)
α , deg	77.52 (4)
β , deg	77.93 (4)
γ , deg	70.27 (4)
cell vol, Å ³	2824.0
linear abs coeff, cm ⁻¹	6.97
space group	P1
molecules/unit cell	4
max cryst dimens, mm	0.25 × 0.28 × 0.35
calcd density, g cm ⁻³	1.64

^a Mo K α radiation, $\lambda = 0.71069$ Å. Ambient temperature of 23 ± 1 °C.

given in Table IV. The average angle at the oxygen atom bridge, 170°, is close to 180° but nevertheless exhibits the largest deviation from linearity of any organotitanium structure. The O–Ti–C angle, 95.0°, is near the previously reported values. Steric effects associated with the bulky olefin in **4** are probably responsible for the largest Ti–O bond length yet reported for a bridging situation, 1.857 (6) Å.

Another effect of the size of the σ -bonded moiety is the long Ti–C(sp²) average bond length, 2.239 (4) Å. In $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}[\text{C}_4(\text{C}_6\text{H}_5)_4]$ the distances 2.141 (5) and 2.172 (5) Å are relatively free of steric effects and fit in well with the established values for Ti–C(sp³).¹⁸

The Ti–C(η^5) bond lengths range from 2.372 (5) to 2.457 (6) Å and average 2.421 (23) Å. This is considerably larger than the 2.366 (22) Å average in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}[\text{C}_4(\text{C}_6\text{H}_5)_4]$ ¹⁸ and the 2.385 (20) Å in $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{H}_2\text{O})]_2\text{O}\}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.¹⁴

A stereoscopic view of the unit cell packing is presented in Figure 2, and the closest intermolecular nonbonded approaches are listed in Table III.

Spectral Properties of 4. The ¹H NMR spectrum of **4** in acetone-*d*₆ solution exhibits a singlet at τ 3.63 ppm assignable to the η^5 -cyclopentadienyl protons and a quartet ($J_{\text{H-gem-CF}_3} = 10.1$ Hz) centered at τ 3.75 ppm, arising from coupling of the vinylic protons with the geminal CF₃ groups. A portion of this quartet resonance overlaps with the η^5 -cyclopentadienyl proton resonance. The ¹⁹F NMR spectrum of **4** in acetone-*d*₆ exhibits an apparent quintuplet due to two overlapping quartets centered at 105.5 ppm, assignable to the CF₃ groups geminal to the vinylic protons, and a quartet ($J_{\text{F-F}} = 12.9$ Hz) at 113.0 ppm assignable to the CF₃ groups geminal to the titanium

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Table II. Atomic Positions in Fractional Coordinates and Thermal Parameters^a for (μ -O)[(C₅H₅)₂TiCF₃C=C(H)CF₃]₂

Atom	x/a	y/b	z/c	B11	B22	B33	B12	B13	B23
Ti(1)	0.60476(8)	0.19951(7)	0.64433(5)	0.02641(8)	0.00499(6)	0.00234(3)	-0.00205(6)	-0.00092(4)	-0.00097(3)
Ti(2)	0.87791(7)	0.26374(6)	0.06481(4)	0.08020(8)	0.00325(5)	0.00177(3)	-0.00197(5)	-0.00002(4)	-0.00076(3)
Ti(3)	0.37303(8)	0.25857(7)	0.62380(5)	0.00743(9)	0.00476(6)	0.00228(3)	-0.00212(4)	-0.00051(4)	-0.00110(3)
Ti(4)	0.17689(7)	0.21848(6)	0.50486(4)	0.00585(8)	0.00324(5)	0.00165(3)	-0.00061(5)	-0.00062(4)	-0.00043(3)
F(1)	0.2930(3)	0.2523(3)	0.0961(2)	0.8087(4)	0.0195(5)	0.0070(2)	-0.0065(3)	-0.0007(2)	-0.0052(2)
F(2)	0.2988(3)	0.2484(4)	0.2117(2)	0.0123(4)	0.0222(5)	0.0047(2)	-0.0110(4)	-0.0007(2)	0.0012(2)
F(3)	0.2450(3)	0.3802(3)	0.1382(3)	0.0071(4)	0.0107(3)	0.0154(4)	0.0005(4)	-0.0025(3)	-0.0014(3)
F(4)	0.5029(4)	0.4402(4)	0.2416(3)	0.0173(6)	0.0203(5)	0.0127(3)	-0.0066(4)	0.0029(3)	-0.0133(4)
F(5)	0.3618(5)	0.3772(3)	0.2732(2)	0.0324(8)	0.0106(3)	0.0052(2)	-0.0078(4)	0.0077(3)	-0.0032(2)
F(6)	0.3474(5)	0.4918(3)	0.1874(3)	0.0247(7)	0.0088(3)	0.0072(2)	0.0047(4)	-0.0002(3)	-0.0025(2)
F(7)	0.6148(5)	0.1760(6)	0.3314(2)	0.0221(7)	0.060(2)	0.0054(2)	-0.0211(7)	0.0010(3)	0.0024(3)
F(8)	0.7236(7)	0.2366(5)	0.3600(2)	0.060(2)	0.0283(8)	0.0032(2)	-0.029(1)	0.0067(4)	-0.0052(3)
F(9)	0.7875(6)	0.1016(5)	0.3495(3)	0.036(1)	0.0216(6)	0.0054(2)	0.0079(7)	0.0041(4)	0.0056(3)
F(10)	0.9050(4)	0.3122(3)	0.2790(2)	0.8200(6)	0.0149(4)	0.0073(2)	-0.0068(4)	-0.0022(3)	-0.0067(2)
F(11)	0.9966(4)	0.1645(3)	0.2885(3)	0.0253(7)	0.0129(4)	0.0102(3)	-0.0081(4)	-0.0128(4)	0.0031(3)
F(12)	1.0532(3)	0.2583(4)	0.1961(2)	0.0141(5)	0.0238(5)	0.0053(2)	-0.0134(4)	-0.0007(2)	-0.0034(2)
F(13)	-0.0476(4)	0.3621(4)	0.8051(2)	0.0219(6)	0.0157(4)	0.0052(2)	0.0072(4)	0.0056(3)	0.0036(2)
F(14)	-0.0333(5)	0.4929(4)	0.7514(4)	0.0272(8)	0.0098(4)	0.0151(4)	0.0003(4)	0.0062(5)	-0.0075(3)
F(15)	-0.1064(4)	0.4222(4)	0.7003(3)	0.0132(5)	0.0241(6)	0.0066(2)	0.0058(4)	0.0003(3)	-0.0053(3)
F(16)	0.3621(4)	0.3747(3)	0.7712(2)	0.0248(6)	0.0137(4)	0.0062(2)	-0.0082(4)	-0.0034(3)	-0.0043(2)
F(17)	0.1950(6)	0.3588(5)	0.8359(2)	0.039(1)	0.0371(9)	0.0034(2)	-0.0249(8)	0.0036(3)	-0.0074(3)
F(18)	0.2000(6)	0.4843(4)	0.7558(4)	0.045(1)	0.0119(4)	0.0155(4)	-0.0002(6)	-0.0107(6)	-0.0101(4)
F(19)	-0.1368(4)	0.1493(4)	0.7451(3)	0.0143(5)	0.0227(6)	0.0062(2)	-0.0058(5)	0.0038(3)	0.0005(3)
F(20)	0.0115(5)	0.1374(4)	0.8003(2)	0.0378(9)	0.0201(5)	0.0026(1)	-0.0180(6)	0.0023(3)	-0.0023(2)
F(21)	0.0064(5)	0.0213(3)	0.7575(2)	0.041(1)	0.0096(3)	0.0055(2)	-0.0109(5)	0.0032(3)	0.0008(2)
F(22)	-0.0490(3)	0.1201(3)	0.5028(2)	0.0140(4)	0.0117(3)	0.0047(1)	-0.0068(3)	-0.0026(2)	-0.0114(2)
F(23)	-0.0739(4)	0.0492(3)	0.6171(2)	0.0247(6)	0.0127(4)	0.0068(2)	-0.0136(4)	-0.0041(3)	0.0013(2)
F(24)	-0.1695(3)	0.1975(3)	0.5887(3)	0.0065(3)	0.0161(4)	0.0092(2)	-0.0024(3)	-0.0011(2)	-0.0044(3)
O(1)	0.7346(3)	0.2348(2)	0.0618(2)	0.0063(3)	0.0033(2)	0.0020(1)	-0.0011(2)	-0.0005(1)	-0.0006(1)
O(2)	0.2634(3)	0.2383(2)	0.5736(2)	0.0064(3)	0.0035(2)	0.0021(1)	-0.0011(2)	-0.0004(1)	-0.0007(1)
C(1)	0.4624(6)	0.3117(5)	-0.0414(3)	0.0109(7)	0.0123(6)	0.0030(2)	-0.0011(5)	-0.0030(3)	-0.0002(3)
C(2)	0.5702(6)	0.3388(5)	-0.0573(3)	0.0146(8)	0.0095(5)	0.0026(2)	-0.0033(5)	-0.0025(3)	0.0006(3)
C(3)	0.4678(6)	0.2459(5)	-0.0878(3)	0.0111(7)	0.0129(6)	0.0020(2)	-0.0040(5)	-0.0008(3)	-0.0004(3)
C(4)	0.6227(6)	0.1913(5)	-0.0890(3)	0.0352(9)	0.0120(6)	0.0035(2)	-0.0033(6)	-0.0018(4)	-0.0032(3)
C(5)	0.4940(6)	0.2213(6)	-0.0615(3)	0.0135(8)	0.0143(7)	0.0037(3)	-0.0059(6)	-0.0031(4)	-0.0016(3)
C(6)	0.7168(5)	0.0315(4)	0.0640(4)	0.0133(7)	0.0042(3)	0.0064(3)	-0.0027(4)	-0.0001(4)	-0.0020(3)
C(7)	0.6029(6)	0.0375(5)	0.0441(4)	0.0158(9)	0.0075(5)	0.0071(4)	-0.0058(5)	-0.0019(4)	-0.0032(3)
C(8)	0.5081(6)	0.0733(5)	0.1018(4)	0.0094(7)	0.0073(5)	0.0084(4)	-0.0050(5)	-0.0013(4)	-0.0011(3)
C(9)	0.5626(6)	0.0884(4)	0.1593(3)	0.0121(7)	0.0046(3)	0.0046(3)	-0.0032(4)	0.0001(3)	0.0003(2)
C(10)	0.6915(5)	0.0605(3)	0.1362(3)	0.0110(6)	0.0031(3)	0.0047(3)	-0.0023(3)	-0.0017(3)	-0.0000(2)
C(11)	0.3253(5)	0.2959(4)	0.1446(3)	0.0072(5)	0.0086(4)	0.0034(2)	-0.0012(4)	-0.0012(3)	-0.0004(2)
C(12)	0.4602(4)	0.2925(4)	0.1233(3)	0.0055(5)	0.0052(3)	0.0023(2)	-0.0012(3)	-0.0004(2)	0.0002(2)
C(13)	0.4972(4)	0.3458(4)	0.1582(3)	0.0079(5)	0.0049(3)	0.0023(2)	-0.0010(3)	0.0004(2)	-0.0005(2)
C(14)	0.4276(5)	0.4116(4)	0.2160(3)	0.0104(6)	0.0057(4)	0.0040(2)	-0.0013(4)	0.0008(3)	-0.0015(2)
C(15)	0.7237(6)	0.1825(3)	0.3164(3)	0.0135(7)	0.0107(5)	0.0021(2)	-0.0024(3)	-0.0006(3)	0.0004(2)
C(16)	0.7652(4)	0.2062(4)	0.2327(2)	0.0078(5)	0.0054(3)	0.0018(2)	-0.0021(3)	-0.0001(2)	-0.0002(2)
C(17)	0.8632(4)	0.2317(3)	0.1936(2)	0.0072(5)	0.0045(3)	0.0021(2)	-0.0021(3)	-0.0009(2)	-0.0008(2)
C(18)	0.9535(5)	0.2402(5)	0.2392(3)	0.0103(6)	0.0093(5)	0.0032(2)	-0.0045(4)	-0.0015(3)	-0.0014(2)
C(19)	0.7958(6)	0.4205(4)	0.1038(3)	0.0185(9)	0.0039(3)	0.0034(2)	-0.0047(4)	0.0011(4)	-0.0017(2)
C(20)	0.9235(6)	0.4074(4)	0.0761(4)	0.0177(9)	0.0058(4)	0.0057(3)	-0.0069(5)	-0.0013(4)	-0.0015(3)
C(21)	0.9400(6)	0.4031(4)	-0.8028(4)	0.0149(8)	0.0039(3)	0.0056(3)	-0.0050(4)	-0.0029(4)	-0.0011(3)
C(22)	0.8263(6)	0.4099(4)	-0.0223(3)	0.0169(8)	0.0038(3)	0.0030(2)	-0.0033(4)	0.0006(3)	-0.0004(2)
C(23)	0.7368(5)	0.4246(3)	0.0433(3)	0.0126(7)	0.0026(3)	0.0042(2)	-0.0014(3)	0.0007(3)	-0.0008(2)
C(24)	1.0666(5)	0.1309(4)	0.0856(3)	0.8074(5)	0.0074(4)	0.0032(2)	-0.0005(4)	-0.0011(3)	-0.0014(2)
C(25)	0.9861(4)	0.0937(4)	0.0623(3)	0.0071(5)	0.0043(3)	0.0034(2)	-0.0005(3)	-0.0005(3)	-0.0008(2)
C(26)	0.9690(4)	0.1372(3)	-0.8130(3)	0.8071(5)	0.0044(3)	0.0031(2)	-0.0007(3)	0.0000(3)	-0.0011(2)
C(27)	1.0368(5)	0.2017(4)	-0.0364(3)	0.0082(5)	0.0048(3)	0.0029(2)	-0.0014(3)	0.0009(2)	-0.0010(2)
C(28)	1.0980(5)	0.1982(4)	0.0242(3)	0.0061(5)	0.0071(4)	0.0047(3)	-0.0025(4)	0.0003(3)	-0.0024(3)
C(29)	0.4148(8)	0.4124(5)	0.5973(4)	0.022(1)	0.0086(5)	0.0049(3)	-0.0098(6)	0.0012(5)	-0.0019(3)
C(30)	0.5277(7)	0.3401(6)	0.5984(4)	0.0158(9)	0.0131(7)	0.0052(3)	-0.0098(7)	-0.0013(4)	-0.0012(4)
C(31)	0.5464(6)	0.2895(5)	0.5378(4)	0.8109(7)	0.0110(6)	0.0046(3)	-0.0057(5)	-0.0007(4)	-0.0012(3)
C(32)	0.4441(6)	0.3328(5)	0.4983(3)	0.0146(8)	0.0092(5)	0.0033(2)	-0.0072(5)	0.0005(3)	-0.0005(3)
C(33)	0.3615(6)	0.4078(4)	0.5344(4)	0.0142(8)	0.0066(4)	0.0054(3)	-0.0061(5)	-0.0084(4)	0.0003(3)
C(34)	0.5536(6)	0.1376(5)	0.8770(4)	0.0085(7)	0.0109(6)	0.0065(4)	-0.0019(5)	-0.0034(4)	-0.0000(4)
C(35)	0.4719(7)	0.1745(5)	0.7400(4)	0.020(1)	0.0087(5)	0.0049(3)	-0.0028(6)	-0.0043(5)	-0.0009(3)
C(36)	0.3635(6)	0.1515(4)	0.7477(3)	0.0135(7)	0.0064(4)	0.0030(2)	0.0016(4)	-0.0009(3)	0.0003(2)
C(37)	0.3764(5)	0.0994(4)	0.6904(3)	0.0098(6)	0.0045(3)	0.0042(2)	-0.0006(4)	-0.0028(3)	0.0005(2)
C(38)	0.4915(5)	0.0922(4)	0.6464(3)	0.0105(7)	0.0065(4)	0.0040(2)	-0.0016(4)	-0.0022(3)	-0.0012(3)
C(39)	0.2423(8)	0.3893(5)	0.7675(4)	0.023(1)	0.0078(5)	0.0053(3)	-0.0039(6)	-0.0018(5)	-0.0037(3)
C(40)	0.2214(5)	0.3462(4)	0.7048(3)	0.0138(7)	0.0041(5)	0.0024(2)	-0.0023(4)	-0.0007(3)	-0.0011(2)
C(41)	0.1060(5)	0.3575(3)	0.6970(3)	0.0117(6)	0.0037(3)	0.0020(2)	0.0000(3)	0.0005(3)	-0.0008(2)
C(42)	-0.0178(6)	0.4068(5)	0.7401(3)	0.0158(8)	0.0070(4)	0.0028(2)	0.0028(5)	-0.0008(3)	-0.0013(2)
C(43)	-0.0152(6)	0.1146(5)	0.7411(3)	0.8152(8)	0.0076(4)	0.0036(2)	-0.0042(5)	0.0014(3)	-0.0008(3)
C(44)	0.0574(5)	0.1490(3)	0.6677(3)	0.0088(5)	0.0043(3)	0.0026(2)	-0.0020(3)	-0.0000(2)	-0.0001(2)
C(45)	0.0453(4)	0.1574(3)	0.5939(3)	0.0060(5)	0.0044(3)	0.0025(2)	-0.0010(3)	-0.0003(2)	-0.0006(2)
C(46)	-0.0595(5)	0.1305(4)	0.5762(3)	0.0079(6)	0.0081(4)	0.0047(3)	-0.0034(4)	-0.0003(3)	-0.0009(3)
C(47)	-0.0172(5)	0.3496(4)	0.5135(3)	0.0079(6)	0.0052(4)	0.0038(2)	0.0011(4)	-0.0005(3)	0.0001(2)
C(48)	-0.0099(5)	0.3127(4)	0.4454(3)	0.0106(6)	0.0060(4)	0.0040(2)	-0.0004(4)	-0.0031(3)	-0.0001(2)
C(49)	0.0925(5)	0.3292(4)	0.3938(3)	0.0128(7)	0.0054(4)	0.0027(2)	0.0002(4)	-0.0020(3)	-0.0001(2)
C(50)	0.1517(5)	0.3729(4)	0.4301(3)	0.8121(6)	0.0042(3)	0.0027(2)	-0.0013(4)	-0.0009(3)	0.0008(2)
C(51)	0.0802(5)	0.3877(3)	0.5034(3)	0.8123(6)	0.0026(3)	0.0030(2)	0.0008(3)	-0.0017(3)	0.0001(2)
C(52)	0.3260(4)	0.0587(3)	0.5117(3)	0.0084(5)	0.0037(3)	0.0027(2)	-0.0001(3)	-0.0006(2)	-0.0001(2)
C(53)	0.2255(5)	0.0547(4)	0.4811(3)	0.8098(6)	0.0042(3)	0.0035(2)	-0.0014(3)	0.0000(3)	-0.0004(2)
C(54)	0.2205(5)	0.1161(4)	0.4098(3)	0.0103(6)	0.0065(4)	0.0032(2)	-0.0006(4)	-0.0014(3)	-0.0026(2)
C(55)	0.3180(5)	0.1573(4)	0.3977(3)	0.0105(6)	0.0052(3)	0.0023(2)	-0.0008(4)	0.0011(3)	-0.0013(2)
C(56)	0.3828(4)	0.1206(3)	0.4603(3)	0.8071(5)	0.0045(3)	0.0030(2)	-0.0005(3)	0.0001(2)	-0.0017(2)

^a Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{11}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

atoms. No coupling between the latter CF₃ groups and the vinylic protons was observed, although the spectrum was well resolved. This result is in accord with a cis configuration for the two nonequivalent CF₃ groups in 4. Both ¹H and ¹⁹F NMR spectra are consistent with many other organometallic compounds containing *cis*-(CF₃)C=C(CF₃)H groups¹⁹⁻²² and

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with the crystallographic structure of 4 as discussed above. The ¹³C NMR spectrum of 4 in acetone-*d*₆ exhibits a resonance at 115.6 ppm which can be assigned to the η⁵-cyclopentadienyl carbon atoms.

The IR spectrum of 4 recorded as a KBr pellet contains intense bands at 1340, 1250, 1200, and 1130 cm⁻¹ assignable to C-F stretching vibrations of the CF₃ groups and bands at 1440 (m), 1110 (s), 1015 (s), and 825 (s) cm⁻¹ which can be

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attributed to C–C and C–H vibrations of the η^5 -cyclopentadienyl substituents. A strong band at 800 cm^{-1} is most likely the C–H out-of-plane bending mode for the two trisubstituted vinylic groups present in **4**. A medium intensity band at 1600 cm^{-1} can be assigned to the C=C stretching vibration in **4**. Although a broad, intense band is present at 665 cm^{-1} in the IR spectrum of **4**, surprisingly, no absorptions are observed between $700\text{--}775\text{ cm}^{-1}$, a region where bands characteristic of M–O–M bonds (M = Ti, Zr, Hf) normally occur.^{23–29}

The mass spectrum of **4** did not exhibit a parent ion peak, in analogy with other compounds containing metaloxane (M–O–M) linkages.^{25,29} However, a number of strong fragmentation peaks representing ions which incorporate the titanoxane linkage and in which the titanium atoms are partially fluorinated are observed at m/e 391, 345, 326, 299, and 280 (see Experimental Section for assignments). Peaks assignable to $(\text{C}_5\text{H}_5)_2\text{TiF}_2^+$, $(\text{C}_5\text{H}_5)_2\text{TiF}^+$, $(\text{C}_5\text{H}_5)_2\text{Ti}^+$, $\text{C}_5\text{H}_5\text{TiF}_2^+$, $\text{C}_5\text{H}_5\text{TiF}^+$, $\text{C}_5\text{H}_5\text{Ti}^+$, and C_5H_5^+ ions were also present. The formation of organometallic fluoride ions during the mass spectral fragmentation of fluorinated organometallics has been observed in related systems.³⁰

Reaction Pathways Leading to 4. Although a detailed mechanism to account for the formation of titanoxane **4** from **1** and hexafluoro-2-butyne under the reaction conditions involved cannot be fully developed on the basis of data presently available, several comments can be put forth. In order to determine whether or not the solvent benzene was responsible as the source of the vinylic hydrogens, the reaction was run under identical conditions as above except that anhydrous benzene- d_6 was used as solvent. Both IR and ^1H NMR spectra of the reaction product proved to be identical with the spectra obtained from reactions carried out in benzene. More specifically, the quartet due to the vinylic protons was still present in the ^1H NMR spectrum, and no shift to lower frequency was observed for the C–H out-of-plane bending vibration at 800 cm^{-1} in the IR spectrum. These results thus rule out the possibility that the vinylic hydrogens in **4** arise from solvent molecules.

The pathway by which the Ti–O–Ti linkage in **4** is formed is difficult to reconcile. Caulton and co-workers³¹ have recently isolated and characterized a novel metal cluster complex of composition $\text{Cp}_6\text{Ti}_6\text{O}_8$ from reactions of **1** with H_2 . The μ_3 -O bridging ligands in this product were presumed to be derived from the carbonyl ligands of **1**. Metal–oxygen bonds are known to be readily formed in other similar reactions of group 4B metallocene dicarbonyls.³² On the basis of these results, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}^{18}\text{O})_2$ was synthesized and allowed to react with hexafluoro-2-butyne under normal conditions. Analysis of the reaction product by mass spectrometry indicated that the ions incorporating the titanoxane linkage did not contain ^{18}O . We therefore conclude that the oxygen atom in **4** is *not* derived from the carbonyl ligands of **1** out from some other source. Additional studies to delineate the mechanism of formation of **4** are in progress.

Table III. Bond Distances (Å) and Angles (Deg) for $(\mu\text{-O})[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CF}_3(\text{H})\text{C}=\text{CCF}_3)]_2^a$

Distances			
Ti(1)–C(12)	2.242 (5)	Ti(1)–O(1)	1.848 (3)
Ti(2)–C(17)	2.241 (4)	Ti(2)–O(1)	1.856 (3)
Ti(3)–C(40)	2.239 (5)	Ti(3)–O(2)	1.856 (3)
Ti(4)–C(45)	2.234 (4)	Ti(4)–O(2)	1.865 (3)
	av 2.239 (3)		av 1.856 (6)
Ti(1)–C(1)	2.443 (6)	Ti(3)–C(29)	2.442 (6)
Ti(1)–C(2)	2.439 (6)	Ti(3)–C(30)	2.401 (6)
Ti(1)–C(3)	2.429 (5)	Ti(3)–C(31)	2.387 (6)
Ti(1)–C(4)	2.386 (6)	Ti(3)–C(32)	2.426 (5)
Ti(1)–C(5)	2.412 (5)	Ti(3)–C(33)	2.457 (6)
Ti(1)–C(6)	2.402 (6)	Ti(3)–C(34)	2.450 (6)
Ti(1)–C(7)	2.441 (6)	Ti(3)–C(35)	2.441 (6)
Ti(1)–C(8)	2.450 (6)	Ti(3)–C(36)	2.426 (6)
Ti(1)–C(9)	2.434 (5)	Ti(3)–C(37)	2.411 (5)
Ti(1)–C(10)	2.423 (5)	Ti(3)–C(38)	2.398 (6)
	av 2.426 (19)		av 2.424 (23)
Ti(2)–C(19)	2.420 (5)	Ti(4)–C(47)	2.432 (5)
Ti(2)–C(20)	2.443 (5)	Ti(4)–C(48)	2.455 (5)
Ti(2)–C(21)	2.432 (5)	Ti(4)–C(49)	2.444 (5)
Ti(2)–C(22)	2.375 (5)	Ti(4)–C(50)	2.372 (5)
Ti(2)–C(23)	2.415 (5)	Ti(4)–C(51)	2.403 (5)
Ti(2)–C(24)	2.436 (5)	Ti(4)–C(52)	2.429 (5)
Ti(2)–C(25)	2.440 (5)	Ti(4)–C(53)	2.443 (5)
Ti(2)–C(26)	2.419 (4)	Ti(4)–C(54)	2.405 (5)
Ti(2)–C(27)	2.390 (5)	Ti(4)–C(55)	2.375 (5)
Ti(2)–C(28)	2.407 (5)	Ti(4)–C(56)	2.407 (5)
	av 2.418 (21)		av 2.416 (27)
C(11)–C(12)	1.506 (7)	C(39)–C(40)	1.509 (7)
C(12)–C(13)	1.332 (6)	C(40)–C(41)	1.316 (7)
C(13)–C(14)	1.503 (7)	C(41)–C(42)	1.502 (7)
C(15)–C(16)	1.483 (7)	C(43)–C(44)	1.497 (7)
C(16)–C(17)	1.326 (6)	C(44)–C(45)	1.337 (6)
C(17)–C(18)	1.503 (6)	C(45)–C(46)	1.505 (7)
Angles			
Ti(1)–O(1)–Ti(2)	171.0 (2)	Ti(3)–O(2)–Ti(4)	169.0 (2)
O(1)–Ti(1)–C(12)	94.3 (1)	O(2)–Ti(3)–C(40)	94.1 (2)
O(1)–Ti(2)–C(17)	94.8 (1)	O(2)–Ti(4)–C(45)	96.5 (1)
Cent(1)–Ti(1)–Cent(2)	129.6	Cent(5)–Ti(3)–Cent(6)	129.7
Cent(3)–Ti(2)–Cent(4)	129.9	Cent(7)–Ti(4)–Cent(8)	130.2

^a Other bond lengths and angles may be found in the supplementary material.

Experimental Section

All reactions were conducted under an argon atmosphere. The argon was dried with P_2O_5 and H_2SO_4 , and trace oxygen was removed by using BTS catalyst (BASF). Benzene, hexane, and toluene were dried over CaH_2 and freshly distilled under argon. Benzene used as the reaction solvent was additionally distilled from LiAlH_4 under argon into the reaction vessel. Column chromatography was carried out under argon by using silica gel which had been dried and degassed. ^1H and ^{19}F NMR spectra were taken on a Varian XL-100 spectrometer and were referenced to internal Me_4Si and C_6F_6 , respectively. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer and were referenced to internal Me_4Si . IR spectra were recorded on a Perkin-Elmer 237-B spectrometer and were calibrated vs. polystyrene. Mass spectra were obtained at 80 eV on a Hitachi Perkin-Elmer RMU 6L instrument. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Hexafluoro-2-butyne was purchased from PCR, Inc., Gainesville, FL, and was dried by means of activated molecular sieves before use. Both dicarbonyltitanocene and its ^{18}O -enriched analogue were prepared by a literature method⁴ and were recrystallized from hexane before use. Carbon monoxide- ^{18}O (99%) was obtained from Stohler Isotope Chemicals, Inc.

Thermolysis of Dicarbonyltitanocene and Hexafluoro-2-butyne. In a typical run, 175–200 mg (0.74–0.85 mmol) of dicarbonyltitanocene (**1**) was placed in a heavy-walled Schlenk tube ($2.2 \times 18\text{ cm}$) which was fitted with a 15-mm threaded connector and Nylon plug (Ace Glass) and a pressure stopcock (Eck and Krebs). Approximately 16 mL of freshly distilled benzene was added, the tube was capped, and

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Table IV. Comparison of Structural Parameters for Oxo-Bridged Early Transition-Metal Compounds

compd	M-O, Å	M-O-M, deg	O-M-X, deg	dihedral angle (X-M···M-X)	ref
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2]_2\text{O}$	1.78 (3)	180	104 (2)		11
$[(\text{CH}_2\text{C}_6\text{H}_4)_3\text{Ti}]_2\text{O}$	1.798	180			12
$\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{H}_2\text{O})_2\text{O}]^{2+}(\text{S}_2\text{O}_8^{2-})\cdot 2\text{H}_2\text{O}$	1.834 (5)	177.0 (3)	95.1	74.1	13
$\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{H}_2\text{O})_2\text{O}]^{2+}(\text{ClO}_4^-)_2\cdot 2\text{H}_2\text{O}$	1.829 (2)	175.8 (5)	94.3		14
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3)_2\text{O}$	1.853, 1.860	171.0 (2), 169.1 (2)	94.6, 95.3	-53.7, +54.1	this study
$\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{O}]^{2+}(\text{BF}_4^-)_2$	1.88 (1)	169.3 (8)	96.2	72.5	15
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2]_2\text{O}$	1.945	168.9 (8)	98.0	74.3	16
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{SC}_6\text{H}_5)_2\text{O}$	1.966	165.8 (2)	100.9	61.7	17

the solution was then frozen by immersing the tube into liquid nitrogen. Once frozen, the tube was evacuated and ca. 0.5–1 mL of hexafluoro-2-butyne was bled into the vessel through the stopcock. The tube was allowed to warm to room temperature and subsequently placed in an oil bath maintained at 55 °C for 16 h. After this period, the color had changed from a deep red to a greenish orange. The pressure was then carefully released from the tube by connecting it to a vacuum line. The solution was concentrated to ca. 5 mL, and 0.75 g of silica gel was added. The remaining solvent was removed in vacuo, and the resulting solid was added to a column of silica gel (1.5 × 37 cm) which had been packed dry under argon. Elution with 2:1 benzene–hexane brought down a yellow-orange band which was collected under argon. Subsequent removal of the solvent under high vacuum gave the titanoxane **4** as a bright orange powder in yields of 30–35%. An analytical sample of **4** was prepared by crystallization of the product from toluene–hexane at low temperatures: orange crystals; mp 222–225 °C dec under argon.

Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{F}_{12}\text{O}_2\text{Ti}$: C, 48.16; H, 3.17; F, 32.64; Ti, 13.72. Found: C, 47.91; H, 3.02; F, 31.94; Ti, 13.93.

The mass spectrum of **4** exhibited principal peaks at m/e 391 [5, $(\text{C}_5\text{H}_5)_4\text{FOTi}_2^+$], 345 [87, $(\text{C}_5\text{H}_5)_3\text{F}_2\text{OTi}_2^+$], 326 [5, 345 - F⁺], 299 [11, $(\text{C}_5\text{H}_5)_2\text{F}_3\text{OTi}_2^+$], 280 [7, 299 - F⁺], 216 [6, $(\text{C}_5\text{H}_5)_2\text{F}_2\text{Ti}^+$], 197 [100, $(\text{C}_5\text{H}_5)_2\text{FTi}^+$], 178 [91, $(\text{C}_5\text{H}_5)_2\text{Ti}^+$], 151 [39, $\text{C}_5\text{H}_5\text{F}_2\text{Ti}^+$], 132 [87, $\text{C}_5\text{H}_5\text{FTi}^+$], 113 [19, $\text{C}_5\text{H}_5\text{Ti}^+$], and 65 [70, C_5H_5^+]. Other spectral properties of **4** are given in the Results and Discussion. The molecular weight of **4** (osmometric in benzene) was 723 (calcd 698).

In a modification of the above experiment dicarbonyltitanocene (1.00 g, 4.3 mmol) was dissolved in 150 mL of pentane in a Schlenk tube, and the solution was cooled to -78 °C. Hexafluoro-2-butyne (1.5 mL) was condensed into a second evacuated Schlenk tube and then added to the pentane solution. The reaction vessel was fitted with a dry-ice reflux condenser, and a mercury overpressure valve was attached. The reaction mixture was stirred at room temperature for 3 h during which time steady gas evolution occurred, the solution lightened in color, and a yellow precipitate formed. The reaction mixture was concentrated under reduced pressure to 50 mL and filtered over a glass frit. The resulting orange powder was shown to be **4** by means of ¹H NMR, IR, and mass spectral analyses.

X-ray Data Collection and Structure Determination for 4. Single crystals of the orange, air-stable compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $[(\sin \theta)/\lambda]^2$ values for 15 reflections ($\theta > 16^\circ$), accurately centered on the diffractometer, are presented in Table I. The crystal system is triclinic, and subsequent structure determination and refinement showed the space group to be $P\bar{1}$ [C_2 , No. 2].

Data were collected on an Enraf-Nonius CAD-4 diffractometer in the usual manner.³³

One independent hemisphere of data was measured out to $2\theta \leq 50^\circ$; a slow scan was performed on a total of 4888 unique reflections. Since the 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 10 was obtained in the prescan. On the basis of these considerations, the data set of 4888 reflections (used in the subsequent structural determination and refinement) was considered observed and consisted of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Full-matrix, least-squares refinement was carried out by using the Busing and Levy program ORFLS.³⁴ The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors for Ti, F, O, and C were taken from the compilations of Cromer and Waber;³⁵ those for H were from ref 36.

Since $Z = 4$ in the space group $P\bar{1}$, it was necessary to locate two complete molecules. Efforts to position the titanium atoms via Patterson methods proved fruitless, and the metal atoms were eventually found with the aid of the program MULTAN.³⁷ At this point $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.54$. The positions of the remaining 82 nonhydrogen atoms in the asymmetric unit were deduced by the repeated application of difference Fourier techniques. Least-squares refinement of the nonhydrogen atoms with isotropic temperature factors led to a reliability index of $R_1 = 0.11$. Conversion to anisotropic thermal parameters and further refinement led to $R_1 = 0.064$. The hydrogen atoms were then placed at calculated positions 1.00 Å from the bonded carbon atom, and their parameters were not refined. Further refinement of the nonhydrogen parameters yielded a final R_1 value of 0.041 and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum(F_o)^2\}^{1/2} = 0.041$. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their standard deviations. The esd of an observation of unit weight was 1.54. No systematic variation of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table II.

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Supplementary Material Available: Tables of hydrogen atom coordinates, other bond lengths and angles, and least-squares plane results and a listing of observed and calculated structure factor amplitudes (36 pages). Ordering information is given on any current masthead page.

(34) Crystallographic programs used on a Univac 1110 include ORFLS (structure factor calculation and least-squares refinement, by W. R. Busing, K. O. Martin, and H. A. Levy), ORFFE (distances and angles with esd's, by W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program), and BPL (least-squares planes, by W. E. Hunter).

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