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Trityltitanium Complexes. X-ray Structural Characterization of $[Ti(CO)_4\{\eta^5\text{-}C(4\text{-}C_6H_4R)_3\}]^-$ (R = H, OCH_3)[1]

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Summary: Reactions of $[Ti(CO)_6]^{2-}$ and chlorotriphenylmethane or chlorotris(4-methoxyphenyl)methane provide the first examples of trityltitanium complexes. These have been shown by IR, NMR, and single-crystal X-ray structural characterizations to have the molecular formula $[Ti(CO)_4\{\eta^5\text{-}C(4\text{-}C_6H_4R)_3\}]^-$ (R = H, OCH_3).

Metal carbonyl anions are key precursors to a tremendous variety of organometallic and inorganic compounds.[2] Their reactions with organic electrophiles are especially useful in the synthesis of new (hydrocarbyl)-metal complexes, which, in turn, are often important as catalysts or intermediates in organic syntheses.[3] Although hydrocarbyl complexes containing titanium in positive oxidation states, especially II to IV, are numerous and well-established,[4] relatively few corresponding zerovalent titanium compounds are known, and all of these have contained only cyclopentadienyl type ligands.[5] Interactions of organic electrophiles with hexacarbonyltitanate(2−), $[Ti(CO)_6]^{2-}$,[6a] represent potentially general, but entirely unexplored, routes to novel Ti(0) organometallics. We now report on the first reactions of this type. These involve the interaction of $[Ti(CO)_6]^{2-}$ with trityl chlorides to generate compounds of the formulation $[Ti(CO)_4\{C(4\text{-}C_6H_4R)_3\}]^-$, (R = H (**1**), OMe (**2**)) (eq 1). Compounds **1** and **2** are of interest as the first examples of group 4 metal trityl complexes and contain substantially more labile hydrocarbyl ligands than does the related $[Ti(CO)_4(\eta^5\text{-}C_5H_5)]^-$, (**3**).[6b]

$$[Ti(CO)_6]^{2-} + C(4\text{-}C_6H_4R)_3Cl \xrightarrow[-50 \text{ to } +20\ ^\circ C]{THF} [Ti(CO)_4\{C(4\text{-}C_6H_4R)_3\}]^- + Cl^- + 2CO \quad (1)$$

$$R = H\ (\mathbf{1}),\ OMe,\ (\mathbf{2})$$

Trityl halides, salts, or substituted versions thereof are often effective one-electron oxidants and usually react with metal carbonyl anions to give metal carbonyl oxidation products and trityl dimer,[7a] rather than isolable metal trityl complexes. For example, the isoelectronic $[V(CO)_6]^-$ reacts with 1 equiv of trityl chloride in CH_2Cl_2 to yield only paramagnetic $V(CO)_6$ and trityl dimer.[7b] To our knowledge, the only prior "successful" reaction of this type was that of $[Re(CO)_5]^-$ and $[CPh_3][PF_6]$, which provided a 37% isolated yield of $Re(CO)_4(\eta^3\text{-}CPh_3)$. Structural characterization of the latter species showed that the trityl group was present as a substituted η^3-benzyl ligand.[8] Thermolysis of this η^3-trityl complex afforded $Re(CO)_3(\eta^5\text{-}CPh_3)$, the only previous structurally characterized η^5-trityl complex.[8c] Reactions of these two species with L = $P(OCH_2)_3CCH_3$ gave $Re(CO)_4L(CPh_3)$ and $Re(CO)_3L_2(CPh_3)$, respectively, which are believed to contain η^1-CPh_3 groups.[9] Trityl−transition-metal complexes are quite rare. Other reported examples include $Ni(CPh_3)Cl$,[10] $Ni(CPh_3)_2$,[10] $[Co(\eta^5\text{-}CPh_3)(C_5H_5)]^+$,[11] $M(CPh_3)Cl$,[12] and $M(\eta^3\text{-}CPh_3)(acac)$[12] (M = Pd, Pt), only the last two of which have been structurally characterized.[13]

A typical synthesis of **1** involved the addition of a solution of trityl chloride (0.340 g, 1.22 mmol) in THF (50 mL, −45 °C) with vigorous stirring to a suspension of finely divided $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$ (1.43 g, 1.22 mmol) in THF (30 mL, −50 °C). The reaction mixture was warmed from −50 to 0 °C over a period of 16 h with efficient stirring. Following filtration at 0 °C, all solvent was removed from the deep red filtrate. Vigorous trituration of the product with diethyl ether (100 mL, 0 °C) caused it to solidify to red microcrystals. These were recrystallized from THF−ether at 0 °C to provide 0.300 g (28% yield) of air-sensitive red microcrystals of pure $[K(15\text{-crown-}5)_2]$[**1**].[14ab] A very similar procedure gave satisfactorily pure $[K(15\text{-crown-}5)_2]$[**2**] in 30% isolated yield.[14c] Attempts to obtain **1** by analogous reactions with $[CPh_3][X]$ (X = BF_4, PF_6) were unsuccessful.

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Infrared spectra for **1** and **2** in the ν(CO) region are virtually identical and show nearly the same two-band pattern previously observed for **3**.[15] NMR spectral data for **1** and **2** are also consistent with the presence of (η^5-dienyl)tetracarbonyltitanate(1−) moieties.[14] Comparison of the IR ν(CO) and ^{13}C NMR δ(CO) positions of **1** (1932 (m) and 1810 (s) cm^{-1} (THF) and 279.6 ppm (THF-d_8)) with corresponding values of **3** (1921 (m) and 1783 (s) cm^{-1} (DME) and 289 ppm (DMSO-d_6))[15] indicates that the trityl group is a significantly weaker donor than is the cyclopentadienyl ligand in these titanium complexes. These data suggested that the bound trityl group should be labile. Indeed, treatment of **1** with excess L = 1,4,7-triazacyclononane (tacn; 2 equiv) or hydridotris(1-pyrazolyl)borate (Tp$^-$; 3 equiv as the K$^+$ salt) in THF gave quantitative conversion (by infrared spectra) within 25 min at 20 °C to the corresponding previously known [Ti(CO)$_4$L].[16] While **3** does not undergo CO exchange reactions at 20 °C under strictly anaerobic conditions,[17] **1** underwent complete carbonyl exchange with ^{13}CO within 3 h in THF at −10 °C.[18] In the latter reaction, no spectral evidence for the formation of a higher carbonyl species, such as the presently unknown [Ti(CO)$_5$(η^3-CPh$_3$)]$^-$, was obtained.

Since structural details for a (η^5-trityl)metal complex have not been previously reported in the scientific literature[8c] and spectral data did not unambiguously specify the nature of the trityl−titanium interactions present in **1** and **2**, single-crystal X-ray structural characterizations were carried out on these species.[19] Only the details of **1** will be described herein, because the structures of **1** (Figure 1) and **2** are very similar. Both anions contain tetracarbonyltitanium units that are best described as being bound to η^5-dienyl groups (vide infra) and are thereby closely related to the "half sandwich" carbonyl species **3**, the only previous structurally characterized (η^5-dienyl)titanium(0) complex.[6a] Important average structural parameters for the Ti(CO)$_4$ unit in **1** are as follows: Ti−C, 2.020(6) Å; C−O, 1.163(7) Å; C−Ti−C (cis), 73(2)°; C−Ti−C (trans), 114(3)°. All of these values are statistically indistinguishable from the corresponding ones reported for **3**, except the Ti−C(carbonyl) distance, which is 0.026 Å (~4σ) longer than the distance of 1.994(7) Å for **3**.[6a] Similarly, the average Ti−C(dienyl) distance of 2.42(3) Å for **1** is appreciably longer than the analogous value of 2.36(1) Å for **3**. These data are in accord with the aforementioned spectral data for **1** and **3** and firmly establish that the trityl group is more weakly bound to titanium than the η^5-cyclopentadienyl group is in these complexes. The coordinated phenyl ring in **1** is folded at C(3) and C(7) with a dihedral angle of only 14.9°, a significantly smaller angle than corresponding values of 46, 33, and 22° reported for Ti(η^5-dmCh)$_2$CO (**4**; dmCh = 6,6-dimethylcyclohexadienyl)[20] Fe(η^5-C$_5$H$_5$)(η^5-C$_6$Me$_5$-

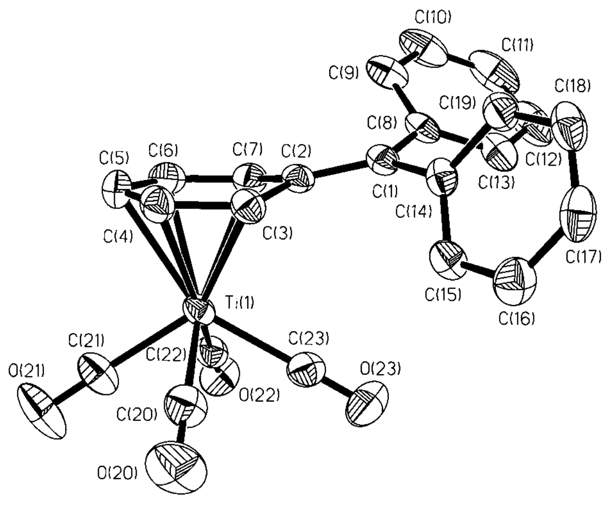

Figure 1. Molecular structure of **1** showing the labeling scheme (50% probability ellipsoids; hydrogens omitted for clarity). Selected bond lengths (Å), and angles (deg): Ti−C(20), 2.024(6); Ti−C(21), 2.017(6); Ti−C(22), 2.022(5); Ti−C(23), 2.016(6); C(20)−O(20), 1.170(7); C(21)−O(21), 1.158(7); C(22)−O(22), 1.159(6); C(23)−O(23), 1.165(6); Ti−C(2), 2.723(5); Ti−C(3), 2.450(5); Ti−C(4), 2.396(5); Ti−C(5), 2.405(5); Ti−C(6), 2.396(5); Ti−C(7), 2.463(5); C(1)−C(2), 1.387(6); C(1)−C(8), 1.490(7); C(1)−C(14), 1.474(7); C(2)−C(3), 1.458(6); C(2)−C(7), 1.458(7); C(3)−C(4), 1.395(7); C(4)−C(5), 1.394(7); C(5)−C(6), 1.411(8); C(6)−C(7), 1.384(7); C(3)−C(2)−C(7), 110.3(4); C(1)−C(2)−C(7), 124.2(4); C(1)−C(2)−C(3), 124.1(4); C(2)−C(1)−C(8), 122.4(4); C(2)−C(1)−C(14), 122.2(4); C(8)−C(1)−C(14), 115.4(4); average Ti−C−O, 178.2(8).

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[14] (a) Satisfactory elemental analyses were obtained for **1** and **2** as unsolvated [K(15-crown-5)$_2$]$^+$ salts. (b) Selected spectral data for **1**: IR ν(CO) (Nujol mull) 1927 (m), 1836 (m, sh), 1794 (s) cm^{-1}; ^{1}H NMR (300 MHz, THF-d_8, 0 °C) δ 7.09 (d, J = 7.5 Hz, 4H, *o*-H, free ring), 6.94 (t, J = 7.5 Hz, 4H, *m*-H, free ring), 6.65 (t, J = 7.8 Hz, 2H, *p*-H, free ring), 5.40 (d, J = 7.8 Hz, 2H, *o*-H, bound ring), 5.07 (t, J = 7.8 Hz, 2H, *m*-H, bound ring), 4.51 (t, J = 6.3 Hz, 1H, *p*-H, bound ring), 3.53 (s, 40H, 15-crown-5) ppm; ^{13}C{^{1}H} NMR (75 MHz, THF-d_8, 0 °C) δ 279.6 (CO), 147.7 (*ipso*-C, free ring), 131.2 (*o*-C, free ring), 131.1 (α-C), 128.3 (*m*-C, free ring), 122.1 (*p*-C, free ring), 111.1 (*m*-C, bound ring), 96.9 (*ipso*-C, bound ring), 92.3 (*o*-C, coord ring), 86.0 (*p*-C, bound ring), 69.5 (15-crown-5) ppm. Heteronuclear chemical shift correlation (HETCOR) spectroscopy was used to assign carbon resonances of bound and free rings. (c) Selected spectral data for **2**: IR ν(CO) (THF) 1932 (m), 1812 (s) cm^{-1}; ^{1}H NMR (300 MHz, THF-d_8, 0 °C) δ 6.98 (d, J = 8.4 Hz, 4H, *m*-H, free ring), 6.54 (d, J = 8.5 Hz, 4H, *o*-H, free ring), 5.08 (m, 4H, *o*-/*m*-H, bound ring), 3.60 (s, 6H, OCH_3, free ring), 3.53 (s, 40H, 15-crown-5), 3.43 (s, 3H, OCH_3, bound ring) ppm; ^{13}C{^{1}H} NMR (75 MHz, THF-d_8, 0 °C) δ 278.5 (CO), 155.2 (*p*-C, free ring), 140.7 (*ipso*-C, free ring), 135.3 (*p*-C, bound ring), 131.4 (*m*-C, free ring), 129.4 (α-C), 113.8 (*o*-C, free ring), 98.7 (*m*-C, bound ring), 91.2 (*ipso*-C, bound ring), 84.3 (*o*-C, bound ring), 69.7 (15-crown-5), 55.6 (OCH$_3$, bound ring), 55.0 (OCH$_3$, free ring). HETCOR NMR spectroscopy was used to assign the carbon resonances of bound and free rings.

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[18] Observed IR ν(^{13}CO) of **1**: 1888 (m), 1770 (s) cm^{-1} (THF). Calcd ν(^{13}CO): 1889, 1770 cm^{-1}.

[19] (a) Crystal data for [K(15-crown-5)$_2$][**1**]·$^1/_2$C$_6$H$_{12}$: C$_{46}$H$_{61}$KO$_{14}$Ti, M_r = 924.95, triclinic, $P1$, red plate, a = 9.4520(2) Å, b = 12.7290(3) Å, c = 20.0869(5) Å, α = 73.330(1)°, β = 85.727(1)°, γ = 86.243(1)°, V = 2306.27(9)Å^3, Z = 2, final residual R = 0.0800, GOF = 1.030 on F^2. The asymmetric unit contained half of a molecule of the solvent cyclohexane. The sandwich bis(15-crown-5)potassium cations are split over two half-occupied units on special positions. One is ordered with an average K−O distance of 2.90(7) Å,which compares well with previous values (cf.: Fischer, P. J.; Young, V. G., Jr.; Ellis, J. E. *Chem. Commun.* **1997**, 1249), but the other is rotationally disordered along its 5-fold axis. The ordered cation was used as a model for the second for restraints. Only the potassium atom was allowed to be anisotropic, while all partially occupied bis(15-crown-5) groups were refined as isotropic groups. (b) Crystal data for [K(15-crown-5)$_2$][**2**]: C$_{46}$H$_{61}$KO$_{17}$Ti, M_r = 972.95, triclinic, $P\bar{1}$, irregular red block, a = 9.1205(1) Å, b = 12.2694(1) Å, c = 22.7257(1) Å, α = 76.382(1)°, β = 86.007(1)°, γ = 83.965(1)°, V = 2455.23(4) Å^3, Z = 2, final residual R = 0.0766, GOF = 1.014 on F^2. One bis(15-crown-5)potassium cation is ordered well, while the other is disordered in a 50:50 ratio. Both potassium ions reside on inversion centers. For further details, see the Supporting Information.

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CH_2) (**5**),[21] and $Re(CO)_3(\eta^5\text{-}CPh_3)$[8c] (**6**), respectively. The large nonbonded Ph_2C group in close proximity to the seven-coordinate titanium center undoubtedly contributes to a partial η^5- to η^3-ring slippage present in **1**; i.e., the titanium is 0.057 Å (~10σ) closer to carbons C(4)−C(6) than to C(3) and C(7) in the bound phenyl group. However, since the five bound carbons, C(3)−C(7), lie in a plane with an average C−C distance of 1.40(1) Å, which is not significantly different than the corresponding value of 1.37(2) Å found for **3**,[6a] **1** is clearly best described as a η^5- rather than a η^3-hydrocarbyl complex. NMR data for **1** are also entirely consistent with this formulation.[14] Compound **4**, which contains two rather bulky η^5-6,6-dimethylcyclohexadienyl ligands bound to seven-coordinate Ti(II), is even more "ring slipped" than **1**, where the difference in corresponding average Ti−C distances is 0.096 Å (~10σ).[20] In contrast, the related Ti(II) species $Ti(\eta^5\text{-dmp})_2(PF_3)$ (dmp = 2,4-dimethylpentadienyl)[22] has more uniform Ti−C distances, where the analogous difference is only 0.019 Å (~6σ).

Compounds **1** and **5**[21] are rare examples of substituted η^5-benzyl complexes and contain exocyclic double bonds, defined by C(1)−C(2), of virtually identical lengths, i.e. 1.387(6) and 1.376(9) Å, respectively. Another similarity in the structures of **1** and **5** is that the trigonal-planar exocyclic carbons, i.e., C(1), are both slightly bent upward by 10° relative to the C(2)−C(3)−C(7) plane. Anions **1** and **2** are well-separated from the $[K(15\text{-crown-}5)_2]^+$ cations in their respective crystalline lattices. Reactions of $[Ti(CO)_6]^{2-}$ with other organic electrophiles are under examination and will be reported on separately.

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Supporting Information Available: Complete crystallographic data for **1** and **2**, including structural details of the counterions (18 pages). Ordering information is given on any current masthead page.

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