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Journal of Organometallic Chemistry 593–594 (2000) 354–360

Journal of Organometallic Chemistry

Highly reduced organometallics Part 49. Reaction of hexacarbonyltitanate(2 –) with azobenzene. Structural characterization of the first hydroxo-carbonyl of titanium $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$ ☆

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Received 28 June 1999; accepted 22 September 1999

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday and for his valued friendship and superb contributions to chemistry over the past 40 + years.

Abstract

Hexacarbonyltitanate(2 –) reacts with azobenzene to provide 40–65% yields of $[Ti(PhNNPh)(CO)_4]^{2-}$, which is formulated as a 1,2-diphenylhydrazido dianion adduct of zerovalent titanium tetracarbonyl. The latter undergoes very facile hydrolysis to provide 1,2-diphenylhydrazine and the first hydroxo-carbonyl of titanium $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$, which has been structurally characterized as the $[K(18\text{-crown-}6)]^+$ salt. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Carbonyl; Azobenzene; Hydroxo complexes

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1. Introduction

Metal carbonyl anions have a rich history in organometallic chemistry and are useful precursors to a wide variety of products containing transition metals, especially in zero or higher formal oxidation states [2]. Over the past 40 years, many of the fundamentally important contributions to our understanding of the syntheses and properties of these reagents are due to the remarkable pioneering efforts of Professor Fausto Calderazzo and members of his dedicated and talented research group. His contributions to Group 5 metal arene and carbonyl chemistry have been particularly significant [3]. Indeed, much of what is presently known about the properties of the hexacarbonylmetallates(1 –) of vanadium, niobium and tantalum, are a result of the careful systematic studies on these species carried out by his group in Pisa [4]. In recent years our interests have focused on the isoelectronic hexacarbonylmetallates(2 –) of the Group 4 elements [5]. We have found $[Ti(CO)_6]^{2-}$ to be a convenient precursor to new classes of zerovalent titanium complexes [6]. Thus, $[Ti(CO)_6]^{2-}$ resembles $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ in that it undergoes facile two-electron processes with a variety of oxidants. However, the titanate(2 –) is far more easily oxidized than the niobium or tantalum complexes.

For example, $[Ti(CO)_6]^{2-}$ quickly reacts with neat methanol and ethanol at room temperature (r.t.) [7], while $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ form stable solutions in these solvents under the same conditions. Formally unsaturated six-coordinate Ti(0) carbonyls of the general formula $[Ti_2(\mu\text{-}OR)_2(CO)_8]^{2-}$, R = Me, Ph, were recently prepared from the interaction of $[Ti(CO)_6]^{2-}$ with the corresponding ROH [8a]. These dimers are of considerable interest since their spectral, chemical, and structural properties indicate that the bridging RO^- groups function as six electron donors and are in this sense electronically equivalent to pentahapto-cyclopentadienide ligands. The isolobal analogy between organoimido, RN^{2-}, and $\eta^5\text{-}C_5R_5^-$ is also important in suggesting new inorganic/organometallic

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☆ For Part 48 see Ref. [1].

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PII: S0022-328X(99)00551-3

'target' molecules [9], so we have been interested in accessing possible organoimido analogs of the dimeric $[Ti_2(\mu\text{-}OR)_2(CO)_8]^{2-}$ [8a] or the monomeric $[Ti(CO)_4(\eta^5\text{-}C_5R_5)]^-$ [8c]. Reports that azobenzene (diphenyl diazene) can be reduced by the formally divalent titanium complex $Ti(TPP)(\eta^2\text{-}RC{\equiv}CR)$, TPP = *meso*-tetra-*p*-tolylporphyrinato, R = Et or Ph, to provide the phenylimido complex, Ti(TPP)(NPh) [10], prompted an examination of the reaction of $[Ti(CO)_6]^{2-}$ with azobenzene. Although this route did not yield the desired phenylimido complex, the first example of a diazene substituted titanium carbonyl was obtained in this reaction. The latter compound was found to undergo extremely facile hydrolysis to provide good yields of the first hydroxo-carbonyl titanium complex.

2. Experimental

2.1. General procedures and starting materials

All operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal or other materials impermeable to air. Solutions were transferred via stainless steel double ended needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line [11]. Glassware was oven dried before use. Syntheses of $X_2[Ti(CO)_6]$, X = K(15-crown-5)$_2$ and K(18-crown-6) were carried out according to modifications of published procedures [12]. Solvents were freed of impurities by standard procedures and stored under argon. Unless otherwise stated, other reagents were obtained from commercial sources and freed of oxygen and moisture before use. Solution IR spectra were recorded on a Mattson Galaxy 6021 FTIR spectrometer with samples sealed in 0.1 mm NaCl or CaF_2 cells. Nujol (mineral oil) mulls of air-sensitive compounds for IR spectra were prepared in a Vacuum Atmospheres Corp. drybox. NMR samples were sealed into 5 mm tubes and were run on a Varian Unity 300 or 500 spectrometers. Titanium analyses were carried out by a standard procedure [13].

2.1.1. Oxidation of $X_2[Ti(CO)_6]$ by azobenzene: synthesis of $X_2[Ti(PhNNPh)(CO)_4]$. X = [K(15-crown-5)$_2$] (**1**)

Only the synthesis of the compound with the bis(15-crown-5)potassium counterion is described in detail. The other, with X = 18-crown-6, was performed in similar fashion. A solution of $[K(15\text{-}C\text{-}5)_2]_2[Ti(CO)_6]\cdot 2py$ (1.78 g, 1.4 mmol) in pyridine (150 ml) was treated at 0°C with a cold (0°C) solution of PhN=NPh (0.26 g 1.4 mmol) in pyridine (20 ml). The reaction mixture turned yellowish–brown at once. After 2 h stirring at 0°C, the solvent was removed in vacuo at 0°C until about 50 ml were left. THF (200 ml) was added. The resulting suspension was filtered and the solvent was removed in vacuo at r.t. THF (50 ml) was added to the residue at 0°C (when starting from $[K(18\text{-}C\text{-}6)]_2[Ti(CO)_6]$ Et_2O was used because the solubility of the product in THF is too high). The resulting greenish–brown suspension was filtered, the dark brown–greenish solid was washed with 2 × 5 ml of THF and dried, providing 1.26 g (65% yield) of **1**. Anal. Found: Ti, 3.37. Calc.: for $[K(15\text{-}C\text{-}5)_2]_2[Ti(PhNNPh)(CO)_4]\cdot py$ ($C_{61}H_{95}K_2N_3O_{24}Ti$): Ti, 3.47%. ^1H-NMR spectra were also consistent with this composition. IR (Nujol): $\nu = 3043$ w, 1893 m, 1749 s, 1725 s, 1578 m, 1542 w, 1376 w, 1321 m, 1294 m, 1273 m, 1251 m, 1122 s, 1088 s, 1039 m, 989 w, 979 w, 940 m, 855 m, 830 w, 735 w, 693 w cm^{-1}. IR (pyridine), ν_{CO}: 1899 m, 1755 s cm^{-1}. IR (CH_3CN), ν_{CO}: 1902 m, 1756 s cm^{-1}. IR (THF), ν_{CO}: 1891 w, 1737 m cm^{-1}. ^1H-NMR (300 MHz, pyridine-d_5, 0°C): $\delta = 3.5$ (s, 15-crown-5), 6.3–8.0 (m, aromatic) 8.7 (s, py) ppm. $^{13}C\{^1H\}$ (75 MHz, pyridine-d_5, 0°C): $\delta = 69$ (s, 15-crown-5), 108–129 (s, aromatic), 164 (s, *ipso*-C), 302 (s, CO) ppm.

2.1.2. X = [K(18-crown-6)] (**2**)

Composition determined by ^1H-NMR, 45% yield. IR (Nujol): $\nu = 3040$ w, 1896 m, 1739 s, 1718 s, 1578 m, 1547 w, 1376 w, 1324 w, 1286 w, 1249 w, 1108 s, 981 m, 869 w, 838 w, 796 w, 740 w, 695 w cm^{-1}. IR (pyridine), ν_{CO}: 1897 m, 1750 s cm^{-1}, IR (THF), ν_{CO}: 1895 w, 1757 m cm^{-1}. ^1H-NMR (300 MHz, pyridine-d_5, 0°C), $\delta = 3.3$ (s, 18-crown-6), 6.2–7.8 (m, aromatic), $^{13}C\{^1H\}$ (75 MHz, pyridine-d$_5$, 0°C), $\delta = 71$ (s, 18-crown-6), 108–129 (s, aromatic), 163.5 (s, *ipso*-C), 301 (s, CO) ppm.

$X_2[Ti(PhNNPh)(CO)_4]$ (X = $[K(15\text{-}C\text{-}5)_2]^+$ or $[K(18\text{-}C\text{-}6)]^+$) is soluble in pyridine, CH_3CN, and slightly soluble in THF. It is insoluble in Et_2O, toluene, pentane at 0°C. It is stable in pyridine at 0°C for a few days, but much less stable in CH_3CN at 0°C.

2.1.3. Reaction of $X_2[Ti(PhNNPh)(CO)_4]$ with H_2O: synthesis of $X_2[Ti_2(\mu\text{-}OH)_2(CO)_8]$. X = [K(15-crown-5)$_2$] (**3**)

Only the preparation of the bis(15-crown-5) potassium salt will be described in detail. The other, X = [K(18-crown-6)] (**4**) was performed in a similar manner. A suspension of $[K(15\text{-}C\text{-}5)_2]_2[Ti(PhNNPh)(CO)_4]\cdot py$ (0.20 g, 0.15 mmol) in 50 ml of THF was cooled to −70°C and then 2.2 ml (0.3 mmol) of a 0.14 M solution of H_2O in THF was added. An immediate color change from brown to red occurred. The suspension was stirred for 3 h at $-70°C \leq T \leq -40°C$, and 0°C for 2 h. An IR spectrum of the supernatant solution showed no bands in the carbonyl stretching region. The suspension was filtered and the red solid was dried in vacuo, 0.080 g (82% yield) of **3** was obtained. Anal. Found: Ti, 7.2. Calc. for unsolvated [K(15-crown-5)$_2$]$_2$[Ti$_2$(μ-OH)$_2$(CO)$_8$] ($C_{48}H_{82}K_2O_{30}Ti_2$): Ti, 7.3. ^{1}H-NMR spectra were also consistent with this composition. IR (pyridine), ν_{CO}: 1897 m, 1751 s cm^{-1}. IR (Nujol): ν = 3708 w, 1892 m, 1739 s, 1357 w, 1304 w, 1249 w, 1121 m-s, 1093 m-s, 1041 m, 925 m, 856 w cm^{-1}. ^{1}H-NMR (300 MHz, pyridine-d_5, 0°C): $\delta = 3.5$ (s, 15-crown-5), 5.0 (s, μ-OH) ppm. ^{13}C{^{1}H}-NMR (75 MHz, pyridine-d_5, 0°C): $\delta = 69$ (s, 15-crown-5), 294 (s, CO) ppm.

2.1.4. X-ray structure determination of [K(18-crown-6)]$_2$ [Ti$_2$(μ-OH)$_2$(CO)$_8$]·2py (4)

The compound was recrystallized by slow diffusion of Et$_2$O into a solution of **4** in pyridine at 0°C. All measurements were carried out with a Siemens SMART system at 173(2) K. Crystal data, data collection parameters and convergence results were compiled in Table 1. The space group $P2_1/c$ was determined based on systematic absences and intensity statistics [14]. A successful direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. A value of $R =$

Table 1
Crystal data and structure refinement for [K(18-C-6)]$_2$[Ti$_2$(μ-OH)$_2$(CO)$_8$]·2py (**4**)

Compound	[K(18-C-6)]$_2$[Ti$_2$(μ-OH)$_2$(CO)$_8$]·2py
Empirical formula	$C_{42}H_{60}K_2N_2O_{22}Ti_2$
Molecular Weight	1118.92
Crystal habit, color	Plate, red
Crystal size (mm)	0.40 × 0.18 × 0.05
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell constants	
a (Å)	15.496(3)
b (Å)	15.374(3)
c (Å)	11.245(2)
β (°)	91.02(3)
Volume (Å^3)	2678.4(9)
Z	2
$D_{calc.}$ (g cm^{-3})	1.387
Absorption coefficient (mm^{-1})	0.530
F(000)	1168
θ range for data collection (°)	1.31–25.03
Measured reflections	9448
Independent reflections	4499 [$R_{int} = 0.0309$]
Weighting scheme	$w = [\sigma^2(F_o^2)+(AP)^2+(BP)]^{-1}$, where $P = (F_o^2+2F_c^2)/3$ $A = 0.0626$, $B = 0.0$
Absorption correction	SADABS (Sheldrick, 1996)
Data/restraints/parameters	4498/0/319
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0593$ $wR_2 = 0.1086$
R indices (all data)	$R_1 = 0.1327$ $wR_2 = 0.1451$
Goodness-of-fit on F^2	0.919

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters for [K(18-C-6)]$_2$[Ti$_2$(μ-OH)$_2$(CO)$_8$]·2py (**4**) [a]

Atom	*x*	*y*	*z*	B_{eq} (Å^2 × 10^2)
Ti(1)	5938(1)	5205(1)	705(1)	34(1)
K(1)	5000	5000	5000	40(1)
K(2)	10 000	5000	5000	35(1)
C(1)	6567(3)	6321(4)	878(5)	56(2)
O(1)	6987(3)	6951(2)	1013(5)	96(2)
C(2)	7134(3)	5190(3)	33(4)	35(1)
O(2)	7850(2)	5225(2)	−287(3)	48(1)
C(3)	6679(3)	4356(3)	1581(4)	37(1)
O(3)	7139(2)	3883(2)	2097(3)	62(1)
C(4)	6080(3)	5532(3)	2423(5)	49(1)
O(4)	6204(2)	5714(3)	3422(4)	79(1)
O(5)	4626(2)	5105(2)	899(3)	51(1)
C(5)	4186(3)	7193(3)	4796(5)	55(2)
O(6)	3831(2)	6353(2)	4562(3)	43(1)
C(6)	3357(3)	6309(3)	3478(5)	51(1)
C(7)	3025(3)	5409(3)	3321(4)	49(1)
O(7)	3740(2)	4838(2)	3151(3)	40(1)
C(8)	3475(3)	3958(3)	2974(5)	49(1)
C(9)	4255(3)	3400(3)	2856(4)	48(1)
O(8)	4708(2)	3387(2)	3970(3)	43(1)
C(10)	5415(3)	2805(3)	3990(5)	53(2)
N(1)	11 096(3)	6436(3)	4700(4)	55(1)
C(11)	10 927(3)	7117(4)	4004(5)	52(1)
C(12)	11 221(3)	7933(4)	4221(6)	60(2)
C(13)	11 712(4)	8068(4)	5224(6)	67(2)
C(14)	11 906(4)	7386(4)	5953(5)	61(2)
C(15)	11 589(3)	6595(3)	5652(5)	53(2)
O(9)	9030(2)	6031(2)	3383(4)	64(1)
C(16)	8820(5)	5624(5)	2280(6)	95(3)
C(17)	9622(6)	5249(5)	1801(5)	99(3)
O(10)	9891(2)	4558(3)	2559(3)	63(1)
C(18)	10 661(5)	4173(6)	2186(6)	109(3)
C(19)	10 905(4)	3467(6)	2976(8)	108(3)
O(11)	11 151(2)	3811(3)	4114(4)	68(1)
C(20)	11 411(4)	3167(4)	4928(9)	103(3)
C(21)	11 709(4)	3584(5)	6040(8)	93(3)

[a] Estimated standard deviations in parenthesis refer to the least significant digit.

0.059 was obtained. The coordinates of the non-hydrogen atoms are listed in Table 2.

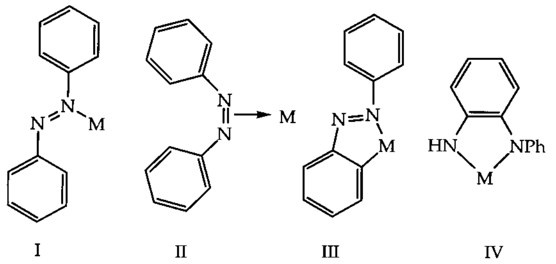
3. Results and discussion

3.1. Interaction of azobenzene with $[Ti(CO)_6]^{2-}$: synthesis of $[Ti(CO)_4(PhNNPh)]^{2-}$, a Ti(0) complex containing a coordinated 1,2-diphenylhydrazido dianion

The transition metal chemistry of azobenzene is both extensive and varied. The resulting metal derivatives may be useful either as stoichiometric reagents or for catalytic applications, especially if unusual heterocyclic systems can be obtained in one- or two-step reactions [15]. The interaction of azobenzene with transition metal derivatives can produce complexes of at least four different types (Scheme 1):

1. the azo compound is bonded to the metal via the nitrogen lone-pair, I;
2. the azo compound is bonded to the metal via the π electrons of the N=N group, II;
3. carbon- and nitrogen-bonded metallated systems, III;
4. a metal-bonded rearranged nitrogen-donor ligand, e.g. *o*-semidine (*o*-aminodiphenylamine), IV.

Salts of $[Ti(CO)_6]^{2-}$ quickly react with azobenzene in pyridine at 0°C to afford greenish–brown compounds identified as $X_2[Ti(PhNNPh)(CO)_4]$ ($X = [K(15\text{-}C\text{-}5)_2]$ (**1**); $[K(18\text{-}C\text{-}6)]$ (**2**)) (Eq. (1)) by elemental analysis of titanium, IR and NMR spectroscopy.



Scheme 1. Coordination modes of azobenzene and rearranged ligand systems derived therefrom.

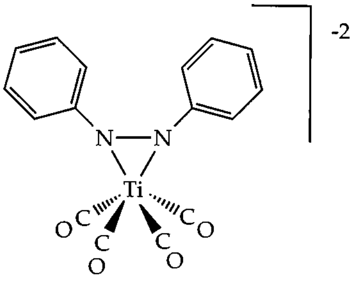


Fig. 1. Proposed structure for $[Ti(PhNNPh)(CO)_4]^{2-}$.

$$X_2[Ti(CO)_6] + PhN{=}NPh \xrightarrow[0°C]{py} X_2[Ti(PhNNPh)(CO)_4] + 2CO \qquad (1)$$

IR spectra of $[Ti(PhNNPh)(CO)_4]^{2-}$ in pyridine are essentially cation independent in the ν_{CO} region and exhibit the band pattern ($A_1 + E$) characteristic of a conventional 18-electron titanium tetracarbonyl moiety of symmetry C_{4v} [16]. The $[Ti(CO)_4]$ fragment in solution appears to be substantially unperturbed, thus excluding ion pairing.

Of substantial interest is the fact that the $\nu(CO)$ values of 1897 m, 1750 s cm^{-1}, in pyridine for **2** are at about the same energy as those reported for the dimeric $[Ti_2(\mu\text{-}OCH_3)_2(CO)_8]^{2-}$, 1900, 1758 cm^{-1}, which was suggested to contain electronically saturated $[Ti(CO)_4]$ units on the basis of spectral, chemical and X-ray structural data [8a]. Also these $\nu(CO)$ values are lower in energy than those reported for the bona fide 18-electron complexes $[Ti(\eta^5\text{-}C_5H_5)(CO)_4]^-$, 1921, 1777 cm^{-1} [17], and $[Ti(\eta^3\text{-}Me_3tacn)(CO)_4]$, 1916, 1769 cm^{-1} [18], for which X-ray data are also available. The carbonyl ^{13}C-NMR resonance position of (**1**, **2**) of + 302 ppm is also consistent with the presence of a very electron rich titanium carbonyl complex. Indeed, this value is more downfield than those previously reported for other titanium tetracarbonyl complexes, including $[Ti(\mu\text{-}OCH_3)_2(CO)_8]^{2-}$, $\delta_c = 293$ ppm [8a], and $[Ti(\eta^5\text{-}C_5H_5)(CO)_4]^-$, $\delta_c = 288$ ppm [8b].

Spectroscopic data for compounds **1** and **2** are consistent with the suggestion that the azobenzene ligand has oxidized the Ti(II-) center to Ti(0) and correspondingly has formally been reduced to the 1,2-diphenylhydrazido(2 −) ligand. Ibers and co-workers rationalized this kind of bonding by proposing donation from the azobenzene π-orbitals to vacant orbitals on the metal with concomitant back-donation from filled metal orbitals to the π*-antibonding orbitals of the azo function [19]. This kind of interaction between azobenzene and a Group 4 metal center is well documented in the literature [20]. On the other hand, azobenzene often reacts with lower-valent transition metal carbonyl complexes to generate species containing *ortho*-metallated azo compounds or *o*-semidine as ligands [15]. As azobenzene and its metal-bonded derivatives often present a fluxional behavior in solution [10,21], an X-ray diffraction study would have been useful to unambiguously determine the structures of **1** and **2**. Unfortunately, many attempts to crystallize the various salts of the $[Ti(PhNNPh)(CO)_4]^{2-}$ ion from several solvents, and by varying concentration and temperature, failed. Nevertheless, available data suggest that $[Ti(PhNNPh)(CO)_4]^{2-}$ has the structure shown in Fig. 1. It is noteworthy, that a corresponding monomeric catecholato complex $[Ti(\eta^2\text{-}O_2C_6H_4)(CO)_4]^{2-}$ has quite similar IR and NMR spectral properties in the carbonyl region (Table 3) and has been established by X-ray

Table 3
Selected spectroscopic data for zerovalent titanium tetracarbonyl anions

Compound	IR [a] ν(CO) (cm^{-1})	$^{13}C\{^1H\}$-NMR δ (CO) (ppm)	Ref.
$[TiCp(CO)_4]^-$	1913 m, 1777 s	288.9 [b]	[8b]
$[TiCp^*(CO)_4]^-$	1912 m, 1801 sh, 1747 s	293.0 [b]	[8b]
$[Ti(C_9H_7)(CO)_4]^-$ [h]	1920 m, 1763 s	288.7 [b]	[8c]
$[Ti(HBpz_3)(CO)_4]^-$ [i]	1908 m, 1743 s	286.0 [b]	[8c]
$[Ti\{\eta^5\text{-}C(C_6H_5)_3\}(CO)_4]^-$ [j]	1927 m, 1836 sh, 1794 s	279.6 [c]	[6a]
$[Ti(\eta^2\text{-}O_2C_6H_4)(CO)_4]^{2-}$ [k]	1895 m, 1732 s, br	294.0 [d]	[7]
$[Ti(\mu\text{-}OPh)(CO)_4]_2^{2-}$	1914 m, 1774 s [d]	290.0 [e]	[8a]
$[Ti(\mu\text{-}OMe)(CO)_4]_2^{2-}$	1901 m, 1758 s [f]	289.9 [e]	[8a]
$[Ti(\mu\text{-}OH)(CO)_4]_2^{2-}$	1892 m, 1739 s	294.0 [g]	This work
$[Ti(PhNNPh)(CO)_4]^{2-}$	1893 m, 1749 s, 1725 s	301.5 [g]	This work

[a] Nujol mull spectra.
[b] Solvent, dimethyl-d_6 sulfoxide.
[c] Solvent, THF-d_8.
[d] Solvent, CH_3CN.
[e] Solvent, CD_3CN.
[f] Solvent, dimethyl sulfoxide.
[g] Solvent, pyridine-d_5.
[h] C_9H_7, indenyl.
[i] $HBpz_3$, hydridotris(1-pyrazolyl)borate.
[j] $C(C_6H_5)_3$, triphenylmethyl.
[k] $O_2C_6H_4$, catecholato.

crystallography to contain the same trigonal prismatic geometry about titanium [7], proposed for the azobenzene complex in Fig. 1.

Finally, it is noteworthy that even though the reaction of azobenzene with some transition metal complexes has been reported in the literature to proceed with the breaking of the N=N bond and formation of imido complexes [21b,22], in the reaction of azobenzene with $X_2[Ti(CO)_6]$ the N–N bond appears to be preserved, on the basis of the spectroscopic and analytical properties of the product. Thus, for example, compounds (**1**, **2**) undergo facile reaction with water to give 1,2-diphenylhydrazine as the only nitrogen containing hydrolysis product. The inability of excess $[Ti(CO)_6]^{2-}$ to react with compounds (**1**, **2**) or 1,2-diphenylhydrazine, PhNHNHPh, also indicates that $[Ti(CO)_6]^{2-}$ is incapable of reducing usual N–N single bonds under mild conditions. Also, it is interesting that $[Ti(CO)_6]^{2-}$ is unreactive towards dialkyldiazenes, such as ^{t}BuN=N^{t}Bu.

3.1.1. Hydrolysis of $[Ti(PhNNPh)(CO)_4]^{2-}$: synthesis of $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$, the first hydroxo carbonyls of titanium

Compounds **1** and **2** are extremely moisture sensitive and readily react with stoichiometric amounts of H_2O to produce 1,2-diphenylhydrazine and the previously uncharacterized hydroxo-bridged titanium carbonyl species $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$, according to Eq. (2). Although IR spectral data also suggest that $[Ti(CO)_6]^{2-}$ reacts with excess H_2O to provide the same hydroxo carbonyl product, all attempts to isolate pure substances from these hydrolysis reactions were unsuccessful [6c].

$$2[Ti(PhNNPh)(CO)_4]^{2-} + 4H_2O \underset{-70°C}{\overset{THF}{\rightarrow}} [Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-} + 2OH^- + 2PhNH\text{–}NHPh \quad (2)$$

Thus, the azobenzene complexes presently provide unique routes to the pure bridging hydroxocarbonyltitanates.

Analytical, IR and ^{1}H- and ^{13}C-NMR spectral data are fully consistent with these formulations. The IR Nujol mull spectra show the stretching vibration of the O–H bond at 3708 cm^{-1}, shifted to 2590 cm^{-1} on deuteration (very close to the theoretical value of 2622 cm^{-1}). Comparison of the IR ν_{CO} and ^{13}C-NMR δ (CO) data of **3** and **4** with corresponding values of other zerovalent carbonyltitanates (Table 3) indicates that the hydroxo ligand, respectively, is quite strongly donating, even stronger than the methoxo ligand.

X-ray quality single crystals of **4** were obtained by slow diffusion of ether into a pyridine solution. Fig. 2 shows the molecular structure of $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$, which confirms our formulations for salts **3** and **4**, since both have virtually identical spectroscopic data for the anionic components.

The dimeric units contain two $Ti(CO)_4$ groups bridged by hydroxo ligands and have an overall structure consisting of two strongly distorted octahedra sharing an edge, defined by the bridging hydroxo oxygens. Distortions of this type for six-coordinate d^4 metal complexes have been previously observed and discussed in some detail by Kubacek and Hoffmann

[23]. The structural units of **4** are substantially similar to related phenoxo- and methoxo-derivatives, but the most striking difference within the structurally characterized complexes, $[Ti_2(\mu\text{-}OR)_2(CO)_8]^{2-}$, R = Ph, Me, H, is the rotation of the planar M_2O_2 core with respect to the two $Ti(CO)_4$ units: 45° when R = Ph, 30° when R = Me and 0° when R = H. We attribute these differences to steric and packing effects. Metrical parameters of the two eclipsed and symmetry-equivalent $Ti(CO)_4$ units in **4** closely resemble those previously reported for $[Ti_2(\mu\text{-}OR)_2(CO)_8]^{2-}$, R = Ph (**5**), Me (**6**), and $Ti(CO)_4(\eta^3\text{-}Me_3tacn)$ (**7**), Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane [18], which indicates that the titanium units in **4** are also best considered to be closed shell or electronically saturated. For example, the average Ti–C and C–O distances in **4** of 2.00(2) and 1.171(8) Å, respectively, are essentially identical to respective values of **7**, i.e. 1.996(6) and 1.17(1) Å. Also, the average *cis* and *trans* C–Ti–C angles in the $Ti(CO)_4$ units in **4**, (*cis* 68(2)°, *trans*, 105(1)°) are experimentally indistinguishable from those in **7**, (*cis* 68(2)°, *trans* 104.6(3)°). Thus, structural and spectral data (Table 3) for **4** and **7** indicate that the individual $Ti(CO)_4$ units in these stoichiometrically different complexes are extraordinarily similar.

The Ti–Ti distance of 3.345(2) Å in **4** is similar to corresponding values observed for **5** and **6** of 3.378(1) and 3.340(6)Å, respectively, and suggests that direct Ti–Ti bonding is unlikely in all three molecules. The average Ti–O distance in **4** of 2.050(3) Å is slightly shorter than those in **5** 2.09(1), and **6** 2.07(1) Å, probably due to the smaller size of the hydroxo group in **4** compared with the phenoxo and methoxo groups present in **5** and **6**, respectively.

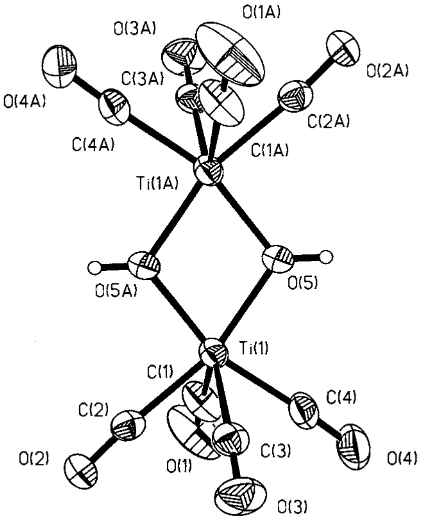


Fig. 2. Molecular structure of $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$, 50% probability thermal ellipsoids. Important bond lengths (Å) and angles (°): Ti(1)–C(1) 1.982(6), Ti(1)–C(2) 2.014(5), Ti(1)–C(3) 1.988(5), Ti(1)–C(4) 2.004(6), Ti(1)–O(5) 2.053(3), Ti(1)–O(5) #1 2.046(3), Ti(1)–Ti(1) #1 3.345(2), C(1)–O(1) 1.174(6), C(2)–O(2) 1.173(5), C(3)–O(3) 1.166(5), C(4)–O(4) 1.171(5), C(1)–Ti(1)–C(2) 65.9(2), C(1)–Ti(1)–C(3) 103.9(2), C(1)–Ti(1)–C(4) 69.1(2), C(2)–Ti(1)–C(3) 69.6(2), C(2)–Ti(1)–C(4) 106.1(2), C(3)–Ti(1)–C(4) 68.5(2), O(5)–Ti(1)–O(5) #1 70.6(1), Ti(1)–O(5)–Ti(1) #1 109.4(1).

There are two different counterions present in the unit cell of **4**. One of these is normal, $[K(18\text{-crown-}6)(py)_2]^+$, and contains potassium ion bound equatorially to 18-crown-6 and axially to two pyridines. The other cation, $[K(18\text{-crown-}6)]^+$ contains a similarly bound 18-crown-6 unit, but in the axial positions are oxygen atoms of coordinated carbonyls, C(4)–O(4), of different dimers. The K–O(4) (carbonyl) distance of 2.819(4) Å is similar to the average K–O (crown ether) distance of 2.80(3) Å, but is much longer than the average K–O (THF) distance of 2.69(4) Å present in $[K(18\text{-crown-}6)(THF)_2]^+$ [24]. The $[K(18\text{-crown-}6)]^+$-carbonyl anion interaction appears to be a weak interaction, since it does not have any obvious influence on the formally 'bridging' C(4)–O(4) carbonyl, which is structurally indistinguishable from the other carbonyl ligands, or the overall structure of the anion.

4. Concluding remarks

Hexacarbonyltitanate(2 −) quickly reacts with azobenzene to provide a thermally stable adduct, which is formulated on the basis of spectral and chemical reactivity data as a 1,2-diphenylhydrazido dianion complex of titanium(0) tetracarbonyl, $[Ti(PhN\text{-}NPh)(CO)_4]^{2-}$. Consistent with this description, the dianion undergoes facile hydrolysis to provide 1,2-diphenylhydrazine and the previously unknown hydroxocarbonyltitanate(0), $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$. As in the case of the azobenzene complex, the latter contains six-coordinate and formally unsaturated zerovalent titanium. Carbonyl IR and NMR spectral data of both species are extremely similar to related electronically saturated seven-coordinate Ti(0) complexes such as $[Ti(CO)_4(\eta^5\text{-}C_5H_5)]^-$ [17] and $[Ti(CO)_4(\eta^3\text{-}Me_3tacn)]$ [18]. Structural data for the hydroxo-bridged Ti(0) dimer also shows that the $Ti(CO)_4$ units in this dimer closely resemble those present in the aforementioned 18-electron complexes. These data indicate that the azobenzene and hydroxo ligands function as effective π-donors to titanium, an interaction that could result in electronic saturation of the respective complexes [25]. In this regard, it is interesting that formally unsaturated Group 6 and 7 metal carbonyls bearing similar potential π-donor ligands have been described [26], but *no analogous substituted Group 5 metal carbonyls are known to date*. However, on the basis of the present and prior studies, it seems very likely that related six-coordinate carbonyl complexes of monovalent V, Nb and Ta will be accessible species.

5. Supplementary material

Crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1E7, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors wish to thank the US National Science Foundation and the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support and the Scuola Normale Superiore, Pisa, Italy, and the Petroleum Research Fund for fellowships to G.T. We also thank Christine Lundby for her expert assistant with the manuscript and Professor Rinaldo Poli for his invitation to contribute to this volume.

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