the highest quantum yield (0.26) of the molecules evaluated. This is consistent with the results we obtained for the corresponding *o*-nitrobenzyl alcohols.[2a,11,12] Surprisingly, the 4,5-dimethoxy-2-nitrobenzyl derivative **8c** photoactivates less efficiently than expected, based on the quantum yield of the 4,5-dimethoxy-2-nitrobenzyl alcohol (0.07);[2a] however, the fluorescence yield for this derivative is still quite high due to its high molar absorptivity (ϵ = 6050 at 350 nm). The phenacyl ether cleavage also is reasonably efficient,[13] but this derivative **5** suffers from very low absorptivity (ϵ = 47 at 350 nm).

The fluorescein monoethers generated as ultimate fluorophores have emission characteristics (λ_{max} = 515 nm) that are virtually identical with fluorescein itself in aqueous solution at neutral to slightly basic pH. Thus, these molecules should be useful in biological environments where fluorescein or other functionalized fluoresceins have been used effectively.

The functionalized fluoresceins described in this paper are excellent PAFs, converting from nonfluorescent precursors to highly fluorescent ultimate fluorophores with reasonable efficiency. Furthermore, the functionality present in **9a–c** makes them ideal molecules for functionalization of biologically interesting macromolecules. FPD studies of molecular transport and diffusion that exploit the capabilities of these unique molecules are underway.

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Highly Reduced Organometallics. 23. Synthesis, Isolation, and Characterization of Hexacarbonyltitanate(2–), Ti(CO)₆²⁻. Titanium NMR Spectra of Carbonyltitanates[†1]

Kai Ming Chi, Scott R. Frerichs, Stephen B. Philson, and John E. Ellis*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

The relatively robust nature of the previously known low spin d^6 octahedral carbonyls, $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$, suggested to us that it should be possible to isolate salts containing the isoelectronic dianion, $Ti(CO)_6^{2-}$.[2] We now report on two independent routes to this previously unknown species which contains titanium in its lowest known formal oxidation state of 2–.[3] Unambiguous characterization of $Ti(CO)_6^{2-}$ has been

(1) Part 22: Chi, K. M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* in press. This article reports on the synthesis of the related $Zr(CO)_6^{2-}$.
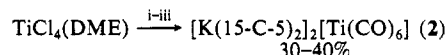(2) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions, A Study of Metal Complexes in Solution*, 2nd ed.; J. Wiley: New York, 1967; Chapter 7.

Scheme I[a]

$$Ti(CO)_3(dmpe)_2 \xrightarrow{i,ii} [K(2.2.2)]_2[Ti(CO)_6] \quad (1)$$
$$\geq 80\%$$
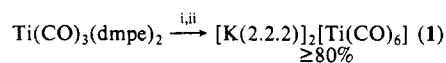
[a] Reagents and conditions: i. $2KC_{10}H_8$ + 2(2.2.2) at –70 °C in THF under argon. ii. Remove argon, add CO, 12 h, and slowly warm to room temperature.

Scheme II[a]

$$TiCl_4(DME) \xrightarrow{i-iii} [K(15\text{-}C\text{-}5)_2]_2[Ti(CO)_6] \quad (2)$$
$$30\text{--}40\%$$

[a] Reagents and conditions: i. $6KC_{10}H_8$, –70 °C, 5 h in DME. ii. Four 15-C-5 at room temperature, 2 h, under argon. iii. Cool to –60 °C, remove Ar, and add CO, 40 h.

provided by elemental analyses, IR, ^{13}C, and Ti NMR spectra. Hexacarbonyltitanate(2–) may be regarded as a saturated and dianionic derivative of the extremely unstable neutral $Ti(CO)_6$ (dec $\geq$ –220 °C) which was observed by matrix isolation spectroscopy.[4] By comparison, the most stable salt of $Ti(CO)_6^{2-}$ obtained so far decomposes above 200 °C, more than 400° higher than the neutral parent! We believe the availability of $Ti(CO)_6^{2-}$ will be of substantial importance in the exploration of new areas of titanium chemistry.

Reductive carbonylations of either $Ti(CO)_3(dmpe)_2$,[5] dmpe = $Me_2PCH_2CH_2PMe_2$, or $TiCl_4(DME)$, DME = 1,2-dimethoxyethane, by alkali metal naphthalenides yield isolable salts of $Ti(CO)_6^{2-}$ *provided* an appropriate crown ether or cryptand is present to effectively complex alkali metal cations. Although the latter appear to prevent formation or cause decomposition of $Ti(CO)_6^{2-}$ at low temperature in these syntheses, little is known concerning this interesting phenomenon, which is presently under examination. Cooper and co-workers have previously noted the ability of cryptands to stabilize $Na_2[M(CO)_5]$ (M = Mo, W) in the solid state, but, in contrast to $Ti(CO)_6^{2-}$, these pentacarbonylmetallates(2–) are readily prepared in tetrahydrofuran (THF) or similar solvents in the absence of effective alkali metal complexants.[6]

Cold (–70 °C) THF solutions containing $Ti(CO)_3(dmpe)_2$ and 2 equiv of $KC_{10}H_8$ and cryptand (2.2.2) were mixed under an argon atmosphere followed by evacuation and addition of carbon monoxide at atmospheric pressure. Stirring was continued for 12 h while the mixture slowly warmed to room temperature. A finely divided orange-red solid was removed by filtration, washed with THF, dried, and then recrystallized from acetonitrile–THF at 0 °C. An 80% yield (1.2 g) of dark violet crystalline product (mp 216–217 °C with dec) was obtained. This material provided satisfactory elemental analyses (C, H, N) for the composition $[K(2.2.2)]_2[Ti(CO)_6]$ (**1**).[7] This procedure is summarized in Scheme I. In the second procedure, cold (–70 °C) DME solutions

(3) Subvalent titanium complexes of the type $Ti(C_6H_5R)_2^-$ (R = H, CH₃) containing Ti(1–) have been reported: Bandy, J. A.; Berry, A.; Green, M. L. H.; Perutz, R. N.; Prout, K.; Verpeaux, J.-N. *J. Chem. Soc., Chem. Commun.* **1984**, 729. The anionic species $[Ti(2,2'\text{-dipyridyl})_3]^z$, where z = 1– and 2–, may also be considered to contain titanium in formally negative oxidation states: Herzog, S.; Zühlke, H. *Z. Chem.* **1966**, *6*, 434. However, these assignments have been questioned on the basis of the ease with which free or complexed 2,2'-bipyridyl undergoes reduction; i.e., the coordinated ligand may be considered to be neutral or anionic: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: London, 1984; p 1133.
(4) Busby, R.; Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 822.
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(6) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354.
(7) Crypt (2.2.2) = (2.2.2) = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane; 15-C-5 = 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane.
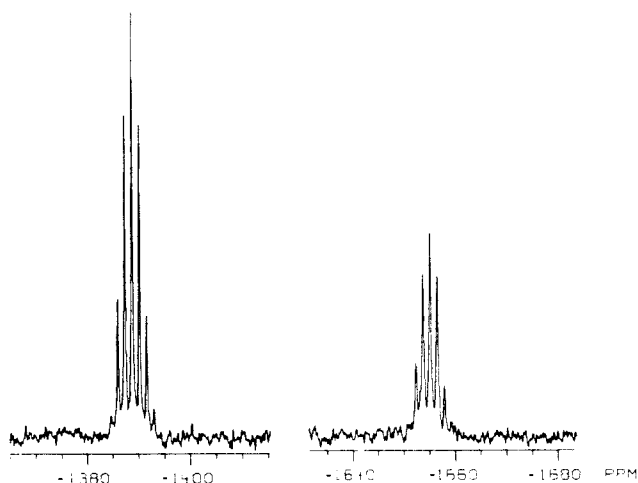
Figure 1. ^{49}Ti and ^{47}Ti NMR spectrum of a 0.05 M solution of 99% ^{13}C enriched [K(2.2.2)]$_2$[Ti(^{13}CO)$_6$] in CH$_3$CN:CD$_3$CN = 10:1 at 23 °C: ^{49}Ti (δ –1389, $J_{^{49}Ti^{-13}C}$ = 23 Hz), ^{47}Ti (δ –1655, $J_{^{47}Ti^{-13}C}$ = 23 Hz).

of TiCl$_4$(DME) and 6 equiv of KC$_{10}$H$_8$ were mixed, stirred for 5 h while warming to room temperature under argon, and then filtered. To the resulting red-brown solution, containing presently uncharacterized intermediate(s), was added 4 equiv of 15-C-5, and stirring was resumed for 2 h. The solution was then cooled to –60 °C, argon was removed by evacuation, and ≥99.9% carbon monoxide was introduced at near atmospheric pressure. After stirring for 40 h at –60 °C a bright red slurry had formed. This was filtered, and the resulting solid was washed with DME, dried in vacuo, and recrystallized from acetonitrile–DME. A 38% yield (3.2 g) of deep red and thermally robust crystalline product (dec 180–182 °C) was isolated. This material provided satisfactory analyses (C, H, K, Ti) for the composition [K(15-C-5)$_2$]$_2$-[Ti(CO)$_6$] (**2**).[7] Product **2** was also obtained from Ti(CO)$_3$-(dmpe)$_2$ in 56% yield as a pure substance. This procedure is summarized in Scheme II.

Spectroscopic properties of **1** and **2** in acetonitrile are consistent with the presence of discrete octahedral Ti(CO)$_6^{2-}$ units. For example, a single intense ν(CO) band at 1745–1750 cm^{-1} is observed in the infrared region which is reasonable for a dianionic mononuclear binary carbonyl of this symmetry.[8] A single ^{13}C resonance is found at δ 245.8 ppm which compares well with previously reported ^{13}C resonance positions of carbonylmetallate dianions (e.g., HV(CO)$_5^{2-}$, δ 250.3[9] and W(CO)$_5^{2-}$, δ 247.4 ppm[6]). The very narrow ^{49,47}Ti NMR resonances observed for **1** [δ –1388 ($W_{1/2}$ ≈ 3 Hz), –1654 ($W_{1/2}$ = 7 Hz) ppm, respectively] and **2** [δ –1386 ($W_{1/2}$ = 5 Hz), –1652 ($W_{1/2}$ = 12 Hz) ppm, respectively] indicate the presence of relatively unperturbed cubic or octahedral titanium species.[10] By comparison our attempts to observe the ^{49,47}Ti NMR resonances of the much less symmetrical (C$_5$H$_5$)$_2$-Ti(CO)$_2$ were unsuccessful. The only other carbonyl of titanium examined for which a Ti NMR spectrum could be obtained was [Et$_4$N][C$_5$H$_5$Ti(CO)$_4$][11] which exhibited much broader ^{49}Ti and ^{47}Ti resonances at –1269 ($W_{1/2}$ = 93 Hz) and –1536 ($W_{1/2}$ = 224 Hz) ppm, respectively, due to the lower symmetry of C$_5$H$_5$Ti-(CO)$_4^-$ relative to that of Ti(CO)$_6^{2-}$.[12] Proof for the formulation of Ti(CO)$_6^{2-}$ has been obtained by the ^{49,47}Ti NMR spectrum of 99% ^{13}C enriched Ti(^{13}CO)$_6^{2-}$ as the K(2.2.2)$^+$ salt.[13] Figure

1 shows the binominal septet of the ^{49}Ti resonance (δ –1389, $J_{^{49}Ti^{-13}C}$ = 23 Hz) due to coupling of six equivalent carbonyl groups to the central titanium and five bands of the expected seven band multiplet of the corresponding ^{47}Ti resonance (δ –1655, $J_{^{47}Ti^{-13}C}$ = 23 Hz). Significantly, there have been no previous reports of resolved ^{49,47}Ti–^{13}C coupling for any organotitanium species. The spectrum in Figure 1 qualitatively resembles that reported for TiF$_6^{2-}$.[14]

In summary, the first binary carbonyl anion of titanium, Ti-(CO)$_6^{2-}$, has been synthesized by two independent methods, isolated, and fully characterized by multinuclear NMR spectroscopy. The importance of employing crown ethers and related alkali metal complexants in the synthesis of certain early transition metal carbonyl anions has been established for the first time.[15] This discovery may prove to be extremely important for future efforts in this emerging area of synthetic chemistry.

(13) Prepared in 95% yield (unrecrystallized) from the reductive carbonylation of Ti(^{13}CO)$_3$(dmpe)$_2$ (ref 5b) under ^{13}CO: IR in CH$_3$CN (ν(CO), cm^{-1}) 1710; ^{13}C{^{1}H} NMR (CD$_3$CN) δ 245.8 (s and satellites due to ^{49,47}Ti–^{13}C coupling, J = 23 Hz); ^{49,47}Ti NMR, see Figure 1. Noteworthy is the ^{13}C isotope effect on the ^{49,47}Ti resonance positions of nearly 1 ppm. Similar isotope effects have been observed previously in the ^{51}V NMR spectra of V(^{12}CO)$_6^-$ and V(^{13}CO)$_6^-$: Ihmels, K.; Rehder, D.; Pank, V. *Inorg. Chim. Acta* **1985**, *96*, L69. See, also: ref 9.

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(15) Stabilization of unusual anions in metal salts by crown ethers and cryptands has been recognized for many years. Two spectacular examples include the electride, [Cs(18-crown-6)$_2$]$^+$e$^-$, and the sodide, [K(2.2.2)]$^+$Na$^-$: Dye, J. L. *Sci. Am.* **1987**, *257*(3), 66. Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 329.

Entrapment of an Anionic, Stable, Moisture-Resistant Oxygen Carrier in Zeolite Y

Russell S. Drago,* Iwona Bresinska, James E. George, Kenneth Balkus, Jr., and Robert J. Taylor

Department of Chemistry, University of Florida
Gainesville, Florida 32611

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Cobalt(II)–cyanide complexes, such as Co(CN)$_5^{3-}$, are known to bind dioxygen and function as homogeneous catalysts.[1] We have succeeded in preparing an anionic cobalt(II)–cyanide complex within the large cavity of zeolite Y. The species present is a low-spin Co(CN)$_4^{2-}$ ion and is probably coordinated to the zeolite framework through a lattice oxygen. The complex combines reversibly with dioxygen, forming a six-coordinate monoadduct, with the zeolite cage inhibiting the formation of the μ-peroxo dimer. This feature, and the stability of the cyanide ligand to oxidation, has resulted in a reversible oxygen carrier that is thermally stable to oxidation at temperatures as high as 250 °C. Both IR and EPR spectroscopy have been used to characterize this material. To our knowledge, this represents the first case in which a large, negative ion has been synthesized within a zeolite cavity,[2] opening the possibility for preparing a whole new class of trapped anionic complexes.

Several Co^{II}–Y zeolites with cobalt contents ranging from 2 to 19 cobalts per mole of zeolite were prepared from Linde LZY-52 zeolite with conventional ion exchange methods. A sample of the Co^{II}–Y zeolite, dried at 160 °C under vacuum (10^{-3} Torr), is stirred for a minimum of 24 h at room temperature in

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