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Highly Reduced Organometallics. 20.[1] The First General Synthetic Route to Zerovalent Titanium Carbonyls. Synthesis and Properties of $Ti(CO)_5(Me_2PCH_2CH_2PMe_2)$

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Abstract: Synthetic procedures developed in this study provide the first general route to zerovalent titanium carbonyls and should facilitate future investigations in this relatively unexplored area of organotitanium chemistry. Sodium naphthalenide reductions of $TiCl_4(THF)_2$ (THF = tetrahydrofuran), in the presence of 2.1–2.3 equiv of $Me_2PCH_2CH_2PMe_2$ (dmpe) in THF at −70 to −80 °C under argon, followed by carbonylation at atmospheric pressure provide 70–80% isolated yields of the previously known but relatively inaccessible $Ti(CO)_3(dmpe)_2$. Under a carbon monoxide atmosphere at room temperature within 3 h, the latter is partially converted to $Ti(CO)_5(dmpe)$, the initial example of a pentacarbonyltitanium species. Addition of about 2 equiv of $BH_3{\cdot}THF$ to the $Ti(CO)_3(dmpe)_2/Ti(CO)_5(dmpe)$ mixture under a CO atmosphere in THF binds free dmpe as $dmpe{\cdot}2BH_3$ and causes disappearance of all $Ti(CO)_3(dmpe)_2$, thereby allowing the isolation of substantially pure $Ti(CO)_5(dmpe)$. The latter is a bright red crystalline material that decomposes within hours at room temperature and has been characterized by infrared, ^{13}C, ^{31}P, and ^1H NMR spectroscopy. Unlike $Ti(CO)_3(dmpe)_2$, the pentacarbonyl compound is quite reactive toward a variety of main group nucleophiles and thereby represents the first accessible synthetic equivalent of the unknown $Ti(CO)_7$. Its reactions with 1,1,1-tris(dimethylphosphinomethyl)ethane (trmpe), sodium cyclopentadienide, sodium indenide, and potassium hydrotris(1-pyrazolyl)borate ($(HB(Pz)_3)^-$) result in the loss of dmpe and provide 70–80% isolated yields of $Ti(CO)_4(trmpe)$, $C_5H_5Ti(CO)_4^-$, $C_9H_7Ti(CO)_4^-$, and $[HB(Pz)_3]Ti(CO)_4^-$. The trmpe derivative is a rare example of a neutral tetracarbonyl of titanium and is one of the most thermally stable organophosphine derivatives of $Ti(CO)_7$ presently known. Thermally robust tetraethylammonium salts of the carbonyl anions were obtained and include the initial indenyl and organonitrogen derivatives of zerovalent titanium. Treatment of $Ti(CO)_5(dmpe)$ with Ph_3ENa, where E = Ge and Sn, results in the retention of dmpe and formation of $Ti(CO)_4(dmpe)(Ph_3E)^-$. These were isolated as Ph_4As^+ salts and are formal derivatives of the presently unknown $Ti(CO)_6^{2-}$.

Metal carbonyls have played an important role in the development of modern transition-metal chemistry[3] and are now of particular significance in chemical synthesis.[4] Good synthetic procedures exist for the preparation of carbonyls of most of the d-block elements;[3,4] however, the situation has been far less satisfactory for the very early or "frontier" transition metals.[5] For example, stable carbonyls are presently unknown for the group 3 elements, as well as the neighboring lanthanoids,[6] while carbonyls of the group 4 elements have been largely limited to those formally containing divalent metals, such as $(C_5H_5)_2Ti(CO)_2$.[7] By comparison, zerovalent metal carbonyls of the group 4 elements are exceedingly rare and, heretofore, no general synthetic routes to these materials have been available.

Ozin and co-workers identified $Ti(CO)_6$ as the highest stoichiometry product arising from the cocondensation of Ti atoms and CO at 10–15 K.[8] Unfortunately, this green substance is so thermally unstable (decomposition point ≥40–50 K) that it is unlikely to be of any use of synthesis in the foreseeable future. More recently, Wreford and co-workers prepared the first thermally stable derivatives of the unknown $Ti(CO)_7$ by high-pressure (1000 psi) Na–Hg reductive carbonylation of $TiCl_4{\cdot}2THF$ (THF = tetrahydrofuran) in the presence of $R_2PC_2H_4PR_2$ (R = CH_3, C_2H_5) at 0 °C. Only low yields (20–30%) of $Ti(CO)_3(R_2PC_2H_4PR_2)_2$ were thereby obtained in these syntheses.[9] Crystal structures of the dmpe product (R = CH_3)[10] and the related $Ti(CO)_2(PF_3)(dmpe)_2$[9] confirmed the formulation of these novel materials. Before 1986, only one Zr(0) carbonyl had been characterized, $Zr(butadiene)_2(dmpe)CO$, which survived as a solid only for *brief* periods at 25 °C under a CO atmosphere.[11] Significantly, no Hf(0) carbonyls have been reported to date in the scientific literature.

Recently, we announced the preparation of quite thermally stable salts containing the anions $C_5R_5M(CO)_4^-$ (R = H, CH_3; M = Ti, Zr) by a two-step reductive carbonylation procedure conducted at low temperature and atmospheric pressure.[1b,12] This method was quite similar to a synthesis of the hexacarbonylmetalates(1−) of niobium and tantalum we had developed earlier.[13] These were the first known carbocyclic and anionic derivatives of zerovalent group 4 carbonyls. In this paper we report on the first application of this reduction procedure to the synthesis of $Ti(CO)_5(dmpe)$, a new and useful organophosphine derivative of $Ti(CO)_7$. This initial example of a titanium pentacarbonyl species reacts readily with nucleophiles and thereby functions as the first accessible synthetic equivalent of $Ti(CO)_7$. Among the most interesting reactions of $Ti(CO)_5(dmpe)$ reported herein are those with 1,1,1-tris(dimethylphosphinomethyl)ethane (trmpe) and hydrotris(1-pyrazolyl)borate ($HB(Pz)_3^-$) which provide one of the most thermally stable carbonylphosphines of Ti(0) presently known, $Ti(CO)_4(trmpe)$, and the first example of an organonitrogen-substituted carbonyltitanate, $[HB(Pz)_3]Ti(CO)_4^-$, respectively. Full details of our improved two-step reductive carbonylation procedure are also presented. We believe that the

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procedures introduced in this paper will be of substantial importance in the future development of highly reduced organometallics of the very early transition metals.

Experimental Section

General Procedures and Starting Materials. Operations were performed under an atmosphere of nitrogen, argon, or carbon monoxide 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 that are impermeable to air.[14] In addition, the carbon monoxide was passed through a column of Ascarite to remove carbon dioxide. Solutions were transferred via stainless steel cannulae whenever possible. Otherwise syringes or standard Schlenk techniques[15] were used in conjunction with a double manifold medium vacuum line.[14] Solvents were dried and distilled under argon before use. All reactants and solvents were obtained from commercial sources except for $TiCl_4(THF)_2$,[16] $TiCl_4(DME)$ (where DME = 1,2-dimethoxyethane),[17] 1,2-bis(dimethylphosphino)ethane (dmpe),[18] 1,1,1-tris(dimethylphosphinomethyl)ethane (trmpe),[19] $TiCl_4(dmpe)$,[20] and $[Na(DME)][C_5H_5]$,[21] which were prepared by standard literature procedures. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer in 0.1 mm sealed NaCl or CaF_2 cells fitted with three-way Nylon stopcocks (Ace Glass 5851) to permit filling outside of the drybox. Nujol mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox filled with nitrogen. NMR samples were sealed into 5-mm tubes (Wilmad 505-PS9) and were run on Nicolet NT-300 WB, IBM NR-200 AF, and NR-300 AF spectrometers. Carbon spectra were acquired with a 45° pulse and a 4 s delay between pulses to aid in the detection of carbonyl ^{13}C resonances. High-resolution mass spectra were obtained on a VG-7070E by xenon bombardment. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by H. Malissa and G. Reuter Analytische Laboratorien, Engelskirchen, West Germany.

Comments Concerning the Reductive Carbonylation Procedure. Of crucial importance to the success of these and related reductive carbonylations (e.g., the syntheses of $Nb(CO)_6^-$, $Ta(CO)_6^-$, and $C_5R_5M(CO)_4^-$ (R = H, Me; M = Ti, Zr)) is the purity of the carbon monoxide. Specifically, technical and CP grade carbon monoxide contain large amounts of CO_2, which are difficult to remove and substantially decrease the yields of products. For this reason, we routinely use ultrahigh purity (99.9%) or research grade (99.99%) carbon monoxide. Although these grades of CO are costly, the improved yields of products justify the additional expense.

Since our publication of the atmospheric pressure synthesis of the hexacarbonylmetalates(1−) of Nb and Ta, significant improvements in this general procedure have been made. Originally, the carbonylations were conducted by passing CO through or sometimes over the solution of reactants.[12] However, this method for adding CO was undesirable since substantial amounts of harmful impurities (e.g., N_2, H_2, or CO_2) were often introduced into the reaction mixture. More satisfactory results are usually obtained if the argon atmosphere is removed by evacuation (ca. 10^{-1}–10^{-3} mmHg) and then replaced by CO, followed by vigorous mechanical stirring (ca. 300 rpm). In this method there is no net flow of CO through the apparatus; the gas pressure is maintained at about 770–780 mmHg throughout the course of the reaction, which permits the use of standard glass vessels. To improve gas–liquid interfacial mixing Morton flasks are used in all reductive carbonylations. Finally it should be emphasized that success in these reductive carbonylations requires strict attention to detail, excellent laboratory technique, proper equipment, and reasonably pure reagents.

Some comments on the preparation of $Na–C_{10}H_8$ are also necessary. Originally, we generated $Na–C_{10}H_8$ by the reaction of commercially available sodium dispersion in mineral oil and naphthalene in THF or DME at 0 °C.[12] Often this reaction was sufficiently exothermic to cause destruction of some $Na–C_{10}H_8$ by the solvent and agglomeration of the sodium. Also the sodium dispersion obtained from two major suppliers was often not of uniform or expected composition even for new samples handled under strict anaerobic conditions. To our dismay the use of Na dispersion often provided much less than the expected amount of $Na–C_{10}H_8$ and caused several failures in initial attempts to prepare $C_5H_5Ti(CO)_4^-$ from $C_5H_5TiCl_3$. When we switched to relatively large pieces of sodium metal (use of sodium sand is not advantageous) our results improved dramatically. Basically, this procedure for the generation of $Na–C_{10}H_8$ is identical with that originally developed by Scott and co-workers[22] and later modified by Chatt and Watson.[23] Since $Na–C_{10}H_8$ reacts with Teflon, glass enclosed magnetic stir bars or glass paddles should be used for agitation; sonication has also been employed.[24] Within *seconds* of adding THF or DME to the mixture of freshly cut sodium (in the form of shiny chunks ca. 2–4 mm on an edge) and naphthalene, the solution should turn green. Otherwise, it is likely that the naphthalene, solvent, and/or atmosphere is contaminated. (Reagent grade naphthalene has generally provided satisfactory results in these preparations without further purification.) After about 3 h of stirring at room temperature, even in the presence of excess sodium metal, almost exactly 1 equiv of sodium will dissolve per equiv of naphthalene in the concentrations employed (0.1–0.5 M) to provide deep green solutions of $Na–C_{10}H_8$. Since our reductions work better in the presence of excess naphthalene, stoichiometric amounts of sodium are used. Although it has been reported that solutions of $Na–C_{10}H_8$ in THF are stable for weeks,[25] we have found that these solutions, as well as those in DME, should be used as soon as possible to minimize decomposition. Scott et al. reported that $Na–C_{10}H_8$ is slowly attacked by DME at room temperature to provide methyl vinyl ether.[22]

All two-step reductive carbonylations presented below were conducted under argon initially since the intermediates react with dinitrogen.

$Ti(CO)_3(dmpe)_2$ (1). A solution of $Na–C_{10}H_8$ in 100 mL of THF, prepared from sodium metal (0.491 g, 21.4 mmol) and naphthalene (4.10 g, 32.0 mmol) as described above, was cooled to −70 °C in a 500-mL, three-necked Morton flask, equipped with a stopcock and mechanical stirrer and immersed in a 2500-mL low-form Dewar.[26] Two milliliters of dmpe (12.0 mmol) was added to a yellow solution of $TiCl_4·2THF$ (1.74 g, 5.21 mmol) in 100 mL of THF. The resulting red solution was cooled to −78 °C and added by cannula to the cold $Na–C_{10}H_8$ solution. After 5 min the color had changed from an inky green-black to a reddish brown and the stirring was stopped. Argon gas was removed by evacuation and replaced by CO. Almost immediately after stirring was resumed the color of the solution changed to a much brighter red. The reaction mixture was then slowly warmed for about 12 h to about −15 (± 15) °C under a CO atmosphere. (Only small decreases in yield occurred when the solution was warmed to room temperature overnight in similar reactions, but the warming should not be abrupt and the impure product should not be kept in solution at room temperature for more than an hour. The reaction vessel remained immersed in the Dewar during this period.) Stirring was again stopped, the CO was replaced by an atmosphere of argon gas, and after about 1 h (to permit settling of finely divided solids) the deep red supernatant was filtered (medium porosity fritted disc; often filter aid (Celite) is added to avoid very slow filtrations). Solvent was removed as quickly as possible under reduced pressure, and the resulting red solid, heavily contaminated by naphthalene, was thoroughly washed with pentane (3 × 50 mL), collected on a coarse porosity frit, and dried under vacuum for about 0.5 h at room temperature. A highly air sensitive, crystalline burgundy solid was thereby obtained in 83% yield (1.87 g), which provided satisfactory analytical data. $^{31}P\{^1H\}$ NMR and IR spectra of this substance were in good agreement with those reported by Wreford and co-workers.[10] The complete ^{13}C NMR spectrum was recorded for the ^{13}C-enriched compound **2**, vide infra. Previously unreported ^1H NMR spectra of **1** were obtained: (tetrahydrofuran-d_8, 23 °C) δ 1.29 (d, J = 4.6 Hz, P–CH_3), 1.60 (apparent d, J = 15.2 Hz, P–CH_2); (toluene-d_8, 23 °C) δ 1.04 (d, J = 4.3 Hz, P–CH_3), 1.12 (d, J = 15.2 Hz, P–CH_2), the latter signal is partially superimposed on the first). IR (tetrahydrofuran) ν(CO): 1848 (s), 1757 (sh), 1747 (s) cm^{-1}; (Nujol) ν(CO): 1825 (s), 1725 (vs br). Anal. Calcd for $C_{15}H_{32}O_3P_4Ti$: C, 41.68; H, 7.46; P, 28.67. Found: C, 41.60; H, 6.84; P, 28.85.

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Although Wreford's group was unable to obtain satisfactory elemental analysis for **1** due to its thermal instability, we find that pure solvent-free samples of this compound, prepared by our method, are thermally stable for several months under nitrogen or argon at room temperature. Rapid decomposition with melting occurs at 122–124 °C, but at 0 °C **1** appears to be stable indefinitely under an inert atmosphere. This material is easily recrystallized from THF–pentane; however, samples obtained from the initial crystallization are generally of sufficient purity for subsequent studies. Crystalline **1** must be handled carefully since it is often pyrophoric and will readily inflame on tissue paper in air. While **1** is only very slightly soluble in saturated hydrocarbons or diethyl ether, it dissolves in toluene, THF, and DME to provide extremely air sensitive deep red solutions. These have virtually identical IR spectra in the ν(CO) region and persist for hours at room temperature under argon. Acetonitrile and methylene chloride dissolve **1** to provide solutions that deteriorate markedly within 1 h and are entirely decomposed within 12 h. The most thermally stable solutions of **1** are obtained in neat dmpe, which does not react with **1** even at 65 °C for several hours.

Ti(^{13}CO)$_3$(dmpe)$_2$ (2). Essentially the same procedure was used for the synthesis of **2** as that shown above for **1**. During the carbonylation, the pressure of ^{13}CO was maintained slightly above atmospheric pressure.[27] In the initial stages of the reaction it was necessary to add additional ^{13}CO three or four times to maintain the pressure. To minimize loss of ^{13}CO, the total volume of glass and metal tubing from the lecture bottle (containing the carbon monoxide) to the reaction vessel and manometer was made as small as practicable. Flexible stainless steel tubing (Cajon, 321-4-x-12) was used instead of butyl rubber tubing to minimize contamination of the ^{13}CO. A 65% yield (1.54 g) of 99% ^{13}C labeled Ti(^{13}CO)$_3$(dmpe)$_2$ was obtained from 1.85 g (5.44 mmol) of TiCl$_4$(dmpe) and 2.0 mL of dmpe. IR (tetrahydrofuran), ν(^{13}CO): 1805 (s), 1718 (sh), 1709 (s) cm^{-1}. Calculated ν(^{13}CO) based on the corresponding ν(^{12}CO) values of **1**: 1806, 1717, 1708 cm^{-1}; (Nujol): 1785 (s), 1687 (vs br) cm^{-1}. NMR (tetrahydrofuran-d_8): ^{13}C{^{1}H} (23 °C) δ 282 (very br apparent singlet, CO), 30.5 (apparent dd, J = 2, 14 Hz, P–*C*H$_2$), 18.3 (d, J = 10 Hz, P*C*H$_3$) (also a weak signal due to free ^{13}CO at δ 185 was present); (–90 °C) δ 300 (m, 1 CO), 276 (br s, 2 CO) (only carbonyl signals were resolved); ^{31}P{^{1}H} (23 °C) δ 28 (very br apparent singlet, Ti–P) (weak singlet δ –48.9 due to free dmpe); (–60 °C) δ 50.1 (s, 1 P), 25.6 (s, 2 P), 8.6 (s, 1 P), –49.0 (free dmpe).

Ti(CO)$_5$(dmpe) (3). Method A. From Ti(CO)$_3$(dmpe)$_2$. A solution containing Ti(CO)$_3$(dmpe)$_2$ (1.00 g, 2.3 mmol) in 60 mL of THF was stirred for 3 h at room temperature under an atmosphere of carbon monoxide. At this time, the solution had changed to a brighter red color and infrared spectra indicated that much Ti(CO)$_3$(dmpe)$_2$ had changed to Ti(CO)$_5$(dmpe) (see Discussion). The solution was cooled to 0 °C and 5 mL (5 mmol) of 1 M BH$_3$·THF in THF was added. After 10 h of stirring under a CO atmosphere at 0 °C, the bands due to Ti(CO)$_3$(dmpe)$_2$ were significantly less intense; within 24 h all reactant carbonyl had disappeared. Filtration of the resulting solution at –78 °C through a medium porosity frit provided a clear orange-red solution, much lighter in color than that of Ti(CO)$_3$(dmpe)$_2$. Subsequently, solvent was removed under vacuum below 0 °C until only about 5 mL remained. Addition of 50 mL of pentane provided a bright red crystalline solid. Removal of the nearly colorless supernatant at –70 °C by cannula and brief drying of the product at room temperature under vacuum provided 0.38 g (49%) of Ti(CO)$_5$(dmpe). The sample was spectroscopically free of **1**, but it contained small amounts of dmpe·2BH$_3$[28] as indicated by the presence of a rather broad weak absorption in the ν(B–H) region centered at 2360 cm^{-1}. IR (tetrahydrofuran) ν(CO): 1996 (w), 1870 (s) cm^{-1}; (Nujol): 1992 (m), 1903 (sh), 1874 vs, 1843 (s) cm^{-1}. NMR ^{1}H (tetrahydrofuran-d_8, 23 °C) δ 1.41 (d, J = 6.4 Hz, P–CH$_3$), 1.80 (d, J = 16.1 Hz, P–CH$_2$); (toluene-d_8, 23 °C) δ 0.846 (d, J = 6.3 Hz, P–CH$_3$), 0.852 (d, J = 16.0 Hz, P–CH$_2$). The latter signal is practically superimposed on the former one in toluene). ^{31}P{^{1}H} (tetrahydrofuran, 23 °C) δ 29.8 (s) (very small amounts of Ti(CO)$_3$(dmpe)$_2$ were also observed in freshly prepared solutions); (toluene-d_8, 23 °C) δ 29.4 (s).

Compound **3** was extremely air sensitive, but less so than **1**. For example, addition of small amounts of oxygen to solutions containing **1** and **3** caused rapid and preferential oxidation of **1**. Compound **3** darkens markedly within 2 h at room temperature even under a CO atmosphere and rapidly decomposes above 80 °C. Due to its poor thermal stability attempts to obtain satisfactory elemental analyses or mass spectra were unsuccessful. Crystalline **3** is stable at –10 °C for at least 1 year under CO. It provides fairly stable solutions in THF, DME, or toluene, which may be stirred at room temperature for 12 h under CO without extensive decomposition.

Method B. From TiCl$_4$·dmpe. The same initial procedure for the synthesis of **1** was used, except only 1 equiv of dmpe was added. The quantities of reactants used in this synthesis were as follows: Na–C$_{10}$H$_8$ (14.3 mmol), C$_{10}$H$_8$ (0.915 g, 7.15 mmol) in 100 mL of THF; TiCl$_4$·dmpe (1.21 g, 3.57 mmol) in 100 mL of THF. After carbonylation and warming of the solution an IR spectrum showed mostly Ti(CO)$_5$(dmpe) in solution, along with some Ti(CO)$_3$(dmpe)$_2$. Treatment of the solution with 1 M BH$_3$·THF (8 mL) in THF and stirring under a CO atmosphere for 24 h caused all Ti(CO)$_3$(dmpe)$_2$ to disappear. Workup as in Method A provided 0.25 g (21% yield) of red crystalline Ti(CO)$_5$(dmpe), which was spectroscopically identical with compound **3**.

Ti(^{13}CO)$_5$(dmpe) (4). By the same procedure used to prepare **3**, Method A, 1.00 g (2.3 mmol) of Ti(^{13}CO)$_3$(dmpe)$_2$ was converted to 0.25 g (32% yield) of product **4** which contained a very small amount of starting material. This is an unoptimized yield that can undoubtedly be improved. IR (tetrahydrofuran) ν(^{13}CO): 1953 (w), 1831 (s) cm^{-1}. Calculated ν(^{13}CO) based on the corresponding ν(^{12}CO) values of **3**: 1951, 1828 cm^{-1}. (Nujol): 1951 (m), 1857 (sh), 1830 (vs), 1807 (s) cm^{-1}. NMR ^{13}C{^{1}H} (tetrahydrofuran-d_8, 23 °C) δ 260.6 (t, J = 8.8 Hz, CO); (–100 °C) δ 266.5 (apparent s, 4 CO), 239.3 (apparent s, 1 CO) weak absorptions at 300.3, 275.8 (Ti(^{13}CO)$_5$(dmpe)$_2$), and 185.2 (free ^{13}CO) were also observed. ^{13}C signals for coordinated dmpe were not resolved. ^{31}P{^{1}H} (tetrahydrofuran, 23 °C) δ 30 (binomial sextet, J = 8.9 Hz, dmpe). The resolved sextet was observed down to –90 °C with no change in coupling constant.

Ti(CO)$_4${CH$_3$C(CH$_2$PMe$_2$)$_3$} (5). Neat (CH$_3$C(CH$_2$PMe)$_2$) (trmpe) (0.68 g, 2.7 mmol) was added to a solution containing 1.00 g (2.3 mmol) of Ti(CO)$_3$(dmpe)$_2$ in 50 mL of THF. The argon atmosphere was replaced by CO and stirred for 5 h at room temperature. At the end of this period all Ti(CO)$_3$(dmpe)$_2$/Ti(CO)$_5$(dmpe) had converted to the product that had partially deposited as shiny red crystals. An additional 20 mL of THF was added to dissolve all product. Filtration provided a deep red solution. All but about 10 mL of solvent was removed under partial vacuum to provide a slurry containing extremely small crystalline flakes. Methylbutane (ca. 200 mL) was then added with swirling to precipitate out virtually all product. This was washed with more methylbutane (2 × 50 mL) and then dried in vacuo at room temperature. Recrystallization from THF–methylbutane by the above procedure provided 0.78 g (82% yield) of orange-red fluffy microcrystalline **5** which provided satisfactory analyses (dec >150 °C). Anal. Calcd for C$_{15}$H$_{27}$O$_4$P$_3$Ti: C, 43.71; H, 6.60; P, 22.54. Found: C, 43.56; H, 6.68; P, 22.30. IR (tetrahydrofuran) ν(CO): 1930 (m), 1833 (sh), 1808 (s) cm^{-1}; (Nujol) 1921 (s), 1828 (sh), 1783 (vs), 1771 (vs) cm^{-1}. NMR (1,2-dimethoxyethane-d_{10}, 23 °C) ^{1}H δ 1.42 (q, J = 2.65 Hz, 6 H), 1.31 (apparent s, 18 H), 1.09 (q, J = 2.4 Hz, 3 H). ^{31}P{^{1}H} δ –10.5 (s). FAB HRMS (M – H$^+$): exact mass calculated for ^{12}C$_{15}$^{1}H$_{26}$^{16}O$_4$^{31}P$_3$^{48}Ti, 411.0523; found, 411.0502.

Crystalline **5** is remarkably resistant toward aerial oxidation and will survive for at least an hour in air without obvious deterioration. In this respect it is far different from most other Ti(0) derivatives described in this paper which are either pyrophoric (e.g., Ti(CO)$_3$(dmpe)$_2$) or oxidize completely within minutes in air (e.g., Et$_4$N$^+$CpTi(CO)$_4^-$). This unusual robustness is undoubtedly due to its high crystalline lattice stability which also is responsible for the relatively low solubility of **5** in most organic solvents in which **1** or **3** is quite soluble. Although solutions of **5** are air sensitive they are much less so than those of Ti(CO)$_3$(dmpe)$_2$. It is nearly insoluble in saturated hydrocarbons, very slightly soluble in ethyl ether, slightly soluble in toluene, and most soluble in THF or DME, in which it provides deep red and very thermally stable solutions. Although it is fairly stable in acetonitrile at 0 °C, the solutions are unstable at room temperature and decompose almost entirely within 3 h to provide an insoluble air sensitive red brown solid of unknown nature.

[Et$_4$N][C$_5$H$_5$Ti(CO)$_4$] (6). A solution containing 0.65 g (1.5 mmol) of Ti(CO)$_3$(dmpe)$_2$ in 50 mL of DME was stirred under a CO atmosphere for 3 h at room temperature and then cooled to 0 °C. Infrared spectra showed that much of the reactant had been converted to Ti(CO)$_5$(dmpe) during this time. A precooled (0 °C) solution of 0.27 g (1.5 mmol) of [Na(DME)]C$_5$H$_5$ in 25 mL of THF was then added rapidly by cannula. After 3 h all Ti(CO)$_5$(dmpe) had been converted to C$_5$H$_5$Ti(CO)$_4^-$ but unconverted Ti(CO)$_3$(dmpe)$_2$ remained. The solution was then gradually warmed to room temperature while being stirred under a CO atmosphere and left for an additional 6 h. At the end of this period an IR spectrum of the solution showed the presence of only bands due to product. The CO atmosphere was then replaced by argon. Anhydrous [Et$_4$N]Br (0.60 g) was added and the solution was stirred for 6 h and then filtered (medium porosity glass frit). After removal of solvent and dmpe in vacuo, the resulting deep red-violet crystalline product was washed with cold (0 °C) anhydrous ethanol (2 × 5 mL), in

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[27] Used as received from Isotec, Inc., 7542 McEwen Road, Dayton, OH 45459. It has been observed that unpurified ^{13}CO from suppliers will often cause substantial decomposition/oxidation of titanium(0) carbonyls, due to the presence of appreciable amounts of CO$_2$ and other contaminants.

[28] Burg, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 2226.

which it is slightly soluble, and dried in vacuo to provide 0.41 g (77% yield) of **6**. The product obtained was spectroscopically identical with bona fide $[\mathrm{Et_4N}][\mathrm{C_5H_5Ti(CO)_4}]$.[1b]

$[\mathrm{Et_4N}][\{\mathrm{HB(Pz)_3}\}\mathrm{Ti(CO)_4}]$ (7). A solution containing 0.50 g (1.16 mmol) of $\mathrm{Ti(CO)_3(dmpe)_2}$ in 70 mL of DME was stirred under CO at room temperature for about 3 h to provide the equilibrium mixture of $\mathrm{Ti(CO)_5(dmpe)}$ and $\mathrm{Ti(CO)_3(dmpe)_2}$. To this was added 0.29 g (1.16 mmol) of potassium hydrotris(1-pyrazolyl)borate ($\mathrm{K[HB(Pz)_3]}$) (Columbia Organics) in 20 mL of DME. After the mixture was stirred for 3 h at room temperature under an atmosphere of CO an infrared spectrum showed that the reaction was complete. As in the preparation of **6**, 0.50 g of powdered, anhydrous $[\mathrm{Et_4N}]\mathrm{Br}$ was added and the mixture was stirred for 6 h and filtered to provide a clear deep red solution. Solvent was removed in vacuo at room temperature and the resulting red-orange solid was purified by washing with toluene, cold ethanol, and ether, followed by drying under a dynamic vacuum. An acetonitrile–toluene recrystallization provided 0.41 g (70% yield) of thermally robust (dec 150–155 °C) and air sensitive red crystals of satisfactory purity. Anal. Calcd for $\mathrm{C_{21}H_{30}O_4N_7BTi}$: C, 50.12; H, 6.01; N, 19.48. Found: C, 49.89; H, 6.04; N, 19.56. IR (acetonitrile) ν(CO): 1912 (m), 1755 (s) cm^{-1}; (Nujol) ν(CO): 1908 (m), 1743 (br s) cm^{-1}. NMR (dimethyl-d_6 sulfoxide) ^{1}H δ {7.89 (d, J = 1.3 Hz), 7.62 (d, J = 2.1 Hz) 6.14 (t, J = 2.0 Hz), $\mathrm{C_3}\mathit{H}_3\mathrm{N_2}$}, 3.18 (q, J = 7.2 Hz, $\mathrm{CH_3C}\mathit{H}_2\mathrm{N}$), 1.15 (t, J = 7.2 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2N}$). We were unsuccessful in observing the signal of the hydrogen attached to the boron which is often broadened by B–H coupling. ^{13}C{^{1}H} (dimethyl-d_6 sulfoxide) δ 286 (s, CO), 143, 134, 104 (s, $\mathit{C}_3\mathrm{H_3N_2}$); 51 (s, $\mathrm{CH_3}\mathit{C}\mathrm{H_2N}$), 7 (s, $\mathit{C}\mathrm{H_3CH_2N}$).

$[\mathrm{Na(1,2\text{-}dimethoxyethane)}][\mathrm{C_9H_7}]$ (8). Indene was purified by passage through a column of activated alumina followed by vacuum distillation. By the same procedure employed to prepare $[\mathrm{Na(DME)}][\mathrm{C_5H_5}]$,[21] the corresponding $[\mathrm{Na(DME)}][\mathrm{C_9H_7}]$ was obtained in 60% yield as a free-flowing light-yellow powder. Although elemental analyses were not obtained for this apparently new substance, its NMR spectra in dimethyl-d_6 sulfoxide were free of impurities and entirely in accord with the proposed formulation: ^{1}H δ 7.09 (dd, J = 5.9, 3.0 Hz, 2 H), 6.35 (t, J = 1.9 Hz, 1 H), 6.21 (dd, J = 5.9, 3.1 Hz, 2 H), 5.70 (d, J = 3.3 Hz, 2 H), 3.43 (br s, $\mathrm{OCH_2}$, 4 H), 3.24 (br s, 6 H). ^{13}C{^{1}H} δ 129.3, 117.3, 117.2, 110.3, 92.6 (indenyl carbons), 71.1, 58.0 (DME carbons).

$[\mathrm{Et_4N}][\mathrm{C_9H_7Ti(CO)_4}]$ (9). Method A. From $\mathrm{Ti(CO)_3(dmpe)_2}$. As previously described, a solution of $\mathrm{Ti(CO)_3(dmpe)_2}$ (0.65 g, 1.5 mmol) in 80 mL of DME was carbonylated to form $\mathrm{Ti(CO)_5(dmpe)}$. To this solution at –30 °C was added $[\mathrm{Na(DME)}][\mathrm{C_9H_7}]$ (0.70 g, 3.1 mmol) in 30 mL of DME. The mixture was then stirred under a CO atmosphere for ca. 12 h while slowly being warmed to room temperature. Powdered $[\mathrm{Et_4N}]\mathrm{Br}$ (0.32 g, 1.5 mmol) was added, and the slurry was stirred for 12 h. After filtration and removal of all but about 10 mL of solvent, ethyl ether was added whereupon dark red crystals precipated. These were washed thoroughly with ether and dried in vacuo to give 0.47 g (77% yield) of compound **9**. Except for slight contamination by $[\mathrm{Na(DME)}][\mathrm{C_9H_7}]$, the product was spectroscopically identical with the analytical sample made by method B.

Method B. From $\mathrm{TiCl_3{\cdot}3THF}$. A cold (0 °C) solution of $[\mathrm{Na(DME)}][\mathrm{C_9H_7}]$ (3.08 g, 13.5 mmol) in 100 mL of THF was added to a slurry of $\mathrm{TiCl_3{\cdot}3THF}$ (5.00 g, 13.5 mmol) in 200 mL of THF also at 0 °C. This greenish mixture, presumably containing (indenyl)$\mathrm{TiCl_2}$, was stirred for 12 h, cooled to –78 °C, and added via cannula to a mechanically stirred slurry of $\mathrm{Na{-}C_{10}H_8}$ (41 mmol) in 200 mL of THF at –78 °C. After 5 min the argon atmosphere was replaced by carbon monoxide and the mixture was allowed to slowly warm to room temperature over a period of about 12 h. After filtration, powdered $[\mathrm{Et_4N}]\mathrm{Br}$ (2.84 g, 13.5 mmol) was introduced and stirring was continued for 12 h. After a second filtration, solvent was removed under vacuum. The resulting dark red solid was washed thoroughly with hexane (3 × 50 mL) and dried to provide 1.85 g (34% yield) of product. The analytical sample was obtained by recrystallization from $\mathrm{THF{-}Et_2O}$ and careful washing with cold anhydrous ethanol and ether. It was then dried in vacuo. Decomposition at 79–80 °C without melting. Anal. Calcd for $\mathrm{C_{21}H_{22}NO_4Ti}$: C, 62.23; H, 6.71; Found: C, 62.10; H, 6.68. IR (tetrahydrofuran) ν(CO): 1925 (m), 1778 (s) cm^{-1}; (Nujol), 1920 (m), 1763 (s; br) cm^{-1}. NMR ($\mathrm{Me_2SO}$-d_6): ^{1}H δ 1.13 (tt, $\mathrm{CH_3}$ of $\mathrm{Et_4N^+}$, $J_{\mathrm{H-H}}$ = 7.2 Hz, $J_{\mathrm{N-H}}$ = 1.9 Hz, 12 H), 3.17 (q, $\mathrm{CH_2}$ of $\mathrm{Et_4N^+}$, $J_{\mathrm{H-H}}$ = 7.2 Hz, 8 H), 5.36 (t, $J_{\mathrm{H-H}}$ = 3.1 Hz, 1 H). 5.60 (d, $J_{\mathrm{H-H}}$ = 3.0 Hz, 2 H), 6.64 (dd, J = 6.4, 3.4 Hz, 2 H), 7.30 (dd, J = 6.4, 3.4 Hz, 2 H). ^{13}C{^{1}H} δ 288.7 (CO) (124.0, 119.1, 114.5, 98.7, 83.8, ($\mathrm{C_9H_7}$)) (51.4, 7.1 ($\mathrm{Et_4N^+}$)).

$[\mathrm{Ph_4As}][\mathrm{Ph_3SnTi(CO)_4(dmpe)}]$ (10). A solution of $\mathrm{Ti(CO)_3(dmpe)_2}$ (0.50 g, 1.16 mmol) in 50 mL of DME was stirred under a CO atmosphere at room temperature for 3 h. Pale yellow $\mathrm{Ph_3SnNa}$ (1.16 mmol), prepared from the reaction of $\mathrm{Na{-}C_{10}H_8}$ (2.32 mmol) and $\mathrm{Ph_3SnCl}$ (0.45 g, 1.16 mmol) in 50 mL of DME, was added and the resulting mixture was stirred under CO for 12 h. After cation exchange with $\mathrm{Ph_4AsCl}$ (0.50 g, 1.19 mmol), filtration, and concentration of the solution to 10 mL, air sensitive red-purple crystals were precipitated by adding 50 mL of ethanol via cannula. The product was washed with ethanol (2 × 20 mL) and dried in vacuo. It was then recrystallized from $\mathrm{CH_3CN}$–toluene. Removal of slightly soluble $\mathrm{Ph_6Sn_2}$ was accomplished by stirring the solid in 100 mL of toluene for 5 h. The analytical sample was then obtained in 73% yield (0.88 g) by washing **10** with 20 mL of pentane and drying under vacuum at room temperature (decomposition at about 110 °C without melting). Anal. Calcd for $\mathrm{C_{52}H_{51}O_4AsP_2SnTi}$: C, 59.86, H, 4.89; Sn, 11.39. Found: C, 59.86; H, 5.00; Sn, 11.35. IR (dimethyl sulfoxide) ν(CO): 1897 (m), 1800 (s), 1770 (s) cm^{-1}; (Nujol): 1909 (m), 1801 (s), 1775 (s), 1749 (s) cm^{-1}. NMR (acetonitrile-d_3, 23 °C): ^{1}H δ 7.95–7.00 (m, $\mathrm{Sn{-}C_6H_5}$, $\mathrm{As{-}C_6H_5}$), 1.57 (d, J = 15.7 Hz, $\mathrm{P{-}CH_2}$ of dmpe), 1.12 (d, J = 5.7 Hz, $\mathrm{P{-}CH_3}$). ^{31}P{^{1}H} δ 37.2 (s, dmpe). Also observed in NMR spectra were peaks due to free dmpe. Solutions of **10** in $\mathrm{CD_3CN}$ or DMSO are not very thermally stable and must be freshly prepared to obtain good spectra. No ^{13}C signal for carbonyl groups in unenriched **10** was detected.

$[\mathrm{Ph_4As}][\mathrm{Ph_3GeTi(CO)_4(dmpe)}]$ (11). By the same procedure as described for compound **10**, the reaction of $\mathrm{Ti(CO)_3(dmpe)_2}$ (0.55 g, 1.27 mmol) and $\mathrm{Ph_3GeNa}$ (1.27 mmol) in 50 mL of DME under a CO atmosphere provided, after cation exchange and recrystallization, 0.66 g (53%) of deep red **11** which is more air and moisture sensitive and much less stable in solution than compound **10** (decomposition at about 90 °C without melting). Anal. Calcd for $\mathrm{C_{52}H_{51}O_4AsGeP_2Ti}$: C, 62.63; H, 5.12; Found: C, 62.29; H, 5.24. IR (dimethyl sulfoxide) ν(CO): 1900 (m), 1800 (s), 1769 (s) cm^{-1}; (Nujol): 1913 (m), 1796 (s), 1777 (s), 1737 (s) cm^{-1}. NMR (dimethyl-d_6 sulfoxide, 23 °C): ^{1}H δ 7.89–6.97 (m, $\mathrm{C_6H_5{-}Ge}$, $\mathrm{C_6H_5{-}As}$), 1.48 (d, J = 15.8 Hz, $\mathrm{P{-}CH_2}$), 0.97 (d, J = 5.4 Hz, $\mathrm{P{-}CH_3}$). ^{31}P{^{1}H} δ 36.1 (s, coord dmpe), –47.7 (s, free dmpe). Both ^{31}P and ^{1}H NMR spectra showed the presence of substantial amounts of free dmpe due to extensive decomposition of **11** in solution.

Results and Discussion

Carbonylation of Naphthalene Complexes of the Early Transition Metals. Datta and Wreford's report in 1976 on the synthesis of $\mathrm{(dmpe)_2Ta(CO)_2Cl}$ by the reduction of $\mathrm{(dmpe)_2TaCl_4}$ with sodium naphthalene under a carbon monoxide atmosphere at room temperature[29] rekindled our long-standing interest in the carbonyl chemistry of the early transition elements.[30] Although Wreford and co-workers later showed that isolated $\mathrm{(dmpe)_2Ta}(\eta^4$-naphthalene)Cl, synthesized from an analogous $\mathrm{Na{-}C_{10}H_8}$ reduction conducted under a nitrogen atmosphere, did not undergo facile carbonylation, we wondered whether more highly reduced naphthalene intermediates might be involved in the carbonylation process. They also prepared the highly reduced anion $[\mathrm{(dmpe)_2Ta}(\eta^4\text{-}\mathrm{C_{10}H_8})]^-$ but did not examine its reactivity toward carbon monoxide.[31] Perhaps very significant in this regard is recent work by Jonas and co-workers who carbonylated the paramagnetic naphthalenevanadate, $\mathrm{CpV(C_{10}H_8)^-}$, at atmospheric pressure and obtained an equimolar mixture of $\mathrm{CpV(CO)_3}^{2-}$, $\mathrm{CpV(CO)_4}$, and free naphthalene.[32] Kundig and Timms's earlier demonstration of the ease with which coordinated naphthalene in $\mathrm{Cr(C_{10}H_8)_2}$ and $\mathrm{Mo(C_{10}H_8)_2}$ was displaced by carbon monoxide and other acceptor ligands emphasized the utility of naphthalene complexes in the syntheses of highly reduced organometallics of the early transition metals.[33] These and related events set the stage for our development of the first atmospheric pressure synthesis of $\mathrm{Nb(CO)_6}^-$ and $\mathrm{Ta(CO)_6}^-$.[13,34] Once we established that this method worked for group 5 elements, it was certainly important to determine whether this synthetic methodology could

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(29) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134.

(30) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

(31) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

(32) Jonas, K.; Wiskamp, V. *Z. Naturforsch.* **1983**, *38B*, 1113. Also see Jonas, K.; Rüsseler, W.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 925.

(33) (a) Kundig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 912. (b) Hawker, P. N.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1983**, *2*, 388. (c) Osborne, J. H.; Trogler, W. C.; Morand, N. D.; Francis, C. G. *Organometallics* **1987**, *6*, 94.

(34) Calderazzo and co-workers [Calderazzo, F.; Englert, U.; Pamploni, G.; Pelizzi, G.; Zamboni, R. *Inorg. Chem.* **1983**, *22*, 1865] independently developed a markedly different atmospheric pressure reductive carbonylation synthesis of $\mathrm{Nb(CO)_6}^-$. However, their process is rather ineffective for the preparation of $\mathrm{Ta(CO)_6}^-$ under these conditions.

be extended to the synthesis of zero or even subvalent group 4 carbonyls and related organometallics.

Our initial attempts in this regard were uniformly discouraging. For example, treatment of $TiCl_4L_2$ (L_2 = 2THF, DME, $Me_2NCH_2CH_2NMe_2$) or $TiCl_3(THF)_3$ with three, four, or more equivalents of alkali-metal naphthalenides at −60 to −80 °C in THF or DME under argon (followed by treatment with CO) or under carbon monoxide at atmospheric pressure invariably gave insoluble non-carbonyl-containing black solids that were not investigated further. Thus, while $VCl_3(THF)_3$ would be converted to $V(CO)_6^-$ in 30–40% (unoptimized) yield by the same procedure,[35a] no evidence was obtained that zero or subvalent titanium carbonyls could be prepared in this way.[70]

Our attention then turned to the prospect of synthesizing phosphine-substituted derivatives of the unknown $Ti(CO)_7$. Wreford had earlier shown that the very good donor ligand dmpe, $Me_2PCH_2CH_2PMe_2$, was capable of stabilizing the zerovalent titanium carbonyl, $Ti(CO)_3(dmpe)_2$.[10] Until recently this substance was the most thermally stable Ti(0) carbonyl known.[36] Since only one reaction of $Ti(CO)_3(dmpe)_2$ had been previously reported, i.e., with PF_3 in the presence of excess dmpe to give $Ti(CO)_2(PF_3)(dmpe)_2$,[9] and Wreford was no longer active in this area,[35b] it was clear that the carbonyl chemistry of Ti(0) was quite an inviting area for exploration. For this reason it was important to determine whether our low-temperature sodium naphthalenide route would provide a facile route to the relatively inaccessible $Ti(CO)_3(dmpe)_2$.

An Improved Synthesis of $Ti(CO)_3(dmpe)_2$. When one or more equivalents of dmpe was added to $TiCl_4L_2$, vide supra, the solutions rapidly changed from yellow to bright orange or orange red.[37a] Subsequent addition to 4 equiv of $Na–C_{10}H_8$ at low temperatures under argon provided a deep red brown solution, which resembled those of the aforementioned niobium and tantalum intermediates, believed to be bis(naphthalene)metalates(−1).[13] Identical solutions were also obtained from corresponding reductions of "$TiCl_4(dmpe)_2$".[37a] These absorbed carbon monoxide at low temperature and changed to a much brighter red color. When about 2.3 equiv of dmpe per titanium was used, excellent and reproducible yields (70–80%) of $Ti(CO)_3(dmpe)_2$ were isolated. With this procedure 5–10 g of the product can be readily obtained in 2 or 3 days by one individual.

Although the nature of the red brown intermediate in this reaction remains unknown, it is very likely that naphthalene as well as dmpe plays an important role in stabilizing this possible zerovalent titanium species. Evidence for active participation by the naphthalene in the reduction process will now be summarized. Attempts to achieve atmospheric pressure reductive carbonylations of $TiCl_4(dmpe)$ in the presence of excess dmpe with a variety of reducing agents including finely divided Mg, Al powder, NaK, Li, other alkali metals, or Na–Hg from 0 to −60 °C in the absence of naphthalene were uniformly unsuccessful and provided only non-carbonyl-containing materials, which were not characterized further.[37b] Also when 1-methylnaphthalene was used as an electron carrier instead of naphthalene, much poorer yields of $Ti(CO)_3(dmpe)_2$ were obtained, suggesting that 1-methylnaphthalene did not bind as well as naphthalene, perhaps for steric reasons.[38] Finally, the presence of 2–4 equiv of additional naphthalene over that required for the sodium metal increased the yields of the $Ti(CO)_3(dmpe)_2$ from about 30–50% to 70–80%. Since naphthalene is inexpensive and easily removed from $Ti(CO)_3(dmpe)_2$, this modification of our sodium naphthalenide procedure has proven to be quite beneficial. Certainly the presence of excess naphthalene during the reduction should aid in the formation and stabilization of a possible labile naphthalene complex.[39] This naphthalene effect is undoubtedly our strongest evidence thus far for the intermediacy of a naphthalene–titanium complex. While it is tempting to formulate the intermediate (shown as [Ti] in the equation below) as $Ti(naphthalene)_x(dmpe)_{3-x}$, where x = 1 or 2 and naphthalene could be tetrahapto, hexahapto, or a combination thereof, depending on whether [Ti] is a 16- or 18-electron species,[40] it could also be a naphthyl hydride species, which are well precedented in the chemistry of group 4 and later transition metals, especially with dmpe as a ligand.[41] Efforts are underway to determine the nature of this and related

$$TiCl_4(dmpe) + 4Na–C_{10}H_8 \xrightarrow{i} [Ti] \xrightarrow{ii} \xrightarrow{iii} Ti(CO)_3(dmpe)_2 \quad (1)$$

i (THF, −70 °C, dmpe, 2–4 equiv of $C_{10}H_8$, argon),
ii (CO, 1 atm P, −70 to 0 °C),
iii (remove CO, add argon)

materials, which function as neutral or anionic "weakly solvated" early transition-metal moieties. Most certainly the general reactivity patterns of such materials with a variety of small molecules should be examined to understand their potential in chemical synthesis.

Many years ago Chatt and Watson examined the reaction of $TiCl_4(dmpe)$ and excess dmpe with $Na–C_{10}H_8$ using a somewhat different procedure and conditions than ours.[23] They titrated solutions of $TiCl_4$–dmpe with 4 equiv of $Na–C_{10}H_8$ under a *nitrogen* atmosphere at low temperature in an attempt to prepare the still unknown $Ti(dmpe)_3$.[42] Addition of the fourth equivalent of $Na–C_{10}H_8$ caused a deep red brown solution to turn black. We repeated their inverse addition procedure under argon and observed essentially the same color changes reported previously, except under this atmosphere the deep red brown solution was fairly stable at low temperature. Subsequent treatment with carbon monoxide provided a 70% isolated yield of bona fide $Ti(CO)_3(dmpe)_2$.[43] On this basis, Chatt and Watson's failure to achieve a positive result from this reaction could well have been due to the reaction of the

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[35] (a) Warnock, G. F. P.; Ellis, J. E., unpublished research: (b) Wreford, S. S., private communication, June 1983.

[36] In this context, it is useful to consider the relative thermal stabilities of $Ti(CO)_6$ [dec ≥ −220 °C: ref 8], $V(CO)_6$ [dec ≥70 °C: Calderazzo, F.; Ercoli, R.; Natta, G. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; J. Wiley: New York, 1968; Vol. 1, p 1], and $Cr(CO)_6$ [mp 152–153 °C: King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1, p 88]. While it has been suggested that the reluctance of titanium to form stable binary carbonyls is a consequence of the high energy of its 3d orbitals compared to those of the later transition metals and the acceptor orbitals on CO [Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*, 3rd ed.; Methuen: London, 1967; Vol. 2, pp 5–6], a more important factor may be that zerovalent titanium is simply too electron poor to effectively participate in back-bonding with CO in the absence of good donor ligands such as dmpe or, for example, $C_5H_5^-$ (ref 1). On this basis, the possibility of stabilizing $Ti(CO)_6$ by reduction to $Ti(CO)_6^-$ (isoelectronic with $V(CO)_6$) or $Ti(CO)_6^{2-}$ (isoelectronic with $Cr(CO)_6$) is of particular interest.

[37] (a) Chatt and Hayter (ref 20) did not mention a reaction of $TiCl_4(dmpe)$ with excess dmpe. However, in THF, the orange hue of $TiCl_4(dmpe)$ rapidly changed to a red color in the presence of an additional equivalent of dmpe. A deep red crystalline product, much different in appearance from that of $TiCl_4(dmpe)$ but very similar to the known $TiCl_4(o\text{-}C_6H_4(AsMe_2)_2)_2$ [Clark, R. J. H.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1962**, 2460], often crystallized at low temperature. This possible bis(dmpe) complex of $TiCl_4$ was not examined further. (b) Recently red-black *trans*-$TiCl_2(dmpe)_2$ has been prepared by the reduction of a mixture of $TiCl_4$ and dmpe in THF by magnesium: Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339.

[38] Naphthalene and 1-methylnaphthalene form radical anions of essentially the same reducing ability as judged from their reported reduction potentials [Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970].

[39] Use of excess naphthalene may well also substantially improve the yields of $Nb(CO)_6^-$ and $Ta(CO)_6^-$ (ref 13), particularly in the case of niobium which forms an especially unstable intermediate.

[40] The known 16-electron species $Ti(\eta^4\text{-butadiene})_2(dmpe)$ is formally analogous to [Ti] with x = 2: Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353.

[41] (a) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 2. (b) Ittel, S.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080. (d) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577; (e) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

[42] Cloke, F. G. N.; Fyne, P. J.; Gibson, V. C.; Green, M. L. H.; Ledoux, M. J.; Perutz, R. N. *J. Organomet. Chem.* **1984**, *277*, 61.

[43] Quantitative transfers of $Na–C_{10}H_8$ were often difficult at low temperatures due to the poor solubility of the naphthalenide salt. For this reason, we prefer to add solutions of the halide to the $Na–C_{10}H_8$ solution/slurry.

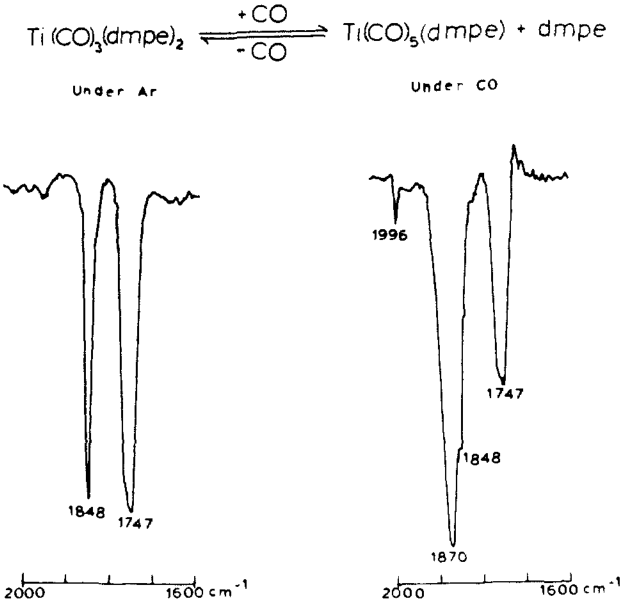

Figure 1. Infrared spectra of $Ti(CO)_3(dmpe)_2$ in tetrahydrofuran under argon (spectrum A) and after stirring under carbon monoxide for about 3 h at room temperature (spectrum B). The two major absorptions at lowest energies are due to $Ti(CO)_3(dmpe)_2$, while the additional bands in spectrum B belong to $Ti(CO)_5(dmpe)$.

red brown intermediate, [Ti], with nitrogen. Reinvestigation of this reaction under nitrogen is warranted; reactions of low-valent group 4 compounds with dinitrogen are well documented.[8,41a,44,45]

Synthesis and Characterization of $Ti(CO)_5(dmpe)$, a New Organophosphine Derivative of $Ti(CO)_7$. Initial attempts to prepare Wreford's compound, $Ti(CO)_3(dmpe)_2$, by the reductive carbonylation of a mixture of $TiCl_4(THF)_2$ and 2 equiv of dmpe gave surprising results. After the carbonylation at low temperature and warming, an infrared spectrum of the unfiltered solution was taken before removal of CO. In addition to IR bands in the ν(CO) region due to $Ti(CO)_3(dmpe)_2$ at 1848 (s), 1757 (sh), and 1747 (s) cm^{-1}, there were new bands at higher energies (1996 (w), 1870 (s) cm^{-1}) due to another titanium carbonyl. Removal of the carbon monoxide and replacement with argon (or nitrogen) caused all bands at higher energies to disappear while those due to $Ti(CO)_3(dmpe)_2$ grew in. Readdition of CO (atmospheric pressure) at room temperature provided within about 3 h the original mixture, which is now known to contain $Ti(CO)_3(dmpe)_2$ and $Ti(CO)_5(dmpe)$. These spectral changes are shown in Figure 1. Evidently Wreford's group never took an infrared spectrum of their original carbonylation product while it was still under a CO atmosphere! We now know their observation that solutions of $Ti(CO)_3(dmpe)_2$ are stabilized under an atmosphere of CO is incorrect since the tricarbonyl under these conditions is substantially converted to $Ti(CO)_5(dmpe)$![9,10]

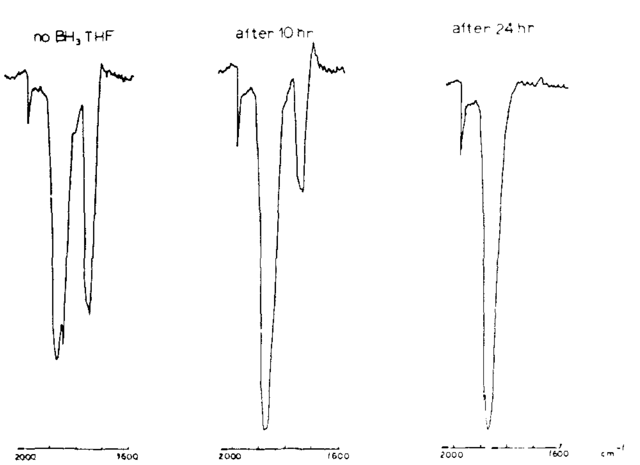

Figure 2. Solution infrared spectra of a mixture of $Ti(CO)_5(dmpe)$ and $Ti(CO)_3(dmpe)_2$ before and after treatment with $BH_3{\cdot}THF$ under carbon monoxide. After 24 h only the pentacarbonyltitanium species remains in solution.

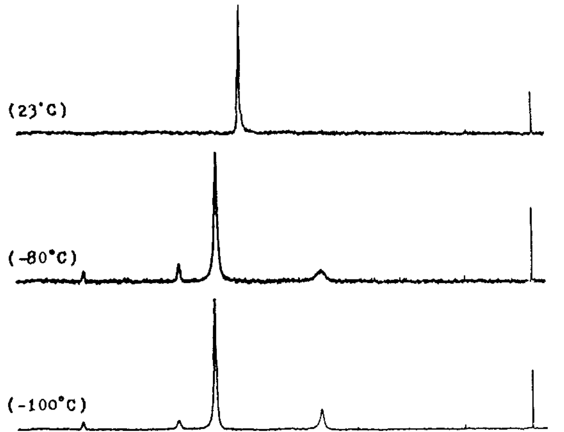

Figure 3. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum of $Ti(^{13}CO)_5(dmpe)$ in tetrahydrofuran.

Relatively pure $Ti(CO)_5(dmpe)$ is best obtained by treating the mixture (eq 2) under CO with about 2.1 equiv of $BH_3{\cdot}THF$, which quantitatively reacts with free dmpe and slowly causes decomposition of $Ti(CO)_3(dmpe)_2$ but has little effect on the pentacarbonyl (eq 3). The slightly soluble $dmpe{\cdot}2BH_3$[28] was mostly removed by filtration at low temperature. As shown in Figure 2, the complete removal of $Ti(CO)_3(dmpe)_2$ from the reaction mixture required about 24 h at 0 °C. At higher temperatures significant decomposition occurred, while below 0 °C the conversion was impracticably slow. (Another "phosphine sponge", 9-borabicyclo[3.3.1]nonane dimer (9-BBN),[46] removed $Ti(CO)_3(dmpe)_2$ more rapidly, but we have been unsuccessful in effectively separating the 9-BBN–dmpe adduct from $Ti(CO)_5(dmpe)$, thus far.) Removal of solvent at 0 °C followed by washing

$$Ti(CO)_3(dmpe)_2 + 2CO \rightleftarrows Ti(CO)_5(dmpe) + dmpe \quad (2)$$

$$dmpe + 2BH_3{\cdot}THF \rightarrow dmpe{\cdot}2BH_3 + 2THF \quad (3)$$

with pentane provided about a 50% (unoptimized) yield of bright red crystalline $Ti(CO)_5(dmpe)$, largely free of $Ti(CO)_3(dmpe)_2$. Although the pentacarbonyl could also be obtained by the $Na{-}C_{10}H_8$ reductive carbonylation of $TiCl_4(dmpe)$ in the absence of any extra dmpe (see Method B in the Experimental Section), much decomposition occurred during this reaction and significant amounts of $Ti(CO)_3(dmpe)_2$ also formed. Only rather poor yields (ca. 20%) of $Ti(CO)_5(dmpe)$ have been obtained from this synthesis. Indeed, in the best syntheses of $Ti(CO)_3(dmpe)_2$, excess dmpe as well as naphthalene helped to maximize product yield.

Even under a CO atmosphere, bright red crystalline $Ti(CO)_5(dmpe)$ darkened markedly within 1 h at room temperature. Elemental analyses or mass spectra have not been obtained due to its thermal instability. However, good evidence for its formulation has been obtained from the ^{13}C and ^{31}P NMR spectra of the 99% ^{13}C-enriched material. These show the binomial triplet and sextet, respectively, expected for a fluxional seven-coordinate molecule of this composition. These spectra were essentially temperature independent from room temperature to −90 °C. The binomial sextet with J_{P-C} = 8.9 Hz arises from five equivalent ^{13}CO groups coupled to the coordinated dmpe group. The cor-

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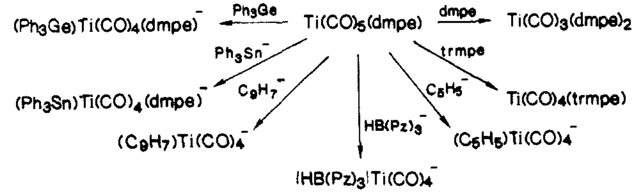
(44) (a) Vol'pin, M. E.; Shur, V. B. In *Organometallic Reactions*; Becker, E., Tsutsui, M., Eds.; J. Wiley: New York, 1970; Vol. 1, p 55. (b) Chatt, J.; Leigh, G. J. *Chem. Soc. Rev.* **1972**, *1*, 121. (c) Van Tamelen, E. E. *Acc. Chem. Res.* **1970**, *3*, 361.

(45) (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087 and references cited therein. (b) Manriquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *J Am. Chem. Soc.* **1976**, *98*, 3042. (c) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

(46) Luck, R.; Morris, R. H. *Inorg. Chem.* **1984**, *23*, 1489.

Scheme I. Reactions of $Ti(CO)_5(dmpe)$ with Various Main Group Nucleophiles



responding $^{13}C\{^1H\}$ NMR spectrum of the same solution of $Ti(^{13}CO)_5(dmpe)$ shows a broad binomial triplet centered at 260.6 ppm with $J_{P-C} \simeq 8.8$ Hz, which arises from coupling of two equivalent ^{31}P atoms of the coordinated dmpe with the five equivalent carbonyl groups.[47] No carbonyl ^{13}C signal could be detected with the unenriched sample. This multinuclear NMR study provides a good example of the use of 99% enriched ^{13}C-labeled carbonyl groups in solving structural and/or compositional problems involving fluxional organometallic compounds. In a previous study, essentially the same strategy was used to unequivocally establish the composition of the thermally unstable $V(CO)_5^{3-}$ in solution.[48] In Figure 3, the proton-decoupled ^{13}C NMR spectra of $Ti(^{13}CO)_5(dmpe)$ in tetrahydrofuran at 23, −80, and −100 °C are shown. At 23 °C the unresolved triplet due to the pentacarbonyltitanium(0) species is observed at 260.6 ppm along with a sharp singlet at 185.2 ppm assigned to free ^{13}CO. Small amounts of $Ti(^{13}CO)_3(dmpe)_2$ are also present in this solution, but the ^{13}C resonance at room temperature (at ca. 282 ppm) is so broad that it is not observed. At −100 °C, the unresolved triplet has changed to two broad singlets (presumably due to unresolved P–C and C–C couplings) at 266.5 and 239.3 ppm of relative area 4:1. These correspond to the weighted average position of the peak at room temperature. The pattern at low temperature is consistent with a carbonyl capped trigonal prismatic structure where the dmpe occupies an edge opposite the unique carbonyl. However, attempts to resolve this structural issue by a single-crystal X-ray diffraction study have been thwarted thus far by our inability to grow suitable single crystals. Weak absorptions at 300.3 and 275.8 ppm of relative areas 1:2 are due to the small amounts of $Ti(^{13}CO)_3(dmpe)_2$ mentioned previously. Wreford previously showed that at −113 °C three inequivalent carbonyl sites are observed at 300.7, 282.1, and 268.3 ppm in THF–toluene for the tricarbonyl complex.[10] A curious feature of the ^1H NMR spectra of $Ti(CO)_5(dmpe)$ in toluene and THF is the unusual change in the chemical shifts of the dmpe protons. Similar spectral changes are observed for $Ti(CO)_3(dmpe)_2$ with the same pair of solvents. We have no good explanation for this apparent anomaly. Infrared spectra of these respective compounds are nearly the same in both solvents.

Chemical Properties of $Ti(CO)_5(dmpe)$. Although $Ti(CO)_3(dmpe)_2$ is fairly resistent to nucleophilic attack by virtue of its very electron rich character, under an atmosphere of carbon monoxide it is readily converted to a new zerovalent titanium species, $Ti(CO)_5(dmpe)$. The latter is quite susceptible to nucleophilic attack and presently is the most useful precursor to other classes of Ti(0) carbonyls. On this basis, $Ti(CO)_5(dmpe)$ may be regarded as a stabilized synthetic equivalent of the unknown $Ti(CO)_7$. We believe that $Ti(CO)_5dmpe$ has the potential to be as important in the development of organotitanium chemistry as, for example, $Cr(CO)_6$ has been for organochromium chemistry.

A survey of the reactions of $Ti(CO)_5(dmpe)$ examined in this study is shown in Scheme I. Free dmpe displaced carbon monoxide within minutes from $Ti(CO)_5(dmpe)$ under a nitrogen or argon atmosphere at room temperature to provide $Ti(CO)_3(dmpe)_2$. Despite Wreford's previous demonstration that PF_3 reacted with $Ti(CO)_3(dmpe)_2$,[9] we have no evidence that additional dmpe reacted with this substance, even in neat dmpe after 8 h at 55–65 °C under argon, or with excess PMe_3 at room temperature. Indeed all attempts to prepare $Ti(dmpe)_3CO$ or $Ti(dmpe)_3$ from $Ti(CO)_3(dmpe)_2$ have failed. Although the reaction chemistry of $Ti(CO)_5dmpe$ has been emphasized in this paper, it is likely that $Ti(CO)_3(dmpe)_2$ will have an interesting chemistry of its own based on its unusually electron rich nature.

In this initial study of the reactions of $Ti(CO)_5(dmpe)$ with main group nucleophiles, only those species that did not react readily with free CO were examined. In this way, the easily isolated $Ti(CO)_3(dmpe)_2$ could be used as the starting material without requiring the isolation of $Ti(CO)_5(dmpe)$, which is not trivial. In all of the reactions examined in this paper, the nucleophiles appeared to react almost exclusively with $Ti(CO)_5(dmpe)$ and were fairly inert toward $Ti(CO)_3(dmpe)_2$. The 3–6-h period generally required for these reactions to go to completion mainly represented the amount of time required for the $Ti(CO)_3(dmpe)_2$ to be converted to $Ti(CO)_5(dmpe)$, which then rapidly reacted with the nucleophile. Thus, when infrared spectra of incomplete reactions were examined, generally only product and unconverted $Ti(CO)_3(dmpe)_2$ were observed. Of course, free dmpe was generated in these reactions, which was deleterious in some cases. For example, under fluorescent lamp radiation, $C_5H_5Ti(CO)_4^-$ slowly reacted with dmpe to generate $\{[C_5H_5Ti(CO)_3]_n(dmpe)\}^{n-}$, where $n = 1$ and 2.[49] Clearly, to study the reactions of $Ti(CO)_5(dmpe)$ with more reactive nucleophiles such as alkyl and aryl carbanions or silyl anions, relatively pure samples of the pentacarbonyl must first be isolated. Results of these studies will be reported in due course.

The reactions in Scheme I proceeded to completion within 6 h under a CO atmosphere to provide 70–80% isolated yields of satisfactorily pure products. The only exception was $(Ph_3Ge)Ti(CO)_4(dmpe)^-$, which was fairly unstable in solution and could only be obtained in about 50% yield as a reasonably pure substance. These reactions and the products will now be discussed in some detail.

Reactions of $Ti(CO)_5(dmpe)$ with Organophosphines; Synthesis and Characterization of $Ti(CO)_4\{CH_3C(CH_2PMe_2)_3\}$, a Remarkably Stable Neutral Carbonyl of Titanium(0). The reaction of $Ti(CO)_5(dmpe)$ with 4 equiv of PMe_3 provided a very small quantity of thermally unstable material that had fairly intense $\nu(CO)$ absorptions at 1940 and 1800 cm^{-1} in toluene and were provisionally assigned to the tetracarbonyl, $Ti(CO)_4(PMe_3)(dmpe)$. Although we have been unsuccessful in detecting any tetracarbonyl species in the reaction of $Ti(CO)_5(dmpe)$ with dmpe, during the decomposition of pure $Ti(CO)_5(dmpe)$ in toluene, much weaker, transient bands, at very similar positions to those observed in PMe_3 reaction, were seen and assumed to be due to a labile tetracarbonyl species, such as $Ti(CO)_4(dmpe)(L)$, whose L could be a η^1-dmpe unit or perhaps η^2-toluene.[50,51] It was important to obtain a stable example of a neutral tetracarbonyltitanium species to unambiguously determine whether these absorptions were actually due to such materials. Attempts to prepare compounds of this type by the reaction of commercially available phenyl substituted triphos

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[47] The triplet pattern for the carbonyl resonance of $Ti(^{13}CO)_5(dmpe)$ was not resolved at 75.46 MHz on two different instruments. However, at 50.32 MHz, the binomial triplet was resolved with $^2J_{PC} = 9$ Hz, in good agreement with that observed for the ^{31}P spectrum.

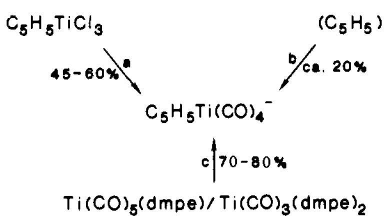
[48] Warnock, G. F. P.; Philson, S. B.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 893.

[49] Frerichs, S. F.; Ellis, J. E., manuscript in preparation.

[50] Thus far we have had no success in preparing arene derivatives of $Ti(CO)_5(dmpe)$, such as $(arene)Ti(CO)_4$ or $(arene)Ti(CO)_2(dmpe)$. In this regard, it is interesting to note that no reactions of carbon monoxide with $[(arene)_2Ti]^z$ species ($z = 0, -1$) have been reported thus far.[51] It has been stated that the neutral bis(arene)titanium complexes are "surprisingly unreactive toward neutral donor ligands (e.g., CO, PPh_3)": Bottrill, M.; Gavens, P. D.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982, Vol. 3, Chapter 22.2.

[51] (a) Anthony, M. T.; Green, M. L. H.; Young, D. *J. Chem. Soc., Dalton Trans.* **1975**, 1419. (b) Hawker, P. N.; Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1978**, 730. (b) Hawker, P. N.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1123. (d) Bandy, J. A.; Berry, A.; Green, M. L. H.; Perutz, R. N.; Prout, K.; Verpeaux, J.-N. *J. Chem. Soc., Chem. Commun.* **1984**, 729. (e) Tairova, G. G.; Krashina, E. F.; Krasochka, O. N.; Kichigina, G. A.; Shvetsov, Y. A.; Lisetsky, E. M.; Atormyan, L. O.; Borodko, Y. G. *Nouv. J. Chim.* **1981**, *5*, 603. (f) Morand, P. D.; Francis, C. G. *Inorg. Chem.* **1985**, *24*, 56.

Scheme II. Routes to $C_5H_5Ti(CO)_4^-$ Involving Ti(IV), Ti(II), and Ti(0) Precursors[a]



[a] Conditions: a, (i) 4Na–$C_{10}H_8$, (ii) CO (1 atm P) −70 to +20 °C (ref 1); b, 2Na–$C_{10}H_8$, CO (1 atm P), −70 to +20 °C (ref 1, footnote 15); c, NaC_5H_5, CO (1 atm P), 20 °C (this work).

type ligands such as $(Ph_2PCH_2)_3CCH_3$ and $(Ph_2PCH_2CH_2)_2PPh$ with $Ti(CO)_5(dmpe)$ were totally unsuccessful. Only the usual slow decomposition of the pentacarbonyl to $Ti(CO)_3(dmpe)_2$ and dark insoluble non-carbonyl-containing materials were observed. Clearly neutral zerovalent titanium carbonyl has a much greater affinity for dmpe than arylphosphines, probably due to both steric and electronic factors.[52]

For these reasons, we were very pleased to discover that trmpe, i.e., 1,1,1-tris(dimethylphosphinomethyl)ethane,[53] readily formed an exceedingly stable (decomposition >150 °C) substituted tetracarbonyltitanium species. Indeed, solutions of $Ti(CO)_3(dmpe)_2$ under an argon atmosphere reacted with trmpe to provide substantial amounts of $Ti(CO)_4(trmpe)$ along with much decomposition material. We do not known whether the formation of the tetracarbonyl under these conditions involved sacrificial scavenging of CO from decomposition products or a more interesting process. When the corresponding reaction was done under a CO atmosphere at room temperature practically quantitative conversion (by IR) to $Ti(CO)_4(trmpe)$ occurred within 5 h. In contrast to $Ti(CO)_3(dmpe)_2$, there was no evidence that $Ti(CO)_4(trmpe)$ reacts with additional CO to give a pentacarbonyl species, although $Ti(CO)_4(trmpe)$ does undergo slow CO exchange at room temperature. About 80% yields of the pure carbonyl have been isolated from this reaction. Significantly, its infrared spectrum in the $\nu(CO)$ region (in THF: 1930 (s), 1833 (sh), 1808 (vs) cm^{-1}) was very similar to the alleged tetracarbonyl, $Ti(CO)_4(dmpe)(PMe_3)$, mentioned above. The relative intensities and positions are also very similar to those observed for $C_5H_5Ti(CO)_4^-$ ($\nu(CO)$: 1921 (m), 1779 (s) cm^{-1}).[1b] A high-resolution mass spectrum confirms its molecular composition. Additionally, a crystal structure of the analogous zirconium complex has been determined,[54] so the formulation of $Ti(CO)_4(trmpe)$ is firmly founded. On the basis of our initial investigation of the early transition metal chemistry of trmpe, it is clear that this is a rather remarkable ligand capable of stabilizing previously unknown types of low-valent metal compounds.[54-56]

Synthesis and Characterization of Cyclopentadienyl, Indenyl, and Hydrotris(1-pyrazolyl)borate Derivatives of $Ti(CO)_7$. $C_5H_5Ti(CO)_4$. In early 1986, the first carbonyl anions of titanium were described, $C_5H_5Ti(CO)_4^-$ and $C_5Me_5Ti(CO)_4^-$.[12] These were obtained by the direct reduction of the $C_5R_5TiCl_3$ (R = H, Me) by Na–$C_{10}H_8$, followed by carbonylation at atmospheric pressure. A single-crystal X-ray study of $C_5H_5Ti(CO)_4^-$ demonstrated that the anion was essentially isostructural with the isoelectronic $C_5H_5V(CO)_4$.[1b] The reaction of NaC_5H_5 with $Ti(CO)_5(dmpe)$ was subsequently shown to provide $C_5H_5Ti(CO)_4^-$ in substantially higher yields than those afforded by the direct reductive carbonylation. Indeed, if dmpe were more available, the synthesis of $C_5H_5Ti(CO)_4^-$ from $Ti(CO)_5(dmpe)$ would be the best route presently available. In ref 1b, it was also noted that $(C_5H_5)_2Ti(CO)_2$ underwent reductive carbonylation to provide $C_5H_5Ti(CO)_4^-$ in about 20% (unoptimized) yield. Although this last method may not be a practical route to the tetracarbonyl anion, it has been used to generate good yields of previously inaccessible disubstituted anions of the type $C_5H_5Ti(CO)_2L_2^-$.[1a] As shown in Scheme II, $C_5H_5Ti(CO)_4^-$ has now been independently prepared from tetravalent, divalent, and zerovalent titanium precursors. The ready accessibility of this interesting material will facilitate investigations of its chemical properties, which to date are largely unexplored.

(Indenyl)$Ti(CO)_4^-$. While indenyl complexes of divalent and higher valent titanium are well known,[57,58] there have not been any previous reports on compounds of this type containing zerovalent titanium. Because of recent research on indenyl complexes of transition metals, owing largely to the "indenyl effect",[59] it was felt that the synthesis of $C_9H_7Ti(CO)_4^-$ would be of interest. The desired substance was prepared in high isolated yield (77%) as the tetraethylammonium salt by the reaction of $Ti(CO)_5(dmpe)$ and sodium indenide, followed by cation exchange. A much lower yield (34%) of the same material was obtained by the two-step reductive carbonylation of "$C_9H_7TiCl_2$", which was prepared from the reaction of $TiCl_3(THF)_3$ and $[Na(DME)][C_9H_7]$ and used in situ.[60] This latter preparation is analogous to that used for the original synthesis of $C_5H_5Ti(CO)_4^-$.[1b] The relatively low yield

$$\text{“}C_9H_7TiCl_2\text{”} + 3Na\text{–}C_{10}H_8 \xrightarrow[\substack{THF \\ -78\ °C}]{Ar} \xrightarrow[\substack{-78\ to\ 20\ °C \\ 12\ h}]{CO} \xrightarrow[12\ h]{Et_4NBr} [Et_4N][C_9H_7Ti(CO)_4] \quad (4)$$

of $C_9H_7Ti(CO)_4^-$ obtained from the reductive carbonylation could have arisen by the poor stability of the intermediate, assumed to be $C_9H_7Ti(naphthalene)_x^-$, or low conversion of $TiCl_3(THF)_3$ to the presumed $C_9H_7TiCl_2$.

Spectroscopic properties of and the analytical data for $[Et_4N][C_9H_7Ti(CO)_4]$ are in complete accord with the proposed formulation. Infrared spectra of this material and $C_5H_5Ti(CO)_4^-$ in the $\nu(CO)$ region were extremely similar (in THF: 1925 (m), 1778 (s) and 1921 (m), 1779 (s) cm^{-1}, respectively) as were the carbonyl ^{13}C NMR chemical shifts (δ 288.7 and 288.9, respectively). These data indicated that the indenyl group is at best only a slightly weaker donor than the cyclopentadienyl group to the $Ti(CO)_4$ unit. The latter moiety is also likely to have nearly the same geometry in each anion. In other systems, e.g., $(indenyl)_2Ti(CO)_2$, the indenyl group has generally been found to be a weaker donor than C_5H_5.[58] The reactivities of both anions toward nucleophilic substitution are qualitatively very similar.[49] In this respect, (indenyl)$Ti(CO)_4^-$ is similar to $(indenyl)_2Ti(CO)_2$, which does not exhibit a significant "indenyl effect".[59] In contrast to (indenyl)$Fe(CO)_2^-$, which binds CO to provide the slipped ring complex (η^3-indenyl)$Fe(CO)_3^-$,[61] we have no evidence that (in-

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[52] Dmpe appears to be a rather special and unusual bidentate ligand in its ability to provide relatively stable neutral derivatives of $Ti(CO)_7$. Analogous reductive carbonylations of $TiCl_4$ in the presence of $Me_2PCH_2CH_2CH_2PMe_2$, dmpp, and $Et_2PCH_2CH_2PEt_2$, depe, provided less stable carbonyls, to be described in another paper in this series. By comparison exceedingly unstable materials were obtained with PMe_3 or $Me_2PCH_2PMe_2$, dmpm, and no evidence for the formation of carbonyltitanium species were obtained when reductive carbonylations were carried out in the presence of PEt_3 or $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$. (Chi, K. M.; Ellis, J. E., unpublished research).

[53] We propose "trmpe" as a reasonable abbreviation for the ligand. It is an acceptable acronym of its full name, related to dmpe which exhibits similar reactivity in many cases and is preferable to the generic name "tripod" which refers to any potentially tris-chelate of this or similar geometry.

[54] Blackburn, D. W.; Ellis, J. E., research in progress.

[55] While this work was in progress, other studies involving the use of trmpe were reported: (a) Arif, A. M.; Hefner, J. G.; Jones, R. A.; Whittlesey, B. R. *Inorg. Chem.* **1986**, *25*, 1080; (b) Thaler, E.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 374; (c) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.

[56] Just before submission of this manuscript we received a preprint by Thomas Gardner and Gregory Girolami on the synthesis and characterization of $Ti(CO)_4[t\text{-}BuSi(CH_2PMe_2)_3]$, which has properties that are very similar to those of $Ti(CO)_4(trmpe)$. Their compound appears to be even more thermally stable than the trmpe complex. Clearly, these electron rich tripodal ligands are unusual in their ability to stabilize early transition metal carbonyls.

[57] Lehmkuhl, H.; Schwickard, R. *J. Organomet. Chem.* **1986**, *303*, C43.

[58] (a) Palmer, G. T.; Basolo, F.; Kool, L. B.; Rausch, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 4417. (b) Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Hunter, W. E. *J. Organomet. Chem.* **1987**, *321*, C9.

[59] (a) Rerek, M. E.; Ji, L. N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33.

[60] We could find no reference to $C_9H_7TiCl_2$ in the literature, although $(C_9H_7)_2TiCl$ has been prepared: Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 1645.

denyl)$Ti(CO)_4^-$ interacts with CO in this fashion, perhaps due to the relatively high coordination number of the titanium and rather bulky nature of the indenyl group.

$[HB(Pz)_3]Ti(CO)_4^-$, the First Organonitrogen Derivative of $Ti(CO)_7$. Several years ago Trofimenko demonstrated that a variety of novel organometallic materials could be obtained with hydrotris(1-pyrazolyl)borate or $HB(Pz)_3^-$. This ligand mimics the cyclopentadienyl group to a certain extent in its ability to form "half-sandwich" complexes but is far more sterically crowded.[62] Curtis has recently observed interesting reactivity patterns for the hydrotris(1-pyrazolyl)borate derivative of $Mo(CO)_6$, $[HB(Pz)_3]Mo(CO)_3^-$,[63] so we felt it would be useful to determine whether a poly(pyrazolyl)borate complex of zerovalent titanium could be prepared. Manzer[64] and later Kouba and Wreford[65] briefly examined the reduction of $[HB(Pz)]_3TiCl_3$ and isolated a trivalent Ti species, $[HB(Pz)_3]TiCl_2{\cdot}THF$. Our attempts to reductively carbonylate $[HB(Pz)_3]TiCl_3$ with the $Na–C_{10}H_8$ procedure were uniformly unsuccessful, so we investigated the reaction of $K[HB(Pz)_3]$ with $Ti(CO)_5(dmpe)$. Under a carbon monoxide atmosphere at room temperature these reactants combined smoothly and nearly quantitatively within 3 h to provide the desired anion $[HB(Pz)_3]Ti(CO)_4^-$. The anion was isolated in 70% yield as a satisfactorily pure and thermally robust (decomposition >150 °C) tetraethylammonium salt. This salt is presently the only known poly(pyrazolyl)borate derivative of $Ti(CO)_7$ and the first stable organonitrogen derivative of any titanium carbonyl, to our knowledge.[7] Interestingly, no reaction was observed when the more sterically crowded hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion (as the potassium salt) was stirred with solutions of $Ti(CO)_5(dmpe)$ in tetrahydrofuran at room temperature.

There is a strong similarity between the infrared spectra of $[HB(Pz)_3]Ti(CO)_4^-$ and $C_5Me_5Ti(CO)_4^-$ in the $\nu(CO)$ region ($[H(Pz)_3]$ complex (CH_3CN): 1912 (m), 1755 (s) cm^{-1}; C_5Me_5 complex (DME): 1914 (m), 1772 (s) cm^{-1}) which indicates that $HB(Pz)_3^-$ and $C_5Me_5^-$ are similar in their donor ability to the $Ti(CO)_4$ unit. However, the energy separation between the two $\nu(CO)$ bands of the $HB(Pz)_3$ complex (157 cm^{-1}) is somewhat larger than the corresponding value for the C_5Me_5 complex (142 cm^{-1}), which suggests that there may be significant differences in the geometries of the respective $Ti(CO)_4$ units. Also the carbonyl ^{13}C chemical shifts for these respective complexes are δ 286 and 293, in $(CD_3)_2SO$, which are not obviously consistent with the corresponding IR spectral values. It will be very interesting to see how the reactivity patterns of $C_5H_5Ti(CO)_4^-$, $C_5Me_5Ti(CO)_4^-$, and $[HB(Pz)_3]Ti(CO)_4^-$ compare. Curtis and co-workers observed striking differences in the chemical properties of $C_5H_5Mo(CO)_3^-$ and $[HB(Pz)_3]Mo(CO)_3^-$ and derivatives thereof.[63] We note that of the three anionic $LTi(CO)_4$ species considered here, the tris(pyrazolyl)borate complex is by far the most resistant toward air oxidation and resembles the neutral $Ti(CO)_4(trmpe)$ in this respect.

Reaction of $Ti(CO)_5(dmpe)$ with Ph_3ENa (E = Ge, Sn). Formal Derivatives of $Ti(CO)_6^{2-}$. Triphenylgermyl- and triphenylstannylsodium were found to be relatively inert to CO and reacted readily with $Ti(CO)_5(dmpe)$ to provide isolable products. In contrast to all other reactions discussed in this paper, except that of free dmpe, a dmpe unit was not displaced by the nucleophile in this reaction. Detailed structures of the product anions $(Ph_3E)Ti(CO)_4(dmpe)^-$ are not known but are likely to contain seven-coordinate titanium units, which, for example, is known to be present in $(Ph_3Sn)_2Ti(CO)_5^{2-}$.[66] Corresponding neutral vanadium compounds such as $(Ph_3Sn)V(CO)_4(dmpe)$[67] have been known for many years; the ability of the smaller vanadium atom to assume seven coordination is well established in related materials such as $(Ph_3Sn)_2V(CO)_5^-$[68] and $HV(CO)_4(Ph_2PCH_2CH_2PPh_2)$.[69] Solution infrared spectra in the $\nu(CO)$ region of $[Ph_4As][(Ph_3Sn)Ti(CO)_4(dmpe)]$ (in DMSO: 1897 (m), 1800 (s), 1770 (s) cm^{-1}) and $(Ph_3Sn)V(CO)_4(dmpe)$ (in THF: 1969 (m), 1875 (vs br)) are similar except the bands of the anion are shifted to lower energy in accord with the more electron rich nature of the titanium complex. Also the broad lowest energy band envelope of the vanadium complex is bifurcated in the titanium species. Since the vanadium compound is derived from $V(CO)_6^-$, these titanium anions may be considered to be the first known derivatives of the unknown $Ti(CO)_6^{2-}$. Attempts to prepare this latter species by the reaction of $Ti(CO)_5(dmpe)$ with suitable reducing agents is an important component of our research program and will be described in the near future.[70]

Concluding Remarks. Several new zerovalent titanium carbonyls have been synthesized from the reactive $Ti(CO)_5(dmpe)$, which is obtained by the atmospheric pressure carbonylation of $Ti(CO)_3(dmpe)_2$. The latter can now be readily obtained in high yield by our two-step reductive carbonylation of $TiCl_4(dmpe)$ in the presence of additional dmpe. An important discovery in this research is the use of trmpe, $CH_3C(CH_2PMe_2)_3$, in the synthesis of a neutral carbonyl of zerovalent titanium of great thermal stability, $Ti(CO)_4(trmpe)$. Extensions of this work to zirconium and hafnium as well as the group 3 transition metals are in progress. It is anticipated that the synthetic methodology introduced in this paper will also be of importance in the stabilization of highly reduced organometallics of the f-block elements.

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