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Highly Reduced Organometallics. 33. Carbonyl Hydrides of Titanium and Corresponding Carbonyltitanates[1]

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Abstract: Photopromoted substitution reactions of $[(C_5R_5)Ti(CO)_4]^-$ (R = H, Me) with organophosphines have been examined for the first time and provided new zerovalent titanium carbonyls of the general formula $[(C_5R_5)Ti(CO)_3(PR_3)]^-$. Disubstituted phosphine derivatives of the formula $[(C_5R_5)Ti(CO)_2(dmpe)]^-$ were obtained by the alkali metal naphthalenide promoted reductive cleavages of titanocene dicarbonyls $(C_5R_5)_2Ti(CO)_2$ (R = H, Me) in the presence of dmpe, i.e., 1,2-bis(dimethylphosphino)ethane. The reductively promoted substitution reaction of $(C_5Me_5)_2Ti(CO)_2$ appears to be the first report of such a reaction involving a bis(pentamethylcyclopentadienyl)metal complex although corresponding reactions involving bis(cyclopentadienyl)metal complexes are well-known. Spectral studies on alkali metal salts of $[(C_5R_5)Ti(CO)_2(dmpe)]^-$ established that the cations interacted strongly with the carbonyl oxygens of the anions and promoted anion decomposition. Alkali metal complexants substantially reduced this site-specific ion-pairing interaction and dramatically improved the thermal stability of the anions in solution and in the solid state. Protonation of the carbonyltitanates provided the first examples of carbonyl hydrides of titanium. While hydrides of the monophosphine derivatives $(C_5R_5)Ti(CO)_3(PR'_3)H$ (R' = Me, Ph) were found to be thermally unstable, the corresponding dmpe derivatives $(C_5R_5)Ti(CO)_2(dmpe)H$ were isolated as pure substances at room temperature. These anions and hydrides have been characterized in solution by IR, ^1H NMR, and ^{13}C NMR spectroscopy. The carbonyl ^{13}C chemical shifts of these carbonyltitanates are of particular interest in that they represent the most downfield values (δ 300–320) observed to date for coordinated terminal carbonyl groups in metal carbonyls.

Introduction

Our recent syntheses of $[(C_5R_5)Ti(CO)_4]^-$ (R = H, Me)[1-3] provided an opportunity to explore the basic chemistry of anionic forms of zerovalent titanium carbonyls for the first time. These materials are potentially valuable reagents for the introduction of low-valent $(C_5R_5)Ti$ units into a variety of materials. Initially, the interactions of $[(C_5R_5)Ti(CO)_4]^-$ with electrophiles were examined and found to provide products that were generally unstable and often intractable. While their reactions with Ph_3SnCl and Ph_3PAuCl gave the expected heterobimetallic compounds, the latter were only marginally stable materials.[1] Also, interaction of $[(C_5R_5)Ti(CO)_4]^-$ with alkylating agents, allyl chloride, nitrosonium salts, and Brønsted acids led to extremely unstable species that defied characterization. On the basis of previous work involving carbonyl hydrides, we suspected that the stability of hydride derivatives would be improved if the anion was made more electron rich by phosphine substitution of one or more carbonyl ligands.[4] At the time we started this research, there were no reports on the synthesis of carbonyl hydrides of titanium.

We have discovered two different routes to phosphine-substituted derivatives of $[(C_5R_5)Ti(CO)_4]^-$, involving either photopromoted substitution of phosphines into the anions or reduction of titanocene dicarbonyls in the presence of phosphines. In the former case, only monophosphines of the general formulation $[(C_5R_5)Ti(CO)_3(PR_3)]^-$ have been obtained, while the latter reaction provided disubstituted phosphines with $Me_2PCH_2CH_2PMe_2$ (dmpe), i.e. $[(C_5R_5)Ti(CO)_2(dmpe)]^-$. While reductive cleavages of metallocenes have been shown previously by Jonas and co-workers to provide extremely useful routes to new classes of highly reduced organometallics,[5] the reduction of $(C_5Me_5)_2Ti(CO)_2$ described herein appears to be the first report of a successful reductive cleavage of a decamethylmetallocene complex. Protonation of the carbonylmetallates gave the initial examples of carbonyl hydrides of titanium, only one of which, $(C_5H_5)Ti(CO)_2(dmpe)H$, has been previously described in the literature.[6]

Experimental Section

For a detailed description of general procedures and sources of most starting materials, see the preceding paper in this series.[1] The unsubstituted titanocene and permethyltitanocene dicarbonyls and their 99% ^{13}CO-labeled analogs were prepared according to published methods.[7a] The photolysis reactions were carried out in an Ace Glass Co. deep-well quartz apparatus with 200-W mercury vapor lamp irradiation filtered through borosilicate glass (Pyrex). In this article, C_5H_5 and C_5Me_5 groups are often designated by Cp and Cp*, respectively. Other abbreviations are THF = tetrahydrofuran, PY = pyridine, DMSO = Me_2SO = dimethyl sulfoxide, DME = 1,2-dimethoxyethane, 12-C-4 = 12-crown-4 = 1,4,7,10-tetraoxacyclododecane, 15-C-5 = 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane, cryptand 2.2.1 = 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, cryptand 2.2.2 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, and dmpe = 1,2-bis(dimethylphosphino)ethane.

$[Et_4N][CpTi(CO)_3(PMe_3)]$ (1). Method A: "Thermal Substitution". A 1.00-g (2.81 mmol) sample of $[Et_4N][CpTi(CO)_4]$ was dissolved in 90 mL of THF, PMe_3 (0.30 mL, 3.6 mmol) was added, and the solution was stirred under argon gas at room temperature for 5 weeks. At this time, the solution was filtered to remove a dark brown, insoluble solid. Additional PMe_3 (0.30 mL, 3.6 mmol) was added, and the solution was

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[4] See, for example: Ellis, J. E.; Faltynek, R. A. *J. Organomet. Chem.* **1975**, *93*, 205.

[5] Jonas, K. *J. Organomet. Chem.* **1990**, *400*, 165 and references cited therein.

[6] Frerichs, S. R.; Stein, B. K.; Ellis, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 5558.

[7] (a) Sikora, D. J.; Moriarty, K. J.; Rausch, M. D. *Inorg. Synth.* **1986**, *24*, 147. (b) ^1H and $^{13}C\{^1H\}$ NMR spectra of coordinated dmpe may show triplets due to virtual coupling of the two phosphorus nuclei with hydrogen and carbon. Poor resolution of these signals results in the observation of apparent broad singlets. See: Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, PA, 1977; p 223.

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Table I. Selected IR and NMR Spectral Data for $[(C_5R_5)Ti(CO)_{4-x}(PR_3)_x]^-$

compound	IR, ν(CO), cm^{-1} (solvent)	$^{13}C\{^1H\}$NMR, δ(CO), ppm[a]	$^{31}P\{^1H\}$NMR, δ, ppm[a]
$[Et_4N][CpTi(CO)_4]$[b]	1923 m, 1777 s (DME)	289 (s)	
$[Et_4N][CpTi(CO)_3(PMe_3)]$ (**1**)	1823 m, 1712 s (THF)	299 (d, J_{PC} = 20 Hz, 2 C), 308 (d, J_{PC} = 14 Hz, 1C)	41 (s)
$[Et_4N][CpTi(CO)_3(PPh_3)]$ (**2**)	1831 m, 1721 s (THF)	300 (d, J_{PC} = 18 Hz, 2 C), 306 (d, J_{PC} = 4 Hz, 1C)	98 (s)
$[Et_4N][CpTi(CO)_3(\eta^1\text{-dmpe})]$ (**3**)	1823 m, 1711 s, 1680 sh (THF)	*c*	51 (d, J_{PP} = 20 Hz, 1P), –47 (d, J_{PP} = 20 Hz, 1P)
$[Et_4N]_2[\{CpTi(CO)_3\}_2(\mu\text{-dmpe})]$ (**4**)	1828 m, 1698 s (DMSO)	299 (t, J_{PC} = 9 Hz, 2C), 308 (t, J_{PC} = 6 Hz, 1C)	50 (s)
$[Et_4N][Cp^*Ti(CO)_4]$[b]	1914 m, 1769 s (DME)	293 (s)	
$[Et_4N][Cp^*Ti(CO)_3(PMe_3)]$ (**5**)	1815 m, 1704 s, 1676 sh (THF)	304 (d, J_{PC} = 17 Hz, 2C), 307 (d, J_{PC} = 13 Hz, 1C)	36 (s)
$Na[CpTi(CO)_2(dmpe)]$ (**6**)	1658 s, br, 1563 m, br (DME)	*c*	63 (s)
$Na[CpTi(^{13}CO)_2(dmpe)]$ (**7**)[d,e]	1613 s, br, 1524 m, br (DME)[e]	320 (t, J_{PC} = 18 Hz)	63 (t, J_{PC} = 18Hz)
[Na(cryptand 2.2.1)]$[CpTi(^{13}CO)_2(dmpe)]$ (**8**)[d,e]	1680 s, 1596 m (DME)[e]	311 (t, J_{PC} = 16 Hz)	78 (t, J_{PC} = 15Hz)
$[Et_4N][Cp^*Ti(CO)_2(dmpe)]$ (**12**)	1680 s, 1600 m (THF)	316 (t, J_{PC} = 17 Hz)	60 (s)
$[Et_4N][Cp^*Ti(^{13}CO)_2(dmpe)]$ (**12**)[d,e]	1638 s, 1566 m (THF)[e]	316 (t, J_{PC} = 17 Hz)	60 (t, J_{PC} = 16 Hz)

[a] NMR spectra were obtained for DMSO-d_6 solutions at +20 °C except for the following compounds: **6** and **7** in DME (–10 °C); **8** in DME (–30 °C); **12** in THF-d_8 (20 °C). [b] Values from ref 1. [c] δ(CO) could not be detected. [d] 99% ^{13}C-enriched CO compounds. [e] $\nu(^{13}CO)$ values. Calcd $\nu(^{12}CO)$: (**7**) 1650, 1559; (**8**) 1718, 1632; (**12**) 1675, 1601 cm^{-1}.

stirred for 2 more weeks. The solution was filtered, and then the volume was reduced to about 20 mL in vacuo to cause a deep red solid to crystallize. Approximately 100 mL of Et_2O was then added to precipitate most of the product. The resulting solid was washed with 20 mL of Et_2O and then dried in vacuo to give 0.60 g (53%) of a red microcrystalline solid, which provided satisfactory analysis for **1**, dec pt 107–109 °C without melting.

Anal. Calcd for $C_{19}H_{34}NO_3PTi$: C, 56.58; H, 8.50; P, 7.68. Found: C, 56.10; H, 8.12; P, 7.44. IR (mineral oil mull) ν(CO): 1820 (m), 1690 (sh), 1665 (s). NMR (Me_2SO-d_6, 20 °C): ^1H δ 4.92 (d, J = 0.86 Hz, C_5H_5), 3.19 (q, J = 6.7 Hz, NCH_2), 1.15 (t, J = 6.7 Hz, NCH_2CH_3), 1.08 (d, J = 5.7 Hz, PCH_3); $^{13}C\{^1H\}$ δ 307.6 (d, J = 14.2 Hz, trans CO), 298.7 (d, J = 20.3 Hz, cis CO), 92.6 (s, C_5H_5), 51.6 (s, NCH_2), 20.2 (d, J = 14.0 Hz, PCH_3), 7.1 (s, NCH_2CH_3).

Method B: Low-Temperature Photolysis. A 1.0-g sample (2.8 mmol) of $[Et_4N][CpTi(CO)_4]$ was dissolved in 500 mL of THF, and PMe_3 (0.40 mL, 4.7 mmol) was added. The solution was transferred into the photolysis apparatus and cooled to –70 °C. With vigorous stirring of the cold solution, the photolysis was performed under partial vacuum (to aid in removal of CO) and the progress of the reaction was monitored by infrared solution spectroscopy. After about 65 min, the reaction was judged to be complete. Following filtration, the volume of the solution was reduced to about 10 mL. Addition of 200 mL of Et_2O caused precipitation of a red solid. Recrystallization of this product from THF/Et_2O provided 0.80 g (72%) of product identical to that prepared by method A. Anal. Calcd: C, 56.58; H, 8.50. Found: 56.27; H, 8.29.

$[Et_4N][CpTi(CO)_3(PPh_3)]$ (2). A solution (50 mL of DME) containing $[Et_4N][CpTi(CO)_4]$ (0.65 g, 1.83 mmol) was added to PPh_3 (0.88 g, 3.63 mmol), and the resulting mixture was heated to 65 °C for 3 days under an argon atmosphere. The hot solution was then filtered through a medium porosity frit to remove the insoluble decomposition and some crude product. As the filtered solution cooled, the product began to crystallize. The solution was concentrated to a total volume of about 20 mL, and then the supernatant was decanted away and saved. The red-violet crystals were then washed with 2 × 10 mL fresh DME to remove starting material and PPh_3, and finally washed with 2 × 10 mL Et_2O. After drying in vacuo, 0.45 g (45%) of dark red-violet crystals was isolated. The supernatant of the original solution yielded another 0.20 g of material for a combined yield of 65%, which provided satisfactory analyses for **2**, dec pt 124–130 °C without melting.

Anal. Calcd for $C_{34}H_{40}NO_3PTi$: C, 69.27; H, 6.84. Found: C, 69.06; H, 6.93. The compound was insoluble in THF and DME at room temperature but dissolved in dimethyl sulfoxide and pyridine and slowly decomposed in the latter solvent. IR (pyridine) ν(CO): 1833 (m), 1721 (s). IR (mineral oil mull) ν(CO): 1823 (m), 1715 (sh), 1696 (s). NMR (Me_2SO-d_6, 25 °C): ^1H δ 7.4–7.2 (m, Ph-H), 4.78 (s, C_5H_5), 3.19 (q, J = 7.2 Hz, NCH_2), 1.14 (t, J = 7.2 Hz, NCH_2CH_3); $^{13}C\{^1H\}$ δ 306.3 (d, J = 4 Hz, trans CO), 299.5 (d, J = 18 Hz, cis CO), 140.6 (d, J = 19.7 Hz, Ph-C), 132.6 (d, J = 11.6 Hz, Ph-C), 127.9 (s, Ph-C), 127.2 (d, J = 7.4 Hz, Ph-C), 93.9 (s, C_5H_5), 51.3 (s, NCH_2), 7.1 (s, NCH_2CH_3).

$[Et_4N][CpTi(CO)_3(\eta^1\text{-dmpe})]$ (3). A solution containing $[Et_4N][CpTi(CO)_4]$ (1.00 g, 2.81 mmol) and dmpe (0.40 mL, 2.4 mmol) in 500 mL of THF was cooled to –60 °C and irradiated under partial vacuum for 2 h. An IR spectrum of the resulting solution in the ν(CO) region (see Table I) was very similar to that of **2** in THF and indicated that all $[CpTi(CO)_4]^-$ had been consumed. The turbid dark red-orange solution was filtered, and as much solvent as possible was removed at room temperature in vacuo to leave a dark red oil, which was shown by NMR spectroscopy to contain mainly **3**, a small amount of **4**, and free dmpe. $^{31}P\{^1H\}$ NMR (Me_2SO-d_6, 20 °C): δ 51.0 (d, J = 20 Hz, coordinated Me_2P of η^1-dmpe), 50.2 (s, μ-dmpe of **4**), –47.0 (s, free dmpe), –47.3 (d, J = 20 Hz, uncoordinated Me_2P of η^1-dmpe). Attempts to isolate a pure sample of **3** from this oil were unsuccessful.

$[Et_4N]_2[\{CpTi(CO)_3\}_2(\mu\text{-dmpe})]$ (4). A 1.00-g (2.81 mmol) sample of $[Et_4N][CpTi(CO)_4]$ was dissolved in 100 mL of DME, and dmpe (0.80 mL, 4.8 mmol) was added. The solution was stirred for 2 weeks at room temperature, and at this time, its solution infrared spectrum showed ν(CO) bands at 1823 (m) and 1716 (s) cm^{-1}. It was then filtered to remove an insoluble reddish-white solid. The solution was concentrated in vacuo to a total volume of about 20 mL, and a dark red microcrystalline solid precipitated from solution. The solid was washed with 10 mL of DME and 2 × 10 mL of Et_2O. After drying in vacuo, 0.30 g (27%) of a red microcrystalline solid was isolated, dec pt 132–134 °C.

Anal. Calcd for $C_{38}H_{66}N_2O_6P_2Ti_2$: C, 56.72; H, 8.27; P, 7.70. Found: C, 56.38; H, 8.24; P, 7.89. IR (mineral oil mull) ν(CO): 1815 (m), 1690 (sh), 1660 (s). NMR (Me_2SO-d_6): ^1H δ 4.95 (s, C_5H_5), 3.19 (q, J = 7.2 Hz, NCH_2), 1.60 (m, PCH_2), 1.15 (t, J = 7.1 Hz, NCH_2CH_3), 1.01 (t, J = 2.4 Hz, PCH_3); $^{13}C\{^1H\}$ δ 308.2 (t, J = 6 Hz, trans CO), 298.8 (t, J = 9 Hz, cis CO), 92.6 (s, C_5H_5), 51.4 (s, NCH_2), 29.4 (s, br, PCH_2), 17.2 (t, J = 7 Hz, PCH_3), 7.1 (s, NCH_2CH_3).[7b]

$[Et_4N][Cp^*Ti(CO)_3(PMe_3)]$ (5). A 2.3-g (5.4 mmol) sample of $[Et_4N][Cp^*Ti(CO)_4]$ was dissolved in about 500 mL of THF and transferred into the photolysis apparatus. A 1.4-mL sample (17 mmol) of PMe_3 was added, and the solution was cooled to –60 °C. The solution was irradiated under a partial vacuum on the system for a total of 2.5 h, at which time the reaction was judged complete by infrared spectroscopy. The solution was then concentrated in vacuo to a 20-mL total volume. After filtration, the solution was cooled to –78 °C. Pentane (200 mL) was slowly added, and the solvents were mixed to give a red powder. The solid was thoroughly washed with pentane. The yield was 2.3 g (91%) of a dark red-violet solid, dec pt ca. 120 °C. Satisfactory elemental analyses were obtained for the unrecrystallized product.

Anal. Calcd for $C_{24}H_{44}NO_3PTi$: C, 60.88; H, 9.37. Found: C, 60.69; H, 9.12. IR (mineral oil mull) ν(CO): 1810 (s), 1678 (s, br). NMR (Me_2SO-d_6): ^1H δ 3.19 (q, J = 7.2 Hz, NCH_2), 1.84 (d, J = 0.5 Hz, $C_5(CH_3)_5$), 1.15 (t, J = 7.1 Hz, NCH_2CH_3), 1.03 (d, J = 4.9 Hz, PCH_3); $^{13}C\{^1H\}$ δ 306.7 (d, J = 13.2 Hz, trans CO), 304.2 (d, J = 17.4 Hz, cis CO), 103.7 (s, $C_5(CH_3)_5$), 51.4 (s, NCH_2), 19.7 (d, J = 12.5 Hz, PCH_3), 12.4 (s, $C_5(CH_3)_5$), 7.1 (s, NCH_2CH_3).

$[Et_4N][CpTi(CO)_4]$ from the Reductive Carbonylation of $Cp_2Ti(CO)_2$. A cold solution (–78 °C) of $NaC_{10}H_8$ (17.9 mmol, prepared by the reaction of sodium metal (0.413 g, 17.9 mmol) and excess naphthalene (6.56 g, 42.7 mmol) in 100 mL of THF) was added to a mechanically stirred cold solution (–78 °C) of $Cp_2Ti(CO)_2$ (2.00 g, 8.54 mmol) in 50 mL of THF under an atmosphere of CO. The reaction mixture turned dark red, and the solution was allowed to slowly warm to room temperature over a period of 12 h under a CO atmosphere. The resulting mixture was filtered and stirred with finely ground $[Et_4N]Cl$ (1.41 g, 8.54 mmol) for 12 h. After another filtration, solvent was removed in vacuo and the resulting red microcrystalline product was washed with 2 × 20 mL of pentane to afford 0.60 g (20% yield) of solid which was spectroscopically identical to that of previously reported $[Et_4N][CpTi(CO)_4]$.[3]

$Na[CpTi(CO)_2(dmpe)]$ (6). A solution of $NaC_{10}H_8$ (7.0 mmol) in 30 mL of DME at 0 °C was added under argon to a rapidly stirred solution at − 60 °C containing $Cp_2Ti(CO)_2$ (0.75 g, 3.2 mmol) and dmpe (0.53 mL, 3.2 mmol). An infrared spectrum of the warmed (+10 °C) solution showed $\nu(CO)$ bands at 1658 (s, br) and 1563 (m, br) cm^{-1}. The ^{31}P NMR spectrum of the reaction mixture (−10 °C, DME) showed singlets at δ 63 ($CpTi(CO)_2(dmpe)^-$) and −48 (free dmpe). The deep red product was thermally unstable and decomposed on attempted isolation to an uncharacterized black solid.

$Na[CpTi(^{13}CO)_2(dmpe)]$ (7). Exactly the same procedure for the synthesis of **6** was employed, except 99% ^{13}CO-enriched $Cp_2Ti(^{13}CO)_2$ was substituted. See Table I for the IR solution spectrum in the $\nu(CO)$ region of thermally unstable **7**. NMR (DME, −10 °C): $^{13}C\{^1H\}$ δ 320 (t, J_{PC} = 18 Hz, $[CpTi(^{13}\mathit{CO})_2(dmpe)]^-$), 134, 128, 126 (s, $C_{10}H_8$), 102.5 (br s, $[\mathit{Cp}Ti(^{13}CO)_2(dmpe)]^-$), 93 (s, NaCp), 72 (s, DME), 58 (s, DME); $^{31}P\{^1H\}$ δ 63 (t, J_{PC} = 18 Hz, $[CpTi(^{13}CO)_2(\mathit{dmpe})]^-$), −47 (free dmpe). As in the case of **6**, this product decomposed on removal of solvent.

$[Na(cryptand\ 2.2.1)][CpTi(^{13}CO)_2(dmpe)]$ (8). To a cold solution (−50 °C) of **7**, prepared as described previously, was added a solution of cryptand 2.2.1 (1.2 g, 3.5 mmol) in 10 mL of DME. The resulting deep red solution was thermally stable at room temperature for hours. See Table I for the IR spectrum of **8**. NMR (DME, −30 °C): $^{13}C\{^1H\}$ δ 311 (t, J_{PC} = 16 Hz, $[CpTi(^{13}\mathit{CO})_2(dmpe)]^-$), 134, 128, 126 (s, $C_{10}H_8$), 103 (s, $[\mathit{Cp}Ti(^{13}CO)_2(dmpe)]^-$), 72 (s, DME), 58 (s, DME); $^{31}P\{^1H\}$ δ 78 (t, J_{PC} = 15 Hz, $[CpTi(^{13}CO)_2(\mathit{dmpe})]^-$), −48 (s, free dmpe). Compound **8** could be isolated as a thermally stable red powder, but attempts to free it from associated NaCp were unsuccessful, so no attempts were made to obtain elemental analyses on the substance.

$K[CpTi(CO)_2(dmpe)]$ (9). A solution of $KC_{10}H_8$ (3.6 mmol) in 20 mL of DME at 0 °C was added under argon to a rapidly stirred solution at −60 °C containing $Cp_2Ti(CO)_2$ (0.40 g, 1.7 mmol) and dmpe (0.29 mL, 1.7 mmol) in 20 mL of DME. The IR solution spectrum of the products showed $\nu(CO)$ bands at 1664 (s, br) and 1542 (m, br) cm^{-1}, which decreased in intensity with time. Two peaks at 1924 (s) and 1851 (m) cm^{-1}, due to $CpTi(CO)_2(dmpe)H$, vide infra, grew as the peaks due to the anion diminished in intensity. The solution rapidly decomposed at room temperature. Attempts to isolate **9** were unsuccessful due to its extreme thermal instability.

$K[CpTi(^{13}CO)_2(dmpe)]$ (10). Exactly the same procedure for the synthesis of **9** was employed, except 99% ^{13}CO-enriched $Cp_2Ti(^{13}CO)_2$ was substituted. The resulting thermally unstable solution had the following spectroscopic properties in the CO region. IR (DME) $\nu(CO)$: 1628 (s), 1510 (m). NMR (DME, −60 °C: $^{13}C\{^1H\}$ δ 318 (unresolved t, $[CpTi(^{13}CO)_2(dmpe)]^-$). $^{31}P\{^1H\}$ NMR (−60 °C): δ +68 (br s, $[CpTi(^{13}CO)_2(\mathit{dmpe})]^-$), −48 (s, free dmpe). Calcd $\nu(^{12}CO)$: 1665, 1544. Observed $\nu(^{12}CO)$: (**9**) 1664, 1542.

$[K(cryptand\ 2.2.2)][CpTi(CO)_2(dmpe)]$ (11). A solution of $KC_{10}H_8$ (5.4 mmol, prepared from K (0.21 g, 5.4 mmol) and naphthalene (1.03 g, 8.0 mmol) in 30 mL of THF) was cooled to −20 °C and added with stirring to a solution of 0.62 g (2.65 mmol) of $Cp_2Ti(CO)_2$ and 0.40 mL (2.4 mmol) of dmpe in 25 mL of THF at −70 °C. The reaction mixture was stirred for 12 h at −70 °C and filtered through a short column of dry diatomaceous earth (prewashed with THF) at −70 °C to remove insoluble KCp (identity verified by comparison of its ^1H NMR spectrum with that of bona fide KCp (Me_2SO-d_6, 20 °C, δ 5.41 (s))). The red-orange filtrate at this point was very thermally unstable, decomposing to a black suspension, which showed no discernible infrared absorptions in the $\nu(CO)$ region. A solution of 1.00 g of cryptand and 2.2.2 (2.66 mmol) in 10 mL of THF was cooled to −70 °C and added to the filtrate. There was no apparent color change, but the solution infrared spectrum showed a thermally stable compound was now present with $\nu(CO)$ bands at 1725 (s) and 1647 (s, br) cm^{-1}. This solution was warmed to room temperature and then filtered through filter aid (prewashed with THF) on a medium porosity frit. The dark solid was rinsed until the filtrate was clear, and the solvent was removed in vacuo. The resulting dark red solid was dried in vacuo for 0.5 h, thoroughly washed with 3 × 50 mL of Et_2O, then dried in vacuo for 1 h. In this manner, 1.37 g (70% yield) of crude **11** was isolated. The analytical sample was recrystallized twice from THF/Et_2O to give 0.98 g (50% overall yield) of a dark red microcrystalline solid, dec pt 110 °C.

Anal. Calcd for $C_{31}H_{57}KN_2O_8P_2Ti$: C, 50.68; H, 7.82; N, 3.81. Found: C, 50.56; H, 7.37; N, 3.95. IR (THF) $\nu(CO)$: 1725 (s), 1647 (s). IR (mineral oil mull) $\nu(CO)$: 1705 (s), 1621 (s). The compound was not soluble enough in unreactive solvents (DME-d_{10} or THF-d_8) to obtain good NMR spectra. However, in view of its satisfactory elemental analysis and supporting IR and NMR spectra of the uncryptated potassium salt precursors **9** and **10**, the formulation of **11** is firmly founded.

$[Et_4N][Cp^*Ti(CO)_2(dmpe)]$ (12). A solution of $Cp^*{}_2Ti(CO)_2$ (0.40 g, 1.07 mmol) and 0.18 mL of dmpe (1.1 mmol) in 20 mL of DME was cooled to −78 °C. To this was added with stirring an ice-cold solution of $NaC_{10}H_8$ (2.26 mmol) in 20 mL of DME. On warming the solution to room temperature, its color changed from dark green to red within 0.5 h. Removal of the solvent left a light orange powder, which was washed with Et_2O (70 mL). The solid was dissolved in 50 mL of THF and filtered off into a vessel containing 0.36 g (2.18 mmol) of powdered $[Et_4N]Cl$. The resulting red-orange slurry was stirred for 0.5 h at 0 °C. After another filtration, the volume of the solution was reduced to about 5 mL and then it was cooled to −78 °C. The cold solution was layered with 150 mL of Et_2O and allowed to stand for 1 h at −78 °C. A dark red microcrystalline solid thereby formed. It was isolated by filtration and washed thoroughly with Et_2O at room temperature. Recrystallization from THF/Et_2O provided 0.28 g (50% yield) of dark red crystals, which gave satisfactory elemental analyses for **12**.

Anal. Calcd for $C_{26}H_{51}NO_2P_2Ti$: C, 60.11; H, 9.89; P, 11.92. Found: C, 59.87; H, 9.65; P, 11.71. IR (mineral oil mull) $\nu(CO)$: 1664 (s), 1588 (s). NMR (THF-d_8): ^1H δ 3.42 (q, J = 7.2 Hz, $NC\mathit{H}_2$), 1.95 (s, $C_5(C\mathit{H}_3)_5$), 1.30–1.24 (m, $PC\mathit{H}_2$, $PC\mathit{H}_3$, $NCH_2C\mathit{H}_3$); $^{31}P\{^1H\}$ δ 60.0 (s, br); $^{13}C\{^1H\}$ δ 316.0 (t, J = 17 Hz, $\mathit{C}O$), 104.1 (s, $\mathit{C}_5(CH_3)_5$), 53.1 (s, $N\mathit{C}H_2$), 31.7 (t, J = 18.5 Hz, $P\mathit{C}H_2$), 23.4 (br s, $P\mathit{C}H_3$), 19.9 (t, J = 18.1 Hz, $P\mathit{C}H_3$), 13.7 (s, $C_5(\mathit{C}H_3)_5$), 8.0 (s, $NCH_2\mathit{C}H_3$).[7b]

Exactly the same procedure was carried out employing 99% ^{13}CO-labeled $Cp^*{}_2Ti(^{13}CO)_2$ to provide a sample of pure $[Et_4N][Cp^*Ti(^{13}CO)_2(dmpe)]$, which had the following spectral properties. IR (mineral oil mull) $\nu(CO)$: 1626 (s), 1553 (s). NMR (THF-d_8): $^{13}C\{^1H\}$ δ 315.8 (t, J = 16.7 Hz, $\mathit{C}O$); $^{31}P\{^1H\}$ δ 59.9 (t, J = 16.2 Hz).

$[Na(12\text{-}crown\text{-}4)_2][Cp^*Ti(CO)_2(dmpe)]$ (13). Sodium naphthalene (3.35 mmol) was combined with an equimolar mixture of $Cp^*{}_2Ti(CO)_2$ (0.60 g, 1.60 mmol) and dmpe (0.27 mL, 1.60 mmol) in 40 mL of DME by the same procedure described above for the synthesis of **12**. After removal of solvent and washing the residue with diethyl ether, an orange solid was obtained. (Spectra indicated that the latter was a mixture of $NaCp^*$ and $Na[Cp^*Ti(CO)_2(dmpe)]$. IR (DME) $\nu(CO)$: 1628 (s), 1545 (m). ^1H NMR (DME-d_{10}, 20 °C): δ 1.97 (s, NaC_5Me_5), 1.94 (s, TiC_5Me_5), 1.32–1.25 (m, coordinated dmpe). The δ value for $NaCp^*$ was established by comparison with that of an independently prepared sample of the pure material.) The latter solid was dissolved in THF (25 mL), cooled to −78 °C, and stirred with 0.26 g (1.58 mmol) of Et_4NCl. The slurry was warmed slowly over a 1 h period to −10 °C and stirred for another 0.5 h as it warmed to 0 °C. The solution was then filtered to separate a white solid, believed to contain $C_5Me_5^-$, and the solvent was removed. After dissolution of the red-orange solid in DME (40 mL), the resulting solution was cooled to −78 °C and a solution of 12-crown-4 (0.80 mL, 3.2 mmol) in 20 mL of DME was added. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 1 h. A red solid precipitated during this period. It was separated by filtration, washed with DME (2 × 5 mL) and Et_2O (2 × 10 mL), and dried in vacuo. An orange powder (0.35 g, 28% yield based on $Cp^*{}_2Ti(CO)_2$) containing substantially pure **13** was thereby obtained, dec pt 137 °C.

Anal. Calcd for $C_{34}H_{63}NaO_{10}P_2Ti$: C, 53.41; H, 8.30; P, 8.10. Found: C, 52.71; H, 7.91; P, 8.44. IR (Nujol) $\nu(CO)$: 1632 (s), 1552 (m). $[Na(12\text{-}C\text{-}4)_2][Cp^*Ti(CO)_2(dmpe)]$ was not sufficiently soluble in unreactive solvents to obtain solution IR or NMR spectra. However, the formulation of **13** is consistent with its infrared spectrum, elemental analyses, and the supporting IR and NMR spectra of **12**.

$CpTi(CO)_3(PMe_3)H$ (14). To a cold (−78 °C) solution of **1** (0.35 g, 0.87 mmol) in 40 mL of THF was added neat CF_3CO_2H (0.060 mL, 0.78 mmol) whereupon the solution immediately changed from dark red to red-violet. IR (THF) $\nu(CO)$: 1993 (m), 1920 (s, br). Also a strong peak at 1693 cm^{-1} due to $CF_3CO_2^-$ was observed. The product was quite unstable under ambient conditions. Attempts to stabilize (or derivatize) the product in the presence of excess PMe_3 were unsuccessful. Similarly, the product could not be isolated without total decomposition. To confirm the formulation of **14**, it was generated at low temperature in methylene chloride by the treatment of **1** with acetic acid. NMR ($\mathrm{CD_2Cl_2}$, −70 °C): ^{1}H δ 5.04 (t, J = 1.4 Hz, $\mathrm{C_5}H_5$), 3.23 (q, J = 6.9 Hz, $\mathrm{NC}H_2$), 2.00 (s, $\mathrm{C}H_3\mathrm{COO^-}$), 1.30 (d, J = 6.7 Hz, $\mathrm{PC}H_3$), 1.27 (s, br, $\mathrm{NCH_2C}H_3$), −1.24 (d, J = 43 Hz, Ti–H); $^1\mathrm{H}\{^{31}\mathrm{P}\}$ (with decoupling at the frequency of the ^{31}P resonance) (as above, with one change) δ −1.22 (s, Ti–H); $^{31}\{^1\mathrm{H}\}$ δ 5.1 (s, coordinated $P\mathrm{Me_3}$); ^{31}P (^{1}H-coupled) δ 5.1 (d, J = 40 Hz). For comparison, corresponding NMR spectra of **1** were determined under identical conditions. NMR ($\mathrm{CD_2Cl_2}$, −70 °C): ^{1}H δ 5.15 (s, $\mathrm{C_5}H_5$), 3.23 (s, br, $\mathrm{NC}H_2$), 1.30 (s, br, $\mathrm{NCH_2C}H_3$), 1.17 (d, J = 6.0 Hz, $\mathrm{P(C}H_3)_3$; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ δ 36.9 (s).

$\mathrm{CpTi(CO)_3(PPh_3)H}$ (15). To a cold (−78 °C) solution of **2** (0.28 g, 0.47 mmol) in 20 mL of $\mathrm{CH_2Cl_2}$ was added 4.5 mL of a 0.105 M solution of acetic acid (0.47 mmol) in $\mathrm{CH_2Cl_2}$ at −70 °C, whereupon the solution immediately changed from an orange-red to a deep red. Infrared spectra in $\mathrm{CH_2Cl_2}$ in the ν(CO) region indicated that **2** (1826 (m) and 1710 (s) $\mathrm{cm^{-1}}$) was converted completely to **15** (1998 (m) and 1933 (m, br) $\mathrm{cm^{-1}}$), but bands due to reactant and especially product rapidly diminished in intensity at ambient temperatures due to thermal instability in this solvent. To confirm the nature of reactant and product in methylene chloride, their NMR spectra were determined independently in $\mathrm{CD_2Cl_2}$ (−70 °C). NMR (**2**): ^{1}H δ 7.38–7.22 (m, Ph-H), 4.94 (s, $\mathrm{C_5}H_5$), 3.26 (s, br, $\mathrm{NC}H_2$), 1.26 (s, br, $\mathrm{NCH_2C}H_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ δ 94.5 (coordinated $P\mathrm{Ph_3}$), −6.4 (free $P\mathrm{Ph_3}$). NMR (**15**): ^{1}H δ 7.38–7.21 (m, PhH), 4.93 (s, $\mathrm{C_5}H_5$), 3.15 (s, br, $\mathrm{NC}H_2$), 1.99 (s, $\mathrm{C}H_3\mathrm{COO^-}$), 1.23 (s, br, $\mathrm{NCH_2C}H_3$), −0.24 (d, J = 35 Hz, Ti–H); $^1\mathrm{H}\{^{31}\mathrm{P}\}$ (decoupling at the resonance frequency of the coordinated ^{31}P) (as above with one change) δ −0.24 (s, Ti–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ δ 60.9 (s, coordinated $P\mathrm{Ph_3}$), −7.2 (s, free $P\mathrm{Ph_3}$); ^{31}P (^{1}H-coupled) δ 60.9 (d, J = 33 Hz, coordinated $P\mathrm{Ph_3}$), −7.2 (s, free $P\mathrm{Ph_3}$). Attempts to isolate **15** from methylene chloride or THF were entirely unsuccessful due to its great thermal instability.

$\mathrm{CpTi(CO)_2(dmpe)H}$ (16). Method A: Protonation of $[\mathrm{CpTi(CO)_3(\eta^1\text{-}dmpe)}]^-$. A solution containing $[\mathrm{CpTi(CO)_3(\eta^1\text{-}dmpe)}]^-$ was prepared in exactly in the same manner as described above under compound **3**. It was cooled to −70 °C and 0.20 mL (2.0 mmol) of neat $\mathrm{CF_3CO_2H}$ was added. An IR spectrum taken of the solution at this time showed two bands in the ν(CO) region, 2000 (w) and 1923 (m, br) $\mathrm{cm^{-1}}$, which are assigned to protonated **3**, i.e., $\mathrm{CpTi(CO)_3(\eta^1\text{-}dmpe)H}$. Bands at 1930 and 1853 $\mathrm{cm^{-1}}$ due to **16** slowly increased in intensity as those attributed to the initial protonation product decayed at room temperature. Solvent was then removed in vacuo. The residue partially dissolved in pentane (80 mL) to provide a red-violet solution. Following filtration, concentration of the pentane solution to about 10 mL and cooling to −78 °C provided dark violet crystals (100 mg). Two more recrystallizations of this product from pentane and toluene/pentane gave 0.040 g (4% yield) of pure **16**, dec pt 86–88 °C.

Anal. Calcd for $\mathrm{C_{13}H_{22}O_2P_2Ti}$: C, 48.77; H, 6.93; P, 19.35. Found: C, 48.54; H, 6.96; P, 19.16. IR (toluene) ν(CO): 1933 (s), 1855 (s). NMR ($\mathrm{C_6D_6}$): ^{1}H δ 4.73 (t, J = 1.3 Hz, $\mathrm{C_5}H_5$), 1.17 (d, J = 6.1 Hz, $\mathrm{PC}H_3$), 1.10–0.85 (m, $\mathrm{PC}H_2$), 0.64 (d, J = 4.8 Hz, $\mathrm{PC}H_3$), 0.75–0.60 (m, $\mathrm{PC}H_2$), −1.65 (t, J = 57.4 Hz, Ti–H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ δ 267.1 (t, J = 9 Hz, $C\mathrm{O}$), 90.0 (s, $C_5\mathrm{H_5}$), 29.6 (t, J = 18 Hz, $\mathrm{P}C\mathrm{H_2}$), 19.9 (t, J = 14 Hz, $\mathrm{P}C\mathrm{H_3}$), 17.0 (s, br, $\mathrm{P}C\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ δ 45.7 (s); ^{31}P (^{1}H-coupled) δ 45.7 (d, J = 56 Hz).[7b]

Method B: Protonation of $[\mathrm{CpTi(CO)_2(dmpe)}]^-$. A solution of Cs-$[\mathrm{CpTi(CO)_2(dmpe)}]$ was prepared by addition of $\mathrm{CsC_{10}H_8}$ (3.8 mmol) in 50 mL of DME at 20 °C to a rapidly stirred and cold (−60 °C) solution containing $\mathrm{Cp_2Ti(CO)_2}$ (0.45 g, 1.9 mmol) and dmpe (0.26 mL, 1.6 mmol) under an argon atmosphere. The resulting red-orange solution was stirred for 1 h at −60 °C and filtered at −60 °C. Neat acetic acid (0.09 mL, 1.5 mmol) was added to the cold solution. Solvent was then removed in vacuo, and the residue was triturated with pentane (2 × 20 mL). The pentane solution was filtered and cooled to −78 °C for 1 h. A mixture of $\mathrm{C_{10}H_8}$ and **16** had precipitated. The hydride was freed from $\mathrm{C_{10}H_8}$ by three fractional recrystallizations from toluene/pentane. Each recrystallization was performed at −78 °C, and a cold pentane wash was used to preferentially remove $\mathrm{C_{10}H_8}$ and a pale brown decomposition material. The drying of the crystals was always performed initially at −78 °C, followed by quick warming to room temperature for a brief period. The yield of deep violet crystals from this procedure was 0.09 g (15%). Spectroscopically this substance was identical to **16** obtained by method A. This sample was used in the preparation of single crystals employed in the X-ray structural characterization of **16** which was previously described.[6]

$\mathrm{Cp^*Ti(CO)_2(dmpe)H}$ (17). Hexane (20 mL) was added to a flask containing 0.80 g (1.04 mmol) of **13**, and the suspension was cooled with stirring to −78 °C. A cold (−78 °C) solution of 0.060 mL (1.05 mmol) of $\mathrm{CH_3COOH}$ in 20 mL of hexane was then added. The solution was stirred at low temperature for 1 h and then gradually warmed to room temperature. After stirring 3.5 h at room temperature, the hexane was removed in vacuo. Pentane (20 mL) was added to the flask, and the dark solid was triturated. The solution was then filtered to remove a black solid and give a dark green filtrate. The solution was concentrated to 5 mL and then quickly cooled to −78 °C. After 0.5 h, dark green crystals were present. The supernatant was removed and saved. The solid was washed with 3 × 10 mL of cold (−78 °C) pentane, and these washings were also saved. The solid was then dried in vacuo to give 0.05 g (12%) of dark gray-green needlelike crystals. A second crop of crystals (0.01 g) was isolated from the washings. In this fashion, an analytically pure sample of **17** was obtained, dec pt 96–97 °C.

Anal. Calcd for $\mathrm{C_{18}H_{32}O_2P_2Ti}$: C, 55.40; H, 8.26. Found: C, 55.16; H, 8.11. IR (hexane) ν(CO): 1928 (s), 1853 (s). IR (mineral oil) ν(CO): 1912 (s), 1833 (s). NMR ($\mathrm{C_6D_6}$): ^{1}H δ 1.86 (s, $\mathrm{C_5(C}H_3)_5$), 1.17 (d, J = 5.5 Hz, $\mathrm{PC}H_3$), 1.09 (m, $\mathrm{PC}H_2$), 0.87 (d, J = 4.1 Hz, $\mathrm{PC}H_3$), −1.71 (t, J = 57.3 Hz, Ti–H); ^{31}P (^{1}H-coupled) δ 32.3 (d, J = 57.7 Hz, coordinated dmpe), −48.1 (s, free dmpe); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ δ 32.3 (s, coordinated dmpe), −48.1 (s, free dmpe); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ δ 273.4 (t, J = 7.0 Hz, $C\mathrm{O}$), 103.5 (s, $C_5\mathrm{(CH_3)_5}$), 30.7 (t, J = 18.1 Hz, $\mathrm{P}C\mathrm{H_2}$), 21.2 (t, J = 16.6 Hz, $\mathrm{P}C\mathrm{H_3}$), 16.0 (s, br, $\mathrm{P}C\mathrm{H_3}$), 12.4 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$).[7b]

Results and Discussion

Syntheses of $[\mathrm{(C_5R_5)Ti(CO)_3(PR_3)}]^-$. Monosubstituted organophosphine derivatives of $[\mathrm{(C_5R_5)Ti(CO)_4}]^-$ were best prepared by low-temperature (−60 °C) photopromoted substitutions, as indicated by eq 1. Photochemical substitution reactions were

$$[\mathrm{(C_5R_5)Ti(CO)_4}]^- + \mathrm{PR_3} \xrightarrow[-60\ ^\circ\mathrm{C}]{h\nu} [\mathrm{(C_5R_5)Ti(CO)_3(PR_3)}]^- + \mathrm{CO} \quad (1)$$

attempted at temperatures as high as 0 °C, but these reactions were accompanied by considerable decomposition of reactant and product. This photosubstitution procedure is essentially identical to that originally developed for the synthesis of phosphine derivatives of the hexacarbonylmetallates (1−) of vanadium, niobium, and tantalum, except the latter reactions are normally conducted at room temperature.[8] All the photochemical reactions were facilitated by application of a vacuum (≤1 Torr) to the solution as the photolysis occurred. This served to remove CO from the system and was important since the monosubstituted species $[\mathrm{(C_5R_5)Ti(CO)_3(PR'_3)}]^-$ (R′ = H, Me) reacted readily with CO to form $[\mathrm{Et_4N}][\mathrm{(C_5R_5)Ti(CO)_4}]$ (R = H, Me). Removal of CO could also be accomplished by purging the solution with a stream of argon, which was the method used in the synthesis of $[\mathrm{CpTi(CO)_3(\eta^1\text{-}dmpe)}]^-$. Similarly, the previously reported photochemical synthesis of $\mathrm{Cp_2Ti(CO)(PMe_3)}$ from $\mathrm{Cp_2Ti(CO)_2}$ required the application of a vacuum or the sweep of an inert purge gas to remove CO and prevent the back-reaction. In the latter study, Rausch et al. emphasized that low-valent Ti complexes often have a strong preference for CO over organophosphines.[9]

Continued irradiation of the solutions of monosubstituted derivatives did not result in disubstitution of $[\mathrm{Et_4N}][\mathrm{CpTi(CO)_4}]$. While the first phosphine substitution was relatively facile for $[\mathrm{(C_5R_5)Ti(CO)_4}]^-$ (R = H, Me), it appeared that this substitution caused the Ti metal center to become so electron rich that the remaining carbonyl ligands could not be removed under our photolysis conditions without destruction of the reactant and potential product. In contrast, photolysis of the less electron rich $\mathrm{CpV(CO)_4}$ in the presence of excess $\mathrm{PMe_3}$ has been shown by Rehder and co-workers[10,11] to provide *cis*- and *trans*-CpV-

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$(CO)_2(PMe_3)_2$. Bidentate phosphines, such as $Ph_2PCH_2CH_2PPh_2$ (diphos), also tend to form bridging complexes like $[\{CpV(CO)_3\}_2(\mu\text{-diphos})]$,[11b] which is similar to what we observed in the $[CpTi(CO)_4]^-$–dmpe system, vide infra.

Although our first syntheses of $[CpTi(CO)_3(PR_3)]^-$ involved apparent very slow "thermal" substitutions of PR_3 into $[CpTi(CO)_4]^-$, these were all accomplished by long-term reactions, sometimes lasting for weeks and were all performed with borosilicate glassware exposed to fluorescent lamp radiation in the laboratory. When solutions of $[CpTi(CO)_4]^-$ and PMe_3 were stirred at room temperature in the dark under the same conditions, no evidence for the formation of compound **1** was obtained. Light was clearly important in promoting these substitution reactions, but we cannot rule out the possibility that small amounts of air might also have helped to facilitate these "thermal" reactions. It is well established in other systems that one-electron oxidations of metal carbonyls facilitate substitution reactions via reactive 17-electron intermediates.[12] Since most of the monosubstituted anions were best obtained by the low-temperature photolysis route, a more detailed investigation of these "thermal" reactions was not carried out. Attempts to obtain phosphine-substituted derivatives of the corresponding zirconates, $[(C_5R_5)Zr(CO)_4]^-$,[2,3] have been unsuccessful to date.

Syntheses of $[(C_5R_5)Ti(CO)_2(dmpe)]^-$. Floriani and co-workers reported in 1976 that vanadocene carbonyl underwent smooth reductive carbonylation in the presence of sodium amalgam to provide high yields of $CpV(CO)_4$ as shown in eq 2.[13] Likewise,

$$Cp_2V(CO) \xrightarrow[CO]{Na/Hg} CpV(CO)_4 + NaCp \qquad (2)$$

the Jonas group has studied the reduction of metallocenes in the presence of a variety of ligands and found that one or two cyclopentadienyl groups can often be selectively removed to form new organometallic species (eqs 3 and 4).[14-16] These prior studies

$$2Li + Cp_2Fe + 2C_2H_4 \xrightarrow{-60\ ^\circ C} Li[CpFe(C_2H_4)_2] + LiCp \qquad (3)$$

$$4Li + Cp_2Fe + 4C_2H_4 \xrightarrow{20\ ^\circ C} Li_2[Fe(C_2H_4)_4] + 2LiCp \qquad (4)$$

demonstrated that metallocenes and their carbonyl adducts are quite valuable precursors in the syntheses of low-valent transition metal complexes. After it was shown that $[CpTi(CO)_4]^-$ could be produced by two independent routes using Ti(IV)[2] and Ti(O)[17] (eqs 5 and 6), it was of interest to determine whether the readily

$$CpTiCl_3 + 4NaC_{10}H_8 + 4CO \xrightarrow[60\ ^\circ C]{THF} Na[CpTi(CO)_4] + 3NaCl + 4C_{10}H_8 \qquad (5)$$

$$Ti(CO)_5(dmpe) + NaCp \xrightarrow[20\ ^\circ C]{THF} Na[CpTi(CO)_4] + dmpe + CO \qquad (6)$$

available Ti(II) complex $Cp_2Ti(CO)_2$ could also be a precursor to $[CpTi(CO)_4]^-$. Our attempts to perform reductive carbonylations of $Cp_2Ti(CO)_2$ with alkali metals or alkali metal amalgams were uniformly unsuccessful. However, alkali metal naphthalenides were successful in producing the desired transformation. Although $[CpTi(CO)_4]^-$ was only producd in a 20% (unoptimized) yield in the reaction, this result was important since it represented the first known conversion of the readily available titanocene dicarbonyl to a zerovalent titanium carbonyl species. Our inability to carry out reductive carbonylations of $Cp_2Ti(CO)_2$ with alkali metals has led us to propose that a naphthalene-stabilized intermediate such as that shown in eqs 7 and 8 is important in the success of our reactions.

$$Cp_2Ti(CO)_2 + 2AC_{10}H_8 \xrightarrow{-60\ ^\circ C} \{A[CpTi(CO)_2(\eta^4\text{-}C_{10}H_8)]\} + ACp + C_{10}H_8 \qquad (7)$$

$$A = Na, K, Cs$$

$$\{A[CpTi(CO)_2(\eta^4\text{-}C_{10}H_8)]\} + 2CO \rightarrow A[CpTi(CO)_4] + C_{10}H_8 \qquad (8)$$

Lee and Cooper recently reported on the facile reaction of the slipped-ring dianion $[(\eta^3\text{-}C_5H_4CH_3)Mn(CO)_3]^{2-}$, following protonation, with naphthalene to provide $[(\eta^4\text{-}C_{10}H_8)Mn(CO)_3]^-$ and methylcyclopentadiene.[18] On this basis it is possible that a similar "slipped-ring" intermediate, such as $[(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Ti(CO)_2]^{2-}$, may be initially formed but rapidly trapped by the naphthalene as suggested by eqs 9 and 10. Potassium cyclopentadienide formation has been established in the synthesis of compound **11** as mentioned in the Experimental Section, vide supra. Although efforts to directly observe either species have been unsuccessful to date, by performing analogous reductions in the presence of dmpe, good yields of the corresponding formal dmpe derivative could be isolated (eq 11). It is noteworthy that we were unable to obtain $[CpTi(CO)_2(dmpe)]^-$ by the direct substitution of $[CpTi(CO)_4]^-$ with dmpe.

$$Cp_2Ti(CO)_2 + 2C_{10}H_8^- \rightarrow [(\eta^3\text{-}Cp)(\eta^5\text{-}Cp)Ti(CO)_2]^{2-} + 2C_{10}H_8 \qquad (9)$$

$$[(\eta^3\text{-}Cp)(\eta^5\text{-}Cp)Ti(CO)_2]^{2-} + C_{10}H_8 \rightarrow [CpTi(CO)_2(\eta^4\text{-}C_{10}H_8)]^- + Cp^- \qquad (10)$$

$$Cp_2Ti(CO)_2 + 2C_{10}H_8^- + dmpe \rightarrow [CpTi(CO)_2(dmpe)]^- + Cp^- + C_{10}H_8 \qquad (11)$$

The successful preparations of $[CpTi(CO)_4]^-$ and $[CpTi(CO)_2(dmpe)]^-$ from $Cp_2Ti(CO)_2$ suggest that corresponding reductive cleavage reactions of the latter reagent should be carried out in the presence of a variety of other ligands to determine the scope of this interesting reaction. Thus far, only PMe_3 has been examined in some detail and provided a much less stable product. For example, reduction of $CpTi(CO)_2$ with $NaC_{10}H_8$ in the presence of 2 equiv of PMe_3 at –70 °C yielded a deep red solution which was quite thermally unstable and decomposed rapidly at room temperature. Because of its instability, no IR evidence for a carbonylmetallate species could be obtained, but low-temperature ^{31}P NMR spectra showed a resonance at 22 ppm (and free PMe_3 at –61 ppm) assigned to coordinated PMe_3. Treatment of this substance with CO (1 atm pressure) at –70 °C provided low yields of $Na[CpTi(CO)_3(PMe_3)]$, which was converted to bona fide compound **1** on exchange with Et_4NBr. Although the initial formation of $[CpTi(CO)_2(PMe_3)_2]^-$ seems possible, no confirmation of the nature of this species has been obtained to date.

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(12) Basolo, F. *Polyhedron* **1990**, *9*, 1503.

(13) Fachinetti, D.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046.

(14) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

(15) Jonas, K.; Schieferstein, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 549.

(16) Jonas, K.; Schieferstein, L.; Krüeger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 550.

(17) Chi, K. M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 163.

(18) Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 716.

While attempts to extend this chemistry to $Cp_2Zr(CO)_2$ have been uniformly unsuccessful so far, we were pleased to discover that decamethyltitanocene dicarbonyl also smoothly underwent cleavage by $C_{10}H_8^-$ in the presence of dmpe to provide good yields of $[Cp^*Ti(CO)_2(dmpe)]^-$ (eq 12). As far as we know, this reaction

$$Cp_2^*Ti(CO)_2 + 2C_{10}H_8^- + dmpe \rightarrow [Cp^*Ti(CO)_2(dmpe)]^- + Cp^{*-} + C_{10}H_8 \quad (12)$$

appears to represent the first successful reductive cleavage of any decamethylmetallocene complex to be reported. As indicated in the Experimental Section, the expelled $[C_5Me_5]^-$ has been unambiguously identified in this reaction.

Simple alkali metal salts of $[CpTi(CO)_2(dmpe)]^-$ proved to be quite thermally unstable and could not be isolated without extensive decomposition. However, addition of efficient alkali metal complexants such as crown ethers or cryptands resulted in dramatic stabilization of the salts in solution and in the solid state and permitted the isolation of satisfactorily pure substances. These observations were of critical importance in our planning of the first successful synthesis of salts containing $[M(CO)_6]^{2-}$ (M = Ti, Zr, Hf).[19]

Corresponding alkali metals salts of $[Cp^*Ti(CO)_2(dmpe)]^-$ were surprisingly more thermally stable in solution and in the solid state. For example, a dark orange solid containing $Na[Cp^*Ti(CO)_2(dmpe)]$ (**18**) contaminated by $NaCp^*$ could be isolated at room temperature. By stirring a THF solution containing approximately (by ^1H NMR) equimolar amounts of **18** and $NaCp^*$ with 1 equiv of Et_4NCl at 0 °C, a precipitate containing $[Et_4N][C_5Me_5]$ and NaCl formed, leaving substantially pure **18** in solution. By subsequent treatment of these solutions of **18** with additional Et_4NCl or 12-crown-4, satisfactorily pure solid samples of $[Et_4N][Cp^*Ti(CO)_2(dmpe)]$ (**12**) or $[Na(12\text{-crown-}4)_2][Cp^*Ti(CO)_2(dmpe)]$ (**13**) could be isolated. The spectroscopic properties of these materials and the other carbonyltitanates will now be described along with pertinent details concerning their behavior in solution.

IR and NMR Spectral Properties of $[(C_5R_5)Ti(CO)_3(PR_3)]^-$. Infrared spectra of tetraethylammonium salts of $[(C_5R_5)Ti(CO)_3(PR_3)]^-$ in the $\nu(CO)$ region (Table I) consist of two intense absorptions, where the one at lower energy is generally an unsymmetrical envelope consisting of two overlapped bands (e.g. Figure 1). For the analogous neutral vanadium complexes $CpV(CO)_3(PR_3)$ the corresponding absorptions are of similar shape and relative intensities, but the third band of medium intensity is often more well resolved. The $\nu(CO)$ bands of the vanadium species are shifted to considerably higher energies (ca. 120 cm^{-1}) than corresponding bands of the titanium complexes, as expected on the basis of the substantially less electron rich nature of the vanadium in $CpV(CO)_3(PR_3)$.[21]

NMR spectra provide further corroboration of our formulations for the monosubstituted products and will be considered in some detail for compounds **1**, **3**, and **4**. The ^{31}P NMR spectra of compound **1** show the presence of bound PMe_3, which has a δ value (40.7 ppm) substantially downfield (ca. 100 ppm) from that of free PMe_3 (−61 ppm). Similar trends have been observed in the past for numerous transition metal phosphine complexes.[22] Integrated intensities of the signals in the ^1H NMR spectrum of **1** are fully in accord with our proposed formulation. In addition, the Cp ring hydrogen resonance shows a small coupling ($J = 0.9$ Hz) due to coordinated PMe_3. Similar $^2J_{PH}$ couplings have been previously observed for cyclopentadienyl metal phosphine complexes.[23] The $^{13}C\{^1H\}$ spectrum of **1** is especially informative in the CO region as it shows well-resolved doublets at δ 307.6 ($J = 14.2$ Hz) and δ 298.7 ($J = 20.3$ Hz) for the trans and cis carbonyls, respectively, where the trans carbonyl is defined as the one more or less trans to the coordinated phosphorus. The integrated intensities of these trans and cis carbonyl peaks have a ratio of 1:2, in accord with the expected configuration of a complex of the general formula $[CpTi(CO)_3L]^-$. While the larger coupling constant to the cis carbonyl carbons appears to be unusual, similar data have been obtained for phosphine-substituted chromium carbonyls.[24] The ^{13}C δ value for the trans CO is about 10 ppm farther downfield than that of the cis CO, in accord with previous reports of ^{13}C NMR spectra of phosphine carbonyls.[25] All of these data, in addition to the elemental analysis, confirm the formulation of the anion in **1** as $[CpTi(CO)_3(PMe_3)]^-$. Compounds $[CpTi(CO)_3(PPh_3)]^-$ (**2**) and $[Cp^*Ti(CO)_3(PMe_3)]^-$ (**5**) were formulated on the same basis but will not be discussed individually.

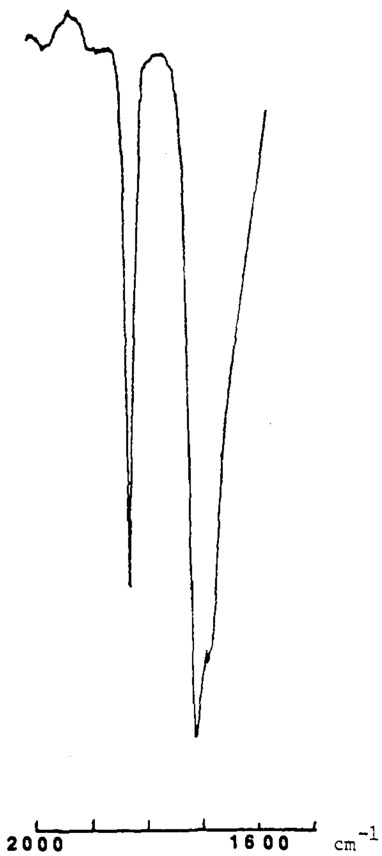

Figure 1. Infrared spectrum of $[Et_4N][(C_5H_5)Ti(CO)_3(PMe_3)]$ in THF. $\nu(CO)$: 1823 (m), 1712 (s), 1680 (sh) cm^{-1}.

1,2-Bis(dimethylphosphino)ethane (dmpe) interacted with $[CpTi(CO)_4]^-$ to provide compounds **3** and **4**, the former of which was only obtained as an impure oil. These products are believed to be generated by the reactions shown in eqs 13–15. No evidence for the formation of $[CpTi(CO)_2(\eta^2\text{-dmpe})]^-$, vide infra, was obtained in these reactions under any conditions. Infrared spectral monitoring showed smooth conversion of $[CpTi(CO)_4]^-$ to a product which we initially believed was pure $[CpTi(CO)_3(\eta^1\text{-dmpe})]^-$, on the basis of the close similarity of its IR spectrum in the $\nu(CO)$ region to that of product **1**. Surprisingly, however, a product slowly precipitated from THF, which had

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[19] Chi, K. M.; Ellis, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 6022 and references cited therein.

[20] For example, the reported IR spectrum for a THF solution of $(C_5H_5)V(CO)_3(PMe_3)$ in the $\nu(CO)$ region is 1947 (s), 1868 (m), and 1840 (s) cm^{-1}.[10]

[21] Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975.

[22] Verkade, J. G., Quin, L. D., Eds. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH Publishers: Deerfield Beach, FL, 1987.

[23] Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haaler, K. J. *Organometallics* **1983**, *2*, 535.

[24] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[25] Mann, B. E.; Taylor, B. F. *Carbon-13 NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

$$[CpTi(CO)_4]^- + dmpe \rightarrow [CpTi(CO)_3(\eta^1\text{-}dmpe)]^- + CO \quad (13)$$

$$[CpTi(CO)_3(\eta^1\text{-}dmpe)]^- + [CpTi(CO)_4]^- \rightarrow [\{CpTi(CO)_3\}_2(\mu\text{-}dmpe)]^{2-} + CO \quad (14)$$

$$2[CpT(CO)_3(\eta^1\text{-}dmpe)]^- \rightarrow [\{CpTi(CO)_3\}_2(\mu\text{-}dmpe)]^{2-} + dmpe \quad (15)$$

virtually an identical IR spectrum in the ν(CO) region. Also, on standing, relatively pure solutions of **3** in THF slowly changed to the insoluble product **4**. Although compound **3** could not be obtained pure, its $^{31}P\{^1H\}$ spectra provide the best evidence for the "dangling" dmpe formulation, i.e., $[CpTi(CO)_3(\eta^1\text{-}dmpe)]^-$. The latter spectra show well-resolved doublets of equal intensity at δ 51.0 (J_{PP} = 20 Hz) due to a coordinated Me_2P unit and δ −47.3 (J_{PP} = 20 Hz) due to an uncoordinated Me_2P unit. The latter δ value is nearly identical to the ^{31}P chemical shift of free dmpe.

In contrast to **3**, product **4** was isolated as an analytically pure substance and was fully characterized in solution by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The ^1H NMR integration data indicated that two equivalent Cp groups per dmpe were present in **4**, while the $^{31}P\{^1H\}$ NMR spectrum established the presence of equivalent coordinated Me_2P units. The $^{13}C\{^1H\}$ NMR spectrum in the CO region for **3** showed triplets of integrated intensity 1:2 for the trans and cis carbonyls, respectively.[7b] Further corroboration of our formulation for **4** was provided by the fact that the carbonyl ^{13}C δ values for **4** are nearly identical to those observed for the PMe_3 derivative, **1**.

IR and NMR Spectral Properties of $[(C_5R_5)Ti(CO)_2(dmpe)]^-$. Corresponding spectral data for the η^2-dmpe complexes $[(C_5R_5)Ti(CO)_2(dmpe)]^-$ are shown in Table I and exhibit dramatic counterion dependences, which can be correlated with their thermal stabilities in solution. Since attempts to observe carbonyl ^{13}C signals for natural abundance $[CpTi(CO)_2(dmpe)]^-$ were unsuccessful, 99% ^{13}C carbon monoxide enriched $Cp_2Ti(^{13}CO)_2$ was prepared[7] and reduced by $NaC_{10}H_8$ in the presence of dmpe to provide solutions of $Na[CpTi(^{13}CO)_2(dmpe)]$ (**7**). The ^{13}C and ^{31}P NMR spectra of this compound showed well-resolved binomial triplets at δ 320 and 63, respectively, with J_{PC} values of 16 Hz, thereby corroborating our formulation for **7**. IR spectra of **7** in the ν(CO) region (Figure 2) showed band positions (1613, 1524 cm^{-1}) which were in satisfactory agreement with those calculated ($\nu(^{13}CO)$: 1622, 1529 cm^{-1}) from the corresponding IR spectrum of **6** ($\nu(^{12}CO)$: 1658, 1568 cm^{-1}) on the basis of the simple harmonic oscillator model.[21] The latter spectrum was otherwise identical to that of **7** with respect to the relative intensities and shapes of the carbonyl absorptions. Further corroboration that the ^{13}C-enriched complex **7** and the natural abundance species **6** were otherwise identical species was provided by the ^{31}P NMR spectrum of **6** which showed a singlet at δ 63, the same ^{31}P chemical shift value observed for **7**. Solutions of **6** and **7** decomposed rapidly at room temperature, and all attempts to isolate these products were unsuccessful.

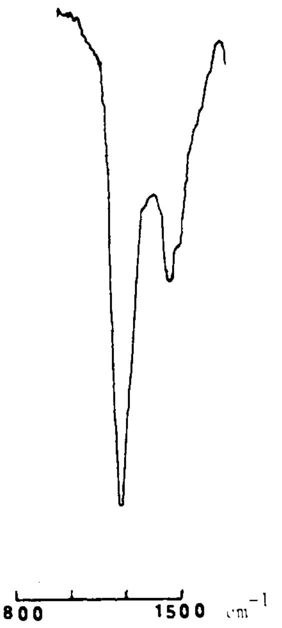

Figure 2. Infrared spectrum of $Na[(C_5H_5)Ti(^{13}CO)_2(dmpe)]$ in DME. ν(CO): 1613 (s), 1524 (m) cm^{-1}.

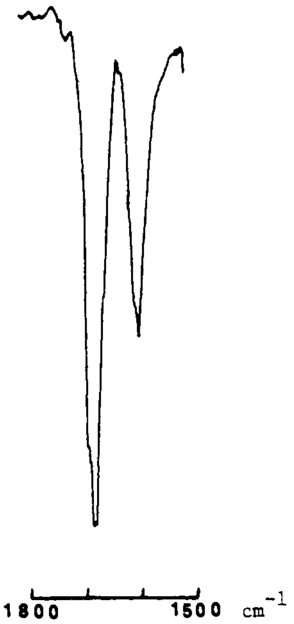

Figure 3. Infrared spectrum of $[Na(cryptand\ 2.2.1)][(C_5H_5)Ti(^{13}CO)_2(dmpe)]$ in DME. ν(CO): 1680 (s), 1596 (m) cm^{-1}.

Treatment of **7** with cryptand 2.2.1 caused no visible change, but solutions of the resulting $[Na(cryptand\ 2.2.1)][CpTi(^{13}CO)_2(dmpe)]$ (**8**), were stable for hours under anaerobic conditions at room temperature. The latter could be isolated as a thermally stable solid, contaminated with NaCp (and/or [Na(cryptand 2.2.1)]Cp) which could not be removed. IR spectra of **8** (Figure 3) closely resembled those for **7** except the bands were shifted about 70 cm^{-1} to higher energies. These shifts in ν(CO) values are indicative of significant reduction of specific ion pairing between Na^+ and carbonyls oxygens of the anion by the cryptand and have been observed for other carbonylmetalates.[26] Substantial differences were also observed in the ^{13}C and ^{31}P NMR spectra of **7** and **8**, where δ(CO) shifted upfield from +320 to +311 ppm, while δ(P, dmpe) shifted downfield from +63 to +78 ppm. The NMR δ(CO) change is consistent with the IR ν(CO) change in that the carbonyl carbons present in **7** are more electron rich than those in **8** by virtue of strong carbonyl oxygen–Na^+ interactions in **7** which effectively transfer electron density from the titanium to the carbonyl group, vide infra.

Our inability to isolate pure samples of **8**, due to contamination by NaCp, led us to prepare the corresponding potassium salts, **9**, since Jonas had previously noted the very poor solubility of KCp in THF.[14,27] Thus, we found that reduction of $Cp_2Ti(CO)_2$ by $KC_{10}H_8$ in the presence of dmpe (eq 16) provided solutions that were virtually free of KCp. IR and NMR spectral properties of **9** and the corresponding 99% ^{13}C carbonyl enriched complex

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(26) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

$$Cp_2Ti(CO)_2 + dmpe + 2KC_{10}H_8 \xrightarrow[THF]{-70\ °C} K[CpTi(CO)_2(dmpe)] + KCp\downarrow + C_{10}H_8 \quad (16)$$

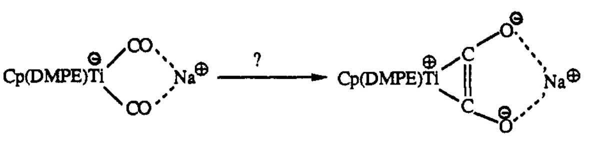
10 were very similar to those of the sodium salts **6** and **7**, respectively, although the potassium salts appeared to be even less stable in solution than the sodium salts. Treatment of **9** with 1 equiv of cryptand 2.2.2 provided thermally stable solutions of [K(cryptand 2.2.2)][CpTi(CO)$_2$(dmpe)] from which 50% yields of analytically pure microcrystalline **11** were isolated, thereby providing valuable additional data in support of our formulations. Although a 99% ^{13}C carbonyl enriched version of **11** was not obtained, it is noteworthy that the calculated ν(^{13}CO) values for THF solutions of **11**, 1687 and 1610 cm^{-1}, are in very good agreement with corresponding observed ν(^{13}CO) values for the [Na(cryptand 2.2.1)]$^+$ salt **8**, 1680 and 1596 cm^{-1}, suggesting that the anion environments for both salts are nearly identical in solution.

Solution IR and NMR spectral properties of [Cp*Ti(CO)$_2$(dmpe)]$^-$ were very similar to those observed for [CpTi(CO)$_2$(dmpe)]$^-$. For example, Na[Cp*Ti(CO)$_2$(dmpe)] (**18**) had the following spectral properties. IR (DME) ν(CO): 1628 (s), 1545 (m). NMR (DME-d_{10}, 20 °C): ^{13}C{^{1}H} δ(CO) 320 (t, J_{PC} = 19 Hz); ^{31}P{^{1}H} δ 47 (s, coordinated dmpe). As expected, on the basis of the better donor ability of Cp* relative to Cp, the ν(CO) values for **18** are somewhat lower in energy than corresponding ones for **6** (see Table I); however, the carbonyl ^{13}C δ values are nearly the same, +320 ppm. As mentioned previously, **18**, unlike **6**, could be isolated at room temperature, though it was invariably contaminated by NaCp*. The Nujol mull IR spectrum of solid **18** showed two bands at significantly lower energy, 1565 (s) and 1512 (m) cm^{-1}, indicating that even stronger Na$^+$–carbonyl oxygen interactions were present. The corresponding Et$_4$N$^+$ salt, **12**, had IR ν(CO) bands (THF, 1680 (s), 1600 (m) cm^{-1}) at significantly higher energies than those of **18**, suggesting that cation–isocarbonyl anion interactions were substantially diminished, if not completely destroyed. Also, **12** exhibited a carbonyl ^{13}C chemical shift of +316 ppm, which was shifted upfield relative to that of **18** by 4 ppm.

One particularly striking feature concerning the ^{13}C NMR spectra of all of the carbonyltitanates in this paper is the unusually positive carbonyl chemical shifts (δ 300–320) observed for these species. These values appear to be the highest ever observed previously for mononuclear metal carbonyl complexes. Prior research has shown that, as the metal center in a mononuclear carbonyl complex becomes more electron rich, the carbonyl ^{13}C chemical shifts tend to assume more positive values while the corresponding IR ν(CO) values shift to lower energies.[28] However, the position of the metal in the periodic table can also be very important in determining the magnitude of the δ(^{13}CO) value, where carbonyls of the earlier transition metals tend to have more positive δ values than those of the later transition metals.[29] For example, the reported δ(^{13}CO) values for the following half-sandwich carbonyl anions [(C$_5$H$_5$)Fe(CO)$_2$]$^-$, [(C$_5$H$_5$)Cr(CO)$_3$]$^-$, and [(C$_5$H$_5$)Ti(CO)$_4$]$^-$ are 229.8 (pyridine-d_5, 25 °C),[30] 246.7 (THF, 20 °C),[31] and 288.9 (DMSO-d_6, 20 °C)[3] ppm, respectively. These are pronounced differences, particularly when they are compared with the corresponding quite similar IR-active ν(CO) values for the same anions. [(C$_5$H$_5$)Fe(CO)$_2$]$^-$ in THF, nBu$_4$N$^+$ salt: 1865 (s), 1788 (s).[32] [(C$_5$H$_5$)Cr(CO)$_3$]$^-$ in DMSO, Et$_4$N$^+$ salt: 1880, 1770.[33] [(C$_5$H$_5$)Ti(CO)$_4$]$^-$ in THF, Et$_4$N$^+$ salt: 1921 (m), 1777 (s).[3] The presence of the relatively electropositive titanium atoms in low formal oxidation states in these complexes undoubtedly gives rise to large paramagnetic shielding contributions, which have been suggested in the past to be the most important factors contributing to carbonyl ^{13}C chemical shift values.[29] As the metal center becomes more electron rich, the carbonyl ^{13}C δ values tend to become more positive due to these paramagnetic contributions, which as demonstrated above are not always related to IR spectral data for carbonyls. Indeed, [Ti(CO)$_6$]$^{2-}$ has an IR active ν(CO) value of about 1750 cm^{-1} and a rather unremarkable δ(^{13}CO) value of 246 ppm.[34]

Solution Stability of [CpTi(CO)$_2$(dmpe)]. Undoubtedly one of the most interesting properties of [CpTi(CO)$_2$(dmpe)]$^-$ is its extreme sensitivity to the nature of the counterion. Some of our observations regarding this subject will now be summarized along with other pertinent studies in this area. In a now classic review, M. Y. Darensbourg emphasized the substantial influence counterions can have on the spectral and chemical properties of carbonylmetallates.[26] Cooper and co-workers previously observed dramatic counterion dependences on ν(CO) and δ(^{13}CO) values for Na$_2$[W(CO)$_5$] and [Na(cryptand 2.2.1)]$_2$[W(CO)$_5$], which have carbonyl ^{13}C δ values of 247 and 257 ppm, respectively.[35] The more shielded carbonyl groups present in Na$_2$[W(CO)$_5$] compared to those in the cryptand complex were attributed to a predominance of direct Na$^+$–tungsten interactions present in Na$_2$[W(CO)$_5$], which would tend to decrease electron density on the carbonyl carbons relative to that in the [Na(cryptand 2.2.1)]$^+$ salt. Undoubtedly, the large steric congestion about seven-coordinate titanium in [CpTi(CO)$_2$(dmpe)]$^-$ forces Na$^+$ to bind exclusively to the carbonyl oxygens in this and the related Cp* complex. On this basis, it is reasonable that addition of cryptand 2.2.1 to Na[CpTi(CO)$_2$(dmpe)] would cause the δ(^{13}CO) values to shift upfield, while in Cooper's system, the corresponding addition caused the δ(^{13}CO) values to shift downfield. While the presence of cryptand 2.2.1 did not appear to have a significant effect on the thermal stability of Na$_2$[W(CO)$_5$] in solution,[35] the presence of the complexant was found to be of critical importance in obtaining thermally stable solutions of Na[CpTi(CO)$_2$(dmpe)] above 0 °C.

Although we have suspected in the past that strong interactions of alkali metal cations with carbonyl oxygens in highly reduced carbonyl anions of the early transition metals were responsible for destabilization of the latter species in solution,[36] this present study is important in that it provides the first unambiguous proof for such an effect. We believe this mode of ion pairing may promote reductive coupling of coordinated CO as suggested by eq 17, perhaps formally analogous to what Lippard and co-workers have observed in the reactions of electron rich group 5 carbonylmetallates with organosilicon electrophiles.[37] The nature(s) of the decomposition products from our reactions remain unknown but are clearly of tremendous importance in understanding the carbonyl chemistry of the early transition metals.



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[27] Jonas, K.; Wiskamp, V. *Z. Naturforsch. B* **1983**, *38*, 1113.

[28] (a) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1. (b) Hickley, J. P.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1979**, *179*, 159.

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[32] Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.

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[35] Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354.

[36] Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1 (in particular, see sections IIIA and -B and VA of this review).

[37] Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 4166 and references cited therein.

Table II. Selected IR and NMR Spectral Data for Carbonyl Hydrides of Titanium

compound	IR, ν(CO), cm^{-1} (solvent)	^{1}H NMR, δ(hydride), ppm	^{31}P NMR, δ ppm^a
$CpTi(CO)_3(PMe_3)H$ (**14**)	1993 m, 1920 s, br (THF)	−1.24 (d, J_{PH} = 43 Hz)^b	5.1 (d, $J_{PH} \approx$ 40 Hz)^b
$CpTi(CO)_3(PPh_3)H$ (**15**)	1998 m, 1933 s, br (CH_2Cl_2)	−0.24 (d, J_{PH} = 36 Hz)^b	60.9 (d, $J_{PH} \approx$ 31 Hz)^b
$CpTi(CO)_2(dmpe)H$ (**16**)	1930 s, 1853 m (THF)	−1.65 (t, J_{PH} = 57 Hz)^c	45.7 (d, $J_{PH} \approx$ 56 Hz)^c
$Cp^*Ti(CO)_2(dmpe)H$ (**17**)	1913 s, 1833 m (THF)	−1.69 (t, J_{PH} = 58 hz)^c	32.3 (d, $J_{PH} \approx$ 58 Hz)^c

^{a} Corresponding $^{31}P\{^1H\}$ NMR spectra showed singlets at identical δ values. ^{b} CD_2Cl_2, −70 °C. ^{c} C_6D_6, +20 °C.

Synthesis and Spectral Properties of Carbonyl Hydrides of Titanium. Protonation of the monophosphine-substituted anions $[(C_5R_5)Ti(CO)_3(PR_3)]^-$ by acetic acid or trifluoroacetic acid at low temperature (eq 18) generally provided much darker red to

$$[(C_5R_5)Ti(CO)_3(PR'_3)]^- + CX_3CO_2H \xrightarrow[-78\,°C]{THF} (C_5R_5)Ti(CO)_3(PR'_3)H + CX_3CO_2^- \quad (18)$$

$$R' = H, Me; X = H, F$$

red-violet and thermally unstable products which could not be isolated as pure materials. However, unambiguous data for their formulation have been obtained by IR and NMR spectroscopy (Table II) for all except $Cp^*Ti(CO)_3(PMe_3)H$. For the latter, only infrared spectra were obtained. For example, protonation of $[Cp^*Ti(CO)_3(PMe_3)]^-$ (ν(CO) in THF: 1815 (m), 1704 (s) cm^{-1}) at −78 °C provided a thermally unstable product attributed to $Cp^*Ti(CO)_3(PMe_3)H$, which had absorptions at much higher energies (ν(CO): 1985 (m), 1908 (s)). These new peaks rapidly decayed at room temperature, and all attempts to remove solvent from the product resulted in total decomposition. The analogous more well characterized $CpTi(CO)_3(PMe_3)H$, vide infra, had an infrared spectrum in the ν(CO) region in THF, 1993 (m) and 1920 (s) cm^{-1}, which closely matched that of $Cp^*Ti(CO)_3(PMe_3)H$, except the bands were shifted to slightly higher energy, as expected since C_5H_5 is not as good a donor group as C_5Me_5. Attempts to observe metal-hydrogen stretching, ν(Ti–H), in these compounds were unsuccessful. Deuteration of the anion provided band envelopes in the ν(CO) region identical to those of the corresponding hydrides, and no new bands at lower energies due to possible ν(Ti–D) absorptions were observed. Convincing evidence for the existence of the hydrides of the monosubstituted derivatives was provided by ^{1}H and ^{31}P NMR experiments at low temperature. The ^{1}H NMR spectra of $CpTi(CO)_3(PR_3)H$ (R = Me, Ph) exhibited substantially downfield Cp resonances relative to those of the anions and also characteristic doublets upfield of TMS for the hydride ligands (see Table II). Although there are few examples for comparison, the coupling constants of 45 and 37 Hz for R = Me and Ph, respectively, are of reasonable magnitude for two-bond phosphorus–hydrogen coupling constants.[38] Corresponding proton-coupled ^{31}P NMR spectra had P–H coupling constants that agreed well with these values. Significantly, ^{1}H NMR experiments with irradiation at the frequency of the phosphorous bound to the metal center caused collapse of the hydride resonance to the expected singlet. Protonation of solutions of the η^1-dmpe complex **3** also appeared to provide a thermally unstable monohydride on the basis of IR data. For example, the product formulated as $CpTi(CO)_3(\eta^1\text{-dmpe})H$ (**19**) had ν(CO) absorptions in THF at 2000 (m) and 1923 (s) cm^{-1}, which were very similar in position, shape, and relative intensities to those observed for $CpTi(CO)_3(PMe_3)H$ (**14**). In contrast to **14**, however, warming the solutions of **19** gave a new thermally stable hydride. IR and NMR spectra and elemental analysis of this deep violet substance provided unambiguous evidence that it was identical to the product **16** obtained from the protonation of $[CpTi(CO)_2(dmpe)]^-$. Thus, the formation of the hydride **16** from **19** almost certainly involved substitution of the dangling phosphine unit on the latter species during its decomposition, as suggested by eq 19. It is not known

$$CpTi(CO)_3(\eta^1\text{-dmpe})H \rightarrow CpTi(CO)_2(\eta^2\text{-dmpe})H + CO \quad (19)$$

whether the uncoordinated Me_2P unit in **19** actively assisted in the elimination of CO or simply provided rapid stabilization of the titanium hydride during the decomposition process. Attempts to obtain a stable bis trimethylphosphine adduct of the unstable $(C_5R_5)Ti(CO)_3(PMe_3)H$ (R = H, Me) by allowing them to decompose in the presence of excess PMe_3 were unsuccessful. These failures suggest that either the desired species, $(C_5R_5)Ti(CO)_2(PMe_3)_2H$, were too unstable to access or that the capture process with PMe_3 was woefully inefficient.

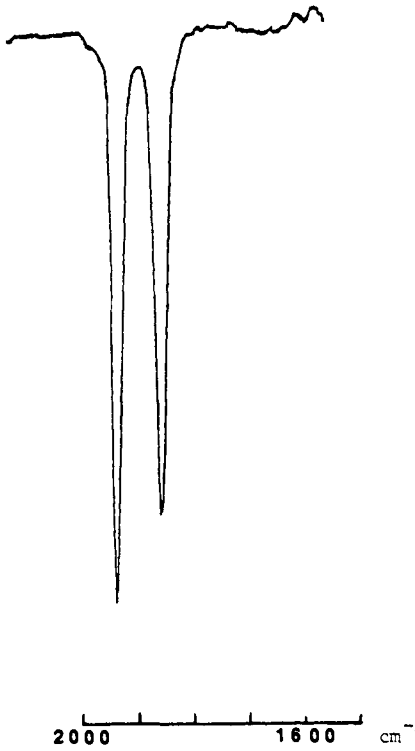

Figure 4. Infrared spectrum of $(C_5H_5)Ti(CO)_2(dmpe)H$ in toluene. ν(CO): 1933 (s), 1855 (m) cm^{-1}.

Since generation of $[CpTi(CO)_3(\eta^1\text{-dmpe})]^-$ was always accompanied by formation of the dinuclear $[\{CpTi(CO)_3\}_2(\mu\text{-dmpe})]^{2-}$ and protonation of the latter gave only decomposition products, the yields of the stable hydride **16** were never very high by this route. For these reasons, the preparation of **16** via the protonation of $[CpTi(CO)_2(dmpe)]^-$ (eq 20) was

$$[(C_5R_5)Ti(CO)_2(dmpe)]^- + CH_3CO_2H \rightarrow (C_5R_5)Ti(CO)_2(dmpe)H + CH_3CO_2^- \quad (20)$$

found to be the superior route. Also, by this latter route, the previously unknown and isolable $Cp^*Ti(CO)_2(dmpe)H$ (**17**) could be obtained. The spectroscopic properties of these carbonyl hydrides of titanium will now be described.

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[38] Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

Infrared spectra for **16** and **17** are very similar (see Figure 4 for **16**) except the ν(CO) values for **17** were about 20 cm^{-1} lower in energy than those for **16** due to the stronger donor nature of C_5Me_5 relative to C_5H_5. As noted previously, we were unsuccessful in observing a titanium–hydrogen absorption in the IR spectrum of these species. However, ^{1}H, ^{13}C, and ^{31}P NMR spectra were all in accord with the proposed formulations of **16** and **17**. The ^{1}H NMR spectra of these hydrides showed sharp binomial triplets ($^2J_{PH} \cong 57$ Hz) for the metal hydride (δ −1.65 and −1.69 for **16** and **17**, respectively, and carbonyl ^{13}C values (δ 267 and 273 for **16** and **17**, respectively) were characteristic of Ti(II) carbonyls and similar to corresponding values observed for $Cp_2Ti(CO)_2$ and $Cp^*{}_2Ti(CO)_2$ (δ 261 in DME and 265 in C_6D_6, respectively).[39] The similarity of the $^{13}C\{^1H\}$ and ^{1}H NMR spectra for the two hydrides, including the practically identical P–H coupling constants, indicates that the geometries of **16** and **17** are likely to be very similar. The single-crystal X-ray structure of **16** was determined[6] and showed the carbonyl and η^2-dmpe groups to reside in an approximate equatorial plane between the "axial" Cp ring centroid and hydride groups of a pseudoctahedral complex. The molecular structure of **16** was very similar to that reported more recently for $CpZr(CO)_2(dmpe)Cl$, in which the chlorine is located nearly opposite the ring centroid of the Cp group.[40] The only significant difference in the spectral properties of **16** and **17** was the $\delta(^{31}P)$ value for coordinated dmpe of +46 and +32 ppm, respectively. The more positive phosphorus chemical shift in **16** suggested that the dmpe group in this complex may be somewhat more tightly bound to the titanium than in **17**, perhaps due to a combination of steric and electronic effects.[41] Slightly shorter titanium–phosphorus bonds in **16** would be expected to result in a larger downfield shift for the coordinated dmpe group. In general, it has been observed for series of very similar phosphine complexes that $\delta(^{31}P)$ values for coordinated phosphines shift downfield as the phosphorus ligand becomes more strongly coordinated to the metal center.[24]

Concluding Remarks. Low-temperature photolyses of $[(C_5R_5)Ti(CO)_4]^-$ (R = H, Me) in the presence of organophosphines, R_3P, have been established to be a good route to previously unknown compounds of the general formula $[(C_5R_5)Ti(CO)_3(PR_3)]^-$. While disubstituted compounds of the type $[(C_5R_5)Ti(CO)_2(PR_3)_2]^-$ were unavailable by this photolysis route, reductive cleavage of titanocene dicarbonyls, $(C_5R_5)_2Ti(CO)_2$ (R = H, Me), by alkali metal naphthalenides in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) provided the desired η^2-dmpe substituted anions $[(C_5R_5)Ti(CO)_2(dmpe)]^-$, whose thermal stabilities and spectral properties were a sensitive function of the counterion. Protonation of these anions gave the first known series of carbonyl hydrides of titanium. Extension of this work to zirconium and hafnium promises to yield a treasure of new results in the still poorly explored area of zerovalent zirconium and hafnium carbonyl chemistry.

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[39] Frerichs, S. R.; Stein, B. K.; Ellis, J. E. Unpublished research.

[40] Wielstra, Y.; Gambarotta, S.; Roedelof, J. B.; Chiang, M. Y. *Organometallics* **1988**, *7*, 2177.

[41] That is, either the smaller size of coordinated Cp vs Cp* or the slightly weaker donor ability of Cp vs Cp* would be expected to make the titanium in **16** more Lewis acidic than that in **17**.