11.4. Found: C, 43.5; H, 7.26; V, 10.0.

Crystallographic Studies. Single crystals of the titanium carbonyl (trimpsi)Ti(CO)$_4$ [or (trimpsi)V(CO)$_3$H; parameters listed in brackets from here on refer to this compound], grown from hot toluene, were sealed in thin-walled glass capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 25 reflections, yielded the cell dimensions given in Table I.

Data were collected in one quadrant [octant] of reciprocal space ($\pm h,+k,+l$) [($+h,-k,+l$)] by using measurement parameters listed in Table I. Systematic absences for $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$ [$0kl$, $k + l \neq 2n$, and $hk0$, $h \neq 2$], were consistent with space groups $P6_3/m$ and $P6_3$ [$Pnma$ and $Pn2_1a$]. The centric space group was investigated initially, and this choice was subsequently confirmed after successful refinement and convergence of the centric model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Absorption corrections were applied, the maximum and minimum transmission factors being 0.948 and 0.909 [0.836 and 0.790], respectively. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged ($R_i = 0.028$) to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods using SHELX-86; correct positions for the titanium [vanadium], phosphorus, and silicon atoms were deduced from an E map. Subsequent least-squares difference Fourier calculations revealed positions for the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where $w = 5.66/(\sigma(F_o)^2 + (pF_o)^2)$ [$w = 1.00/(\sigma(F_o)^2 + (pF_o)^2)$]. The analytical approximations to the scattering factors were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. Carbon atoms C4 and C7 were disordered across the mirror plane, and each was successfully modeled as two half-atoms. Due to the paucity of data, hydrogen atoms were included as fixed contributors in "idealized" positions (for methyl hydrogens, staggered with respect to the attached sp^3 Si or P atom) with C–H = 0.96 Å. In the final cycle of least squares, anisotropic thermal coefficients were refined for non-hydrogen atoms and a group isotropic thermal parameter was varied for the hydrogen atoms. [No evidence of the hydride attached to the vanadium atom was seen in the final difference maps.] Successful convergence was indicated by the maximum shift/error of 0.04[0.006] for the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features, and there were no apparent systematic errors among the final observed and calculated structure factors.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757) and the Office of Naval Research under their Young Investigator Award Program for support of this research. We particularly wish to thank Dr. Scott Wilson of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determinations and Prof. John Ellis of the University of Minnesota for communicating their results in ref 38 prior to publication.

Registry No. 1, 110512-29-3; 2, 110512-30-6; 3, 110512-31-7; [t-BuSi(CH$_2$PMe$_2$)$_3$]VCl$_3$, 110512-32-8.

Supplementary Material Available: Tables of hydrogen atom positions (S1) and anisotropic thermal parameters (S2) for (trimpsi)Ti(CO)$_4$ and (trimpsi)V(CO)$_3$H (2 pages); listings of final observed and calculated structure factors for (trimpsi)Ti(CO)$_4$ (S3) and (trimpsi)V(CO)$_3$H (S4) (9 pages). Ordering information is given on any current masthead page.

Cationic Alkylbis(cyclopentadienyl)titanium Complexes. Synthesis, Reactions with CO and *t*-BuNC, and the Structure of [Cp$_2$Ti{η^2-C(Me)N-*t*-Bu}(CN-*t*-Bu)]BPh$_4$·MeCN

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Cationic methylbis(cyclopentadienyl)titanium complexes [Cp$_2$TiMe(L)]BPh$_4$ (L = MeCN, n-PrCN, t-BuCN, PhCN, PMe$_3$, PMe$_2$Ph, PMePh$_2$, n-Bu$_3$P, pyridine) have been synthesized in high yields by reaction of Cp$_2$TiMeCl with L and sodium tetraphenylborate in polar solvents. A range of bis(indenyl)titanium complexes is similarly accessible. The complex [Cp$_2$TiMe(NCMe)]BPh$_4$ reacts with carbon monoxide to give [Cp$_2$Ti(η^2-COMe)(NCMe)]BPh$_4$ in which the nitrile ligand is retained, while *tert*-butyl isocyanide displaces acetonitrile and inserts into the titanium–methyl bond to give [Cp$_2$Ti{C(N-t-Bu)Me}(CN-t-Bu)]BPh$_4$·MeCN (18) whose crystal structure was determined. The complex crystallizes in space group $P2_1/c$, $a = 13.212$ (10) Å, $b = 9.354$ (2) Å, $c = 33.951$ (4) Å, $\beta = 91.87$ (4)°, $V = 4193.3$ Å^3, $Z = 4$, and $D_{\mathrm{calcd}} = 1.14$ g cm^{-3}. The iminoacyl ligand in 18 is η^2-coordinated, with Ti—C and Ti—N distances of 2.08 and 2.12 Å and a short C=N bond (1.24 Å).

Introduction

Although the polymerization of olefins in the homogeneous phase by catalysts based on bis(cyclopentadienyl)titanium dihalide/aluminum alkyl halide systems has been known for over 30 years, the mechanism of this reaction has continued to attract attention.[1-5] An early suggestion by Breslow et al.[6] involved the intermediacy of electron-

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(1) Boor, J. *Ziegler-Natta Catalysts and Polymerisation*; Academic: New York, 1979; p 349 ff.

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deficient titanium alkyl species carrying a (partial) positive charge to which an ethylene molecule coordinates prior to "insertion" into the titanium–carbon bond. Although some electrochemical evidence for the participation of such charged intermediates has been proposed,[7] general acceptance has been lacking[3] in the absence of knowledge of the chemistry of cationic titanium alkyl complexes, until the recent isolation by Eisch et al.[8] of a cationic titanium vinyl complex derived from the insertion of $PhC{\equiv}CSiMe_3$ into a "$[Cp_2TiMe]^+$" intermediate and the polymerization of ethylene catalyzed by the closely related complex $[Cp_2ZrMe(THF)]BPh_4$ in the absence of aluminum alkyls[9] (THF = tetrahydrofuran). Here we report the synthesis of a number of cationic titanium alkyl complexes and their conversion into acyl and iminoacyl compounds. A preliminary account of this work has appeared.[10]

Results and Discussion

Preparation of Complexes. Tetrahydrofuran solutions of bis(cyclopentadienyl)dimethyltitanium react in the dark smoothly with ammonium hexafluorophosphate with liberation of 1 equiv of methane and the formation of a dark orange ammine complex **1**. The perchlorate can be obtained similarly. The compounds are stable under ambient conditions; however, their use as starting materials for further reactions is limited by the tendency of the highly electrophilic titanium center to react with the anion. For example, although **1** liberates NH_3 when dissolved in acetonitrile, indicating that ligand exchange is facile, the main product eventually isolated is Cp_2TiF_2, presumably via a sequence of transalkylation and halogenation reactions with the anion. The reactions with pyridine and aniline have similar instantaneous results (eq 1–4). The behavior of these titanium complexes closely resembles that of related zirconium compounds.[11]

$$Cp_2TiMe_2 + NH_4PF_6 \rightarrow \underset{\mathbf{1}}{[Cp_2TiMe(NH_3)]PF_6} + CH_4 \quad (1)$$

$$\mathbf{1} + L \rightarrow [Cp_2TiMeL]PF_6 + NH_3 \quad (2)$$

$$[Cp_2TiMeL]PF_6 \rightarrow Cp_2TiMeF + L\text{–}PF_5 \quad (3)$$

$$Cp_2TiMeF + L\text{–}PF_5 \rightarrow Cp_2TiF_2 + L\text{–}PMeF_4 \quad (4)$$

$$L = MeCN,\ pyridine$$

This difficulty is circumvented by the use of tetraphenylborate salts. Acetonitrile solutions of $Cp_2TiMeCl$ soon assume the dark brown color of $[Cp_2TiMe(NCMe)]BPh_4$ (**2**) when treated with 1 equiv of sodium tetraphenylborate. A wide range of complexes with N and P ligands is accessible by chloride substitution of $Cp_2TiMeCl$ in THF in the presence of equimolar quantities of ligand and sodium tetraphenylborate (eq 5).

$$Cp_2TiMeCl + L + NaBPh_4 \rightarrow \underset{\mathbf{2\text{–}10}}{[Cp_2TiMe(L)]BPh_4} + NaCl \quad (5)$$

2, L = MeCN; **3**, L = *n*-PrCN; **4**, L = PhCN;
5, L = *t*-BuCN; **6**, L = pyridine; **7**, L = PMe_3;
8, L = PMe_2Ph; **9**, L = $PMePh_2$; **10**, L = P-*n*-Bu_3

Complexes **2–10** are isolated as dark orange to brown air-sensitive crystalline solids, moderately soluble in THF and best recrystallized from dichloromethane. The solubility of the nitrile adducts increases in the order Me $\ll$ Ph $\simeq$ *n*-Pr < *t*-Bu. There is no reaction between $Cp_2TiMeCl$ in THF and L = triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)methane, 2,2′-bipyridyl, or 1,10-phenanthroline. Surprisingly, in contrast to eq 1, no reaction takes place between Cp_2TiMe_2 or $Cp_2Ti(CH_2SiMe_3)_2$ and solutions of NH_4BPh_4 in THF; the starting materials are recovered. Repeated attempts were made to prepare a THF complex which we expected to be more labile and reactive than nitrile and phosphine complexes. However, there is no reaction between $Cp_2TiMeCl$ and $NaBPh_4$, $AgBPh_4$, or $TlBPh_4$ in THF in the absence of other ligands, while Cp_2TiMe_2 and $AgBPh_4$ give small amounts of as yet unidientified material. The lack of formation of a titanium THF complex is in striking contrast to analogous zirconium complexes where THF readily displaces acetonitrile.[9,11] In view of the ease with which even bulky ligands such as $PMePh_2$ form stable titanium complexes (eq 5) while a sterically more congested complex such as $(C_5Me_5)_2ScMe$ which fails to react with PMe_3 still forms a THF adduct,[12] it appears implausible that steric factors prevent the coordination of THF in the present case, and although one might expect cationic titanium complexes to be potent electrophiles, the finding suggests that the $[Cp_2TiMe]^+$ fragment is a significantly weaker Lewis acid than isostructural Zr,[9,11] Sc,[12,13a] or lanthanide[13] compounds.

A range of bis(indenyl)titanium complexes, $[Ind_2TiMe(L)]BPh_4$ (Ind = η^5-C_9H_7), is similarly accessible from $Ind_2TiMeCl$, $NaBPh_4$, and L = MeCN (**11**), PhCN (**12**), *t*-BuCN (**13**), PMe_3 (**14**), and PMe_2Ph (**15**). While the bis(cyclopentadienyl) complexes react with excess nitrile only very sluggishly under nitrile insertion into the titanium–methyl bond, the bis(indenyl) analogues are significantly more reactive.[10,14] Acetonitrile is the least reactive substrate. Multiple nitrile insertion as with bis(pentamethylcyclopentadienyl)scandium methyl[15] is not observed.

Selected spectroscopic data are listed in Table I. The $C{\equiv}N$ stretching frequencies of the nitrile adducts are found at ca. 50 cm^{-1} wavenumbers higher than in the free ligands. The titanium–methyl groups in **1–10** appear in the ^1H NMR spectra as singlets between δ 0.6 and 1.3,

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Table I. Selected Spectroscopic Data of Cationic Titanium Complexes

compd	IR,[a] cm^{-1}	^1H NMR[b]	^{13}C NMR[e]
$[Cp_2TiMe(NH_3)]PF_6$ (**1**)	3370 (m), 3300 (m), 3210 (w), 1625 (s) (NH_3) 2970, 2895 (CH_3) 840 (vs), 560 (s) (PF_6)	0.96 (s, 3 H, TiMe),[d,g] 6.49 (s, 10 H, Cp)	g
$[Cp_2TiMe(NCMe)]BPh_4$ (**2**)	2970, 2920, 2890 (CH_3) 2310 (w), 2282 (m) ($C\equiv N$)	0.69 (s, 3 H, TiMe),[d] 1.95 (s, 3 H, MeCN), 6.3 (s, 10 H, Cp)	2.1 (*Me*CN),[d] 49.0 (TiMe), 117.5 (Me*C*N) 118.2 (Cp)
$[Cp_2TiMe(NC\text{-}n\text{-}Pr)]BPh_4$ (**3**)	2285 ($C\equiv N$)	1.2 (s, 3 H, TiMe),[c] 0.7–2.1 (m, 7 H, Pr), 6.39 (s, 10 H, Cp)	13.1 ($Me(CH_2)_2CN$), 19.3, 18.7 ($Me(CH_2)_2CN$), 71.1 (TiMe), 116.5 (*C*N), 118.4 (Cp)
$[Cp_2TiMe(NCPh)]BPh_4$ (**4**)	2260 ($C\equiv N$)	1.32 (s, 3 H, TiMe),[c] 6.45 (s, 10 H, Cp), 7.6 (m, 5 H, Ph)	
$[Cp_2TiMe(NC\text{-}t\text{-}Bu)]BPh_4$ (**5**)	2275 ($C\equiv N$)	1.22 (s, 3 H, TiMe),[c] 1.40 (s, 9 H, *t*-Bu), 6.36 (s, 10 H, Cp)	27.4 (CMe_3),[c] 54.2 (CMe_3), 71.6 (TiMe), 116.0 (*C*N), 118.6 (Cp)
$[Cp_2TiMe(py)]BPh_4$ (**6**)	1605, 1490, 1442, 1220, 1010 (py)	0.73 (s, 3 H, TiMe),[d] 6.28 (s, 10 H, Cp), 7.15 (m, 20 H, BPh_4), 7.75–8.35 (m, 5 H, py)	
$[Cp_2TiMe(PMe_3)]BPh_4$ (**7**)	1292 (m), 950 (s) (PMe_3)	0.70 (s, 3 H, TiMe),[d] 1.10 (s, br, 9 H, PMe_3), 6.3 (s, 10 H, Cp)	
$[Cp_2TiMe(PMe_2Ph)]BPh_4$ (**8**)	1295, 1110, 937, 915 (PMe_2Ph)	0.6 (d, 3 H, TiMe, $J_{P-H} = 3$ Hz),[c] 1.42 (d, 6 H, $J = 7.8$ Hz, PMe_2), 6.2 (d, 10 H, Cp, $J_{P-H} = 3$ Hz), 7.15 (25 H, Ph)	14.7 (d, $^1J_{P-C} = 25.1$ Hz, PMe), 81.9 (d, $^2J_{P-C} = 15$ Hz, TiMe), 116.7 (Cp)
$[Cp_2TiMe(PMePh_2)]BPh_4$ (**9**)	1105, 897	0.76 (d, 3 H, TiMe, $J = 3$ Hz),[c] 1.92 (d, $J = 8.4$ Hz, PMe), 6.25 (d, $J = 2.4$ Hz, Cp), 7.15 (m, 30 H, Ph)	
$[Cp_2TiMe(P\text{-}n\text{-}Bu_3)]BPh_4$ (**10**)	1305, 1140 (sh), 845 ($P\text{-}n\text{-}Bu_3$)	0.8 (s, 3 H, TiMe),[c] 0.8–2.0 (m, 27 H, Bu), 6.26 (10 H, Cp)	
$[Ind_2TiMe(NCMe)]BPh_4$ (**11**)	3120 (Ind) 3060 (BPh_4) 2310 (w), 2282 (m) ($C\equiv N$)	−0.24 (3 H, TiMe),[d] 1.95 (3 H, MeCN), 6.0–6.45 (m, 6 H, Ind), 6.8–7.7 (m, 28 H, Ind, BPh_4)	
$[Ind_2TiMe(NCPh)]BPh_4$ (**12**)	2270 ($C\equiv N$)	0.0 (s, 3 H, TiMe),[c] 6.2 (m, 6 H, Ind), 7.3 (m, 28 H, Ind, BPh_4), 7.64 (m, 5 H, *Ph*CN)	
$[Ind_2TiMe(NC\text{-}t\text{-}Bu)]BPh_4$ (**13**)	2275 ($C\equiv N$)	−0.12 (s, 3 H, TiMe),[c] 1.34 (s, 9 H, *t*-Bu), 6.1 (m, 6 H, Ind), 7.3 (m, 28 H, Ind, BPh_4)	
$[Ind_2TiMe(PMe_3)]BPh_4$ (**14**)	3115 (Ind) 950 (s) (PMe_3)	−1.0 (d, 3 H, $J_{P-H} = 3.6$ Hz, Ti–Me),[c] 1.28 (d, $J_{P-H} = 9.6$ Hz, PMe_3), 5.8–6.5 (m, 6 H, Ind), 6.8–7.7 (m, 28 H, BPh_4, Ind)	
$[Ind_2TiMe(PMe_2Ph)]BPh_4$ (**15**)	3120 (Ind) 1295, 950 (PMe_2Ph)	−0.9 (d, $J_{P-H} = 3$ Hz, TiMe),[c] 1.55 (d, $J = 4.2$ Hz, 6 H, PMe_2), 5.9–6.3 (m, 6 H, Ind), 6.6 (m, 5 H, PPh), 6.8–7.7 (m, 28 H, BPh_4, Ind)	15.0 (d, $^1J_{P-C} = 22.6$ Hz, PMe_2), 64.9 (d, $^2J_{P-C} = 15$ Hz, TiMe), 107–108.8, 119.3–132.5 (m, Ind)
$[Cp_2Ti(COMe)(NCMe)]BPh_4$ (**16**)	2315 (w), 2290 (m) ($C\equiv N$) 1630 (s) ($C{=}O$)	1.90 (s, 3 H, MeCN),[c] 2.92 (s, 3 H, MeCO), 5.60 (s, 10 H, Cp)	
$[Cp_2Ti(COMe)(PMe_2Ph)]BPh_4$ (**17**)	1610 (s) ($C{=}O$)	1.76 (d, 6 H, $J_{P-H} = 7.2$ Hz, PMe_2), 2.99 (s, 3 H, CMe), 5.36 (d, 10 H, $J_{P-H} = 2.4$ Hz, Cp), 7.15 (m, 20 H, BPh_4), 7.6 (m, 5 H, PPh)	
$[Cp_2Ti\{C(N\text{-}t\text{-}Bu)Me\}(CN\text{-}t\text{-}Bu)]BPh_4\cdot MeCN$ (**18**)	2290 (w), 2245 (m) (MeCN) 2190 (m) ($t\text{-}BuN\equiv C$) 1740 (s) ($C{=}N$)	1.33 (s, 9 H, $t\text{-}BuN{=}C$),[c] 1.66 (s, 9 H, $t\text{-}BuN\equiv C$), 1.94 (s, 3 H, MeCN), 2.77 (s, 3 H, $MeC{=}N$), 5.4 (s, 10 H, Cp)	1.58 (*Me*CN),[f] 22.9 (s, $MeC{=}N$), 28.5, 29.5 (CMe_3), 59.3, 61.5 (CMe_3), 105.6 (Cp), 212.9 ($C{=}N$)
$[Cp_2Ti\{C(N\text{-t-}Bu)Me\}(CN\text{-}t\text{-}Bu)]BPh_4$ (**19**)	2190 (s) ($C\equiv N$) 1745 (m) ($C{=}N$)	1.34 (s, 9 H, $t\text{-}BuN{=}C$),[c] 1.68 (s, 9 H, $t\text{-}BuN\equiv C$), 2.76 (s, 3 H, Me), 5.42 (s, 10 H, Cp)	

[a] CCl_4 mull. Abbreviations: w, weak; m, medium; s, strong. [b] BPh_4^- signals are not influenced by the cation and are omitted unless they overlap with ligand signals. [c] In CD_2Cl_2. [d] In CD_3CN. [e] BPh_4^- resonances: δ 122.6, 126.5, 136.6, 164.3 (q, $J_{B-C} = 50$ Hz). [f] In $CDCl_3$. [g] Reacts with solvent.

while those in **11–15** experience a high-field shift to δ 0.0 to −1.0 as a result of the magnetic anisotropy of the indenyl ligands. The infrared spectrum shows the C–H vibrations of the titanium–methyl groups at ca. 2970 (ν_{asym}) and 2900 (ν_{sym}) cm^{-1} (CCl_4 mull);[16] lower frequencies that might indicate metal–hydrogen interactions are not observed.[17]

Ligand substitution in nitrile complexes is facile; for example, **5** is readily converted into **6** or **7** on treatment with pyridine and PMe_3, respectively. However, complexes

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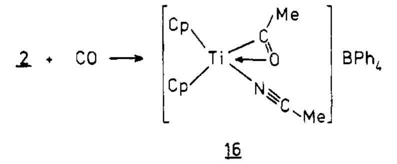
Table II. Selected Bond Lengths (Å) and Angles (deg) of Complex 18

C(1)-Ti	2.080 (6)	N(3)-Ti	2.125 (5)
C(8)-Ti	2.192 (6)	N(3)-C(1)	1.240 (6)
C(1)-C(2)	1.496 (7)	N(3)-C(4)	1.491 (6)
C(4)-C(5)	1.513 (8)	C(8)-N(9)	1.150 (6)
N(9)-C(10)	1.461 (7)		
C(1)-Ti-N(3)	34.3 (1)	C(8)-Ti-C(1)	117.9 (3)
C(8)-Ti-N(3)	83.7 (2)	C(2)-C(1)-Ti	149.0 (3)
N(3)-C(1)-Ti	74.8 (3)	N(3)-C(1)-C(2)	136.2 (4)
C(1)-N(3)-Ti	70.9 (3)	C(4)-N(3)-Ti	153.4 (2)
C(4)-N(3)-C(1)	135.7 (3)	C(5)-C(4)-N(3)	111.9 (4)
N(9)-C(8)-Ti	174.4 (3)	C(10)-N(9)-C(8)	176.7 (4)
C(11)-C(10)-N(9)	109.6 (5)		

2, 8, and 9 failed to react with PhC≡CR (R = $SiMe_3$, Me, Ph) in THF or with ethylene at 1 bar in dichloromethane. Apparently, the nitrile and phosphine ligands are too tightly bonded to be displaced by alkenes or alkynes under these conditions. Attempts to facilitate the removal of coordinated acetonitrile in 2 by the addition of 1 equiv of a Lewis acid, e.g. $AlCl_3$, in the presence of an excess of $PhC{\equiv}CSiMe_3$ resulted in the formation of Cp_2TiCl_2.

As is the case with neutral titanium alkyls, e.g. $Cp_2TiMeCl$,[18] the cationic alkyl complex **2** reacts readily with carbon monoxide (1 bar) to give the acyl complex **16** (eq 6); the nitrile ligand is not replaced.



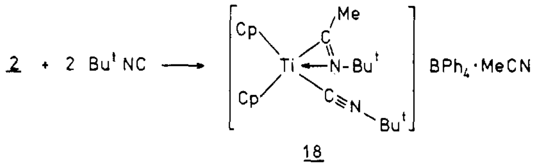
(6)

16

The acyl—C=O band in the IR spectrum is found at 1630 cm^{-1}, only 10 cm^{-1} higher than in $Cp_2Ti(\eta^2\text{-}COMe)Cl$, and suggests an η^2 mode of coordination. By contrast, η^1-bonded acyl groups in cationic complexes tend to give rise to C=O stretching frequencies which are considerably higher than in their neutral counterparts (e.g. $[Ni\{COMe\}\{PMe_3\}_3]^+$, 1715 cm^{-1}; $Ni(COMe)Cl(PMe_3)_2$, 1635 cm^{-1}).[19]

The phosphine complex **8** is surprisingly resistant toward CO insertion. A phosphine acyl complex is, however, obtained by displacement of the acetonitrile ligand in **16** with PMe_2Ph to give $[Cp_2Ti(\eta^2\text{-}COMe)(PMe_2Ph)]BPh_4$ (**17**).

The reaction of **2** with *tert*-butyl isocyanide in acetonitrile solution takes a different course. The dark brown color of **2** immediately pales to light yellow on contact with the isocyanide, and the product **18**, isolated as air-stable crystals in high yield, contains both an iminoacyl group as the result of isocyanide insertion into the Ti–Me bond and a terminally coordinated isocyanide ligand while 1 mol of noncoordinated acetonitrile is present as solvent of crystallization (eq 7).



(7)

18

The nitrile-free complex $[Cp_2Ti\{\eta^2\text{-}C(N\text{-}t\text{-}Bu)Me\}(CN\text{-}t\text{-}Bu)]BPh_4$ (**19**) is obtained if the butyronitrile complex **3** in dichloromethane is used as the starting material.

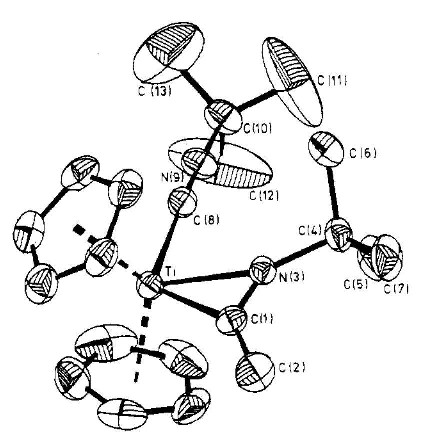


Figure 1. The structure of $[Cp_2Ti\{\eta^2\text{-}C(N\text{-}t\text{-}Bu)Me\}(CN\text{-}t\text{-}Bu)]^+$, indicating the atomic numbering scheme.

Table III. Comparative Data of Selected *tert*-Butyl Isocyanide Complexes

compd	d^n, n =	$\nu_{C{\equiv}N}$, cm^{-1}	$r_{M\text{-}C}$, Å	$r_{C{\equiv}N}$, Å	ref
18	0	2190	2.19	1.15	this work
$Cp_2Ti(CO)(CN\text{-}t\text{-}Bu)$	2	2170	2.11	1.16	29
$VCl_3(CNBu)_3$	2	2200, 2160	2.19	1.13	30
$[CpNbCl(CN\text{-}t\text{-}Bu)_4]^+$	2	2185, 2146	2.20	1.13	31
$[V(CN\text{-}t\text{-}Bu)_6]^{2+}$	3	2197	2.10	1.15	32
$[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$	4	2143, 2138	2.15	1.14	33
$WI_2(CO)_2(CN\text{-}t\text{-}Bu)_3$	4	2160, 2110	2.11	1.13	34
$Ru(PPh_3)(CN\text{-}t\text{-}Bu)_4$	8	2100, 2055	2.00	1.17	
		1830	1.86	1.28	28

Molecular Structure of 18. The structure of the complex titanium cation in **18** is shown in Figure 1. Table II lists selected bond distances and angles. The iminoacyl group is "N-inside" η^2-bonded, in spite of the close proximity of the two *tert*-butyl groups resulting from this geometry. This bonding mode is in agreement with the theoretical predictions for η^2-acyl ligand bonding in bis(cyclopentadienyl)-d^0 metal systems.[20] Both the iminoacyl C and N atoms are nearly equidistant from titanium (2.080 and 2.125 Å, respectively). These values are close to those observed in the Ti(III) complex $Cp_2Ti(\eta^2\text{-}PhCN\text{-}2,6\text{-}Me_2C_6H_3)$ (Ti—C = 2.096 Å, Ti-N 2.149 Å);[21c] the Ti-N bond is, however, longer than analogous distances in the Ti(IV) complexes $Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(t\text{-}BuNCCH_2Ph)(CH_2Ph)$ and $Ti(OAr\text{-}2,6\text{-}Ph_2)_2(PhNCCH_2SiMe_3)(CH_2SiMe_3)$ (2.015 and 2.025 Å, respectively).[22] All these titanium–nitrogen distances are within the range expected for a nitrogen ligand bonded to an sp^2-hybridized carbon, as in $Cp_2Ti(NC_4H_4)_2$ (2.085 Å),[23] while the Ti-N bonds in dialkylamides and bis(trimethylsilyl)amides are considerably shorter, e.g. 1.88 Å in $CpTiCl_2[N(SiMe_3)_2]$[24] and 1.89 Å in $Fe[C_5H_4Ti(NEt_2)_3]_2$.[25] Pure Ti-N donor interactions are long by comparison, e.g. 2.293 Å in the pyridine complex $Ti(OC_6H_3\text{-}t\text{-}BuMe_2CH_2)(OC_6H_3\text{-}t\text{-}Bu_2)(CH_2SiMe_3)$-

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Table IV. Bonding Parameters of η^2-Iminoacyl Ligands

compound	$\nu_{C=N}$, cm^{-1}	$r_{C=N}$, Å	∠R—C=N, deg	∠C=N—R′, deg	$\delta(^{13}C)$	ref
18	1740	1.24	136.2	135.7	212.9	this work
$Cp(CO)_2Mo(\eta^2\text{-}PhNCMe)$	1680	1.23	138.9	134.7	195.15	35
$Cp_2Ti[\eta^2\text{-}PhCN(2,6\text{-}Me_2C_6H_3)]$	1573	1.28	127.4	130.6		21c
$Ti(OAr)_2R(\eta^2\text{-}CRNR')$						
Ar = 2,6-*i*-$Pr_2C_6H_3$, R = CH_2Ph, R′ = CMe_3	1560	1.257			230.5	22
Ar = 2,6-$Ph_2C_6H_3$, R = CH_2SiMe_3, R′ = Ph	1565	1.279			240.7	22
$Zr(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2(\eta^2\text{-}t\text{-}BuNCCH_2Ph)_2$	1570	1.286			244.3	22
$HB(3,5\text{-}Me_2pz)_3ZrMe(O\text{-}t\text{-}Bu)(\eta^2\text{-}CMeN\text{-}t\text{-}Bu)$ (pz = 1-pyrazolyl)	1542	1.27	129	131	243.6	37
$Cp_3U(\eta^2\text{-}CMeN\text{-}c\text{-}C_6H_{11})$	1570	1.25	125	127		40
$Cp(CO)_2\{P(OMe)_3\}Mo(\eta^1\text{-}CMeNPh)$	1570	1.266	119.4	124.3	155.5	35
$PtI(PEt_3)_2(\eta^1\text{-}CMeN\text{-}p\text{-}C_6H_4Cl)$	1593, 1580	1.287	115.4	125.4		42

(py).[26] The C=N bond in 18 (1.24 Å) is shorter than in a number of comparable titanium, zirconium, hafnium, and tantalum complexes[22] but appreciably longer than the C=O bond in $Cp_2Zr(\eta^2\text{-}COMe)Me$ (1.21 Å; $\nu_{C=O}$ 1540 cm^{-1}).[27]

To our knowledge 18 is the first structurally characterized example of a complex containing an isocyanide ligand coordinated to a d^0 metal center. The *tert*-butyl isocyanide ligand maintains a near linear geometry. The C≡N distance (1.15 Å) is normal for coordinated isocyanide, in accord with the $\nu_{C\equiv N}$ frequency of 2190 cm^{-1}, 65 cm^{-1} higher than in the free ligand. A comparison of the bonding parameters in 18 with a selection of Ti(II), V(II, III), Nb(III), Mo(II), and W(II) complexes (Table III) shows the *t*-BuNC ligand to be remarkably unresponsive in geometry and IR frequency to changes in the d-electron count, oxidation state, and overall charge of the metal center. Substantial back-bonding and, as a consequence, a bent geometry of the isocyanide ligand is only observed in very electron-rich systems, for example, in $(Ph_3P)Ru(=C=N\text{-}t\text{-}Bu)_2(C\equiv N\text{-}t\text{-}Bu)_2$.[28]

The compound contains 1 mol of acetonitrile of crystallization. There are no close contacts. Figure 2 shows the molecular packing and the location of the solvent molecules.

Bonding Characteristics of the Iminoacyl Ligand. The C=N stretching frequency of the iminoacyl group in the IR spectrum of 18 is observed at 1740 cm^{-1}. It has been argued[35] that C=N frequencies below 1620 cm^{-1} are typical of η^1-coordination, while bands at higher wavenumbers indicate an η^2-bonding mode. However, there is now ample evidence for η^2-bonded iminoacyl ligands in Ti(III),[21] Ti(IV),[22,36] Zr(IV),[22,37] Ta(III),[38] Ta(V),[22,39] and U(III)[40] complexes, all of which give rise to $\nu_{C=N}$ IR bands below 1600 cm^{-1}; by contrast, η^1-bonded iminoacyl groups in nickel complexes may show bands as high as 1720 cm^{-1}.[41] On the basis of these data and by comparison with the small difference of 10 cm^{-1} in C=O frequencies between the cationic η^2-acyl complex 16 and its neutral analogue $Cp_2Ti(COMe)Cl$, the C=N vibration in 18 should be expected at ca. 1600–1620 cm^{-1}. A survey of the structural and spectroscopic data of iminoacyl complexes (Table IV) shows no satisfactory correlation between the C=N stretching frequency, the ^{13}C NMR resonance of the iminoacyl carbon, and the C=N bond length, although a low-field ^{13}C chemical shift of ca. 200–260 ppm is indicative of η^2-bonding. The position of the $\nu_{C=N}$ band is, however, sensitive to the hybridization of the iminoacyl C and N atoms, as measured by the R—N=C and R′—C=N angles. A widening of these angles beyond the 120° typical for sp^2 hybridization increases the sp character of the C=N bond and can be expected to result in a high-frequency shift of the C=N vibration. A substantial influence on

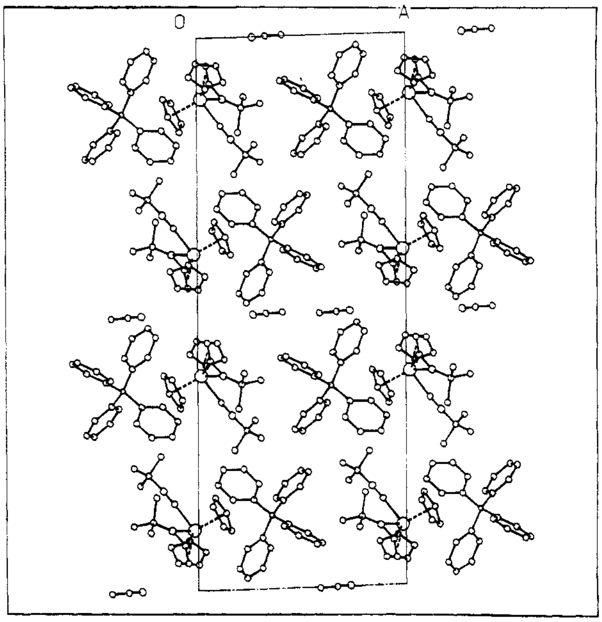

Figure 2. The crystal packing arrangement of 18, including the positions of the solvent molecules of crystallization.

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(36) The complexes $Cp_2Ti(\eta^2\text{-}ArNCAr')X$ (Ar = Ph, o-C_6H_4Me; Ar′ = 2,6-$Me_2C_6H_3$; X = I, SPh) are exceptions and show $\nu_{C=N}$ bands at 1655–1665 cm^{-1}.[21a]

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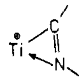
the C=N bond is, however, only noticeable for angles of 135° and larger.

In addition to such hybridization effects we believe that in the case of **18** the charge distribution in the complex may contribute to the strength of the C=N bond and the high IR frequency. Polar resonance structures are useful for describing the bonding in η^2-iminoacyl complexes. While in neutral complexes such formulations imply the (unfavorable) accumulation of negative charge on the metal,[22,40] this is not the case in the cationic compound **18**, and resonance structures such as B are likely to contribute significantly to the ground state of the complex, minimizing the positive charge concentrated on the metal center and strengthening the C=N bond by electrostatic attraction. There is no evidence for the participation of either an aminocarbenoid formulation (C) or a titanaazacyclopropenium structure (D).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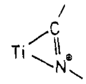
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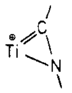
C


D

Conclusion. Although the 14-electron complex $[Cp_2TiR]^+$ has not yet been isolated, a range of stable complexes, $[Cp_2TiMe(L)]^+$, with donor ligands such as nitriles, isocyanides, and phosphines is readily accessible. The insertion of CO, isocyanides, and nitriles[14] into the titanium–alkyl bond is facile. Similar insertion chemistry with alkenes and alkynes, as postulated for the olefin polymerization with $Cp_2TiCl_2/AlClEt_2$ catalysts,[6] is precluded since the ligands L are not displaced by hydrocarbons. The $[Cp_2Ti{-}R]^+$ cation would be expected to exhibit features similar to the structurally and electronically related neutral complexes Cp_2MR of trivalent Sc, Y, and lanthanides, some of which are highly active alkene polymerization catalysts.[13b–d,43] However, it differs from these and from $[Cp_2ZrMe]^+$[9,11] in its low affinity for "hard" bases such as diethyl ether and THF and a higher tendency to form phosphine adducts; I.E., titanium appears to be a comparatively weaker Lewis acid and a "softer" metal center. Efforts to prepare $[Cp_2TiR]^+$ complexes free of neutral ligands L are continuing.

Experimental Section

General Procedures. All experiments were carried out under argon by using standard vacuum line (Schlenk) techniques. Solvents were distilled under nitrogen from sodium–benzophenone (diethyl ether, THF), sodium (toluene), or calcium hydride (dichloromethane, acetonitrile). NMR solvents (CD_2Cl_2, CD_3CN) were stored over activated 4A molecular sieves under nitrogen. Infrared spectra were recorded as CCl_4 mulls (in the region between 4000 and 800 cm^{-1}) or as Nujol mulls between KBr plates on Perkin-Elmer 297 and 684 spectrometers. NMR spectra were measured on JEOL PMX-60 (^1H NMR) and JEOL FX-100 (^{13}C NMR) instruments. Gases were analyzed by GC–MS using a Kratos MS 25 mass spectrometer connected to a 25-m OV-1 capillary gas chromatography column. Melting points were determined in sealed capillaries under argon and are uncorrected. *tert*-Butyl isocyanide,[44] $Cp_2TiMeCl$,[45] Cp_2TiMe_2,[45] $Cp_2Ti(CH_2SiMe_3)_2$,[46] and PhC_2SiMe_3[47] were made according to known procedures. $Ind_2TiMeCl$ was made as described for $Cp_2TiMeCl$; $MBPh_4$ salts (M = NH_4, Ag, Tl) were made by precipitation of the respective nitrates or acetates with BPh_4^- in aqueous solution. Other reagents were used as purchased.

$[Cp_2TiMe(NH_3)]PF_6$ (1). A solution of 2.0 g (9.6 mmol) of Cp_2TiMe_2 in 10 mL of THF was stirred in the dark with an equimolar quantity of NH_4PF_6 at room temperature for 3 h. The bright yellow solution changed to dark orange. Methane evolved and was collected in a gas burette (9.5 mmol) and analyzed by GC–MS. After the mixture was concentrated and cooled, 2.4 g of dark orange crystals was obtained from the solution (6.9 mmol, 72%): decomp pt 128–130 °C; IR (CCl_4 mull) 3370 (m), 3300 (w), 3210 (w) (NH_3), 3115 (w) (Cp), 3036 (m), 3000 (w), 2990 (w) (BPh_4^-), 2970 (w), 2895 (w) (CH_3), 1625 (s), 1585 (m), 1460 (s), 1180 (m), 1150 (m), 840 (vs), 740 (s), 710 (s), 600 (m), 560 (s) cm^{-1}. Anal. Calcd: C, 35.67; H, 4.32; N, 3.78. Found: C, 35.60; H, 4.30; N, 3.76.

$[Cp_2TiMe(NCMe)]BPh_4$ (2). A solution of 2.0 g (8.8 mmol) of $Cp_2TiMeCl$ in 20 mL of acetonitrile–dichloromethane (1:1) was treated with 3.0 g of $NaBPh_4$ at room temperature and the mixture stirred for 30 min. The color changed from red to dark brown. The solution was filtered, the residue washed with acetonitrile (2 × 3 mL), and the filtrate concentrated and cooled to obtain **2** as dark brown crystals which were collected and washed with a little THF: yield 3.5 g (6.3 mmol, 72%); decomp pt 143–145 °C; IR (CCl_4 mull): 3110 (w), 3060 (w), 3005 (w), 2995 (w), 2970 (w), 2920 (w), 2890 (w), 2310 (w), 2282 (m), 1585 (m), 1480 (s), 1432 (s), 1275 (m), 1188 (w), 1156 (w) cm^{-1}. Anal. Calcd: C, 80.3; H, 6.51; N, 2.53. Found: C, 80.0; H, 6.44; N, 2.64.

Other nitrile adducts were made similarly, using *n*-PrCN, PhCN, and *t*-BuCN instead of MeCN. The products were extracted with and recrystallized from dichloromethane.

$[Cp_2TiMe(NC\text{-}n\text{-}Pr)]BPh_4$ (3): yield 82%; mp 80 °C; IR (CCl_4 mull) 3120 (m), 3060 (s), 3005 (w), 2995 (m), 2990 (sh), 2920 (w), 2285 (s), 1585 (m), 1485 (s), 1448 (m), 1430 (s), 1270 (m), 1255 (m), 1150 (m), 1068 (m) cm^{-1}. Anal. Calcd: C, 80.5; H, 6.88; N, 2.41. Found: C, 79.7; H, 6.97; N, 2.42.

$[Cp_2TiMe(NCPh)]BPh_4$ (4): yield 78%; mp 98 °C; IR (CCl_4 mull) 3100 (w), 3040 (s), 2995 (s), 2260 (s), 1590 (w), 1577 (m), 1475 (s), 1425 (s), 1255 (m), 1183 (m), 1175 (w), 1150 (s) cm^{-1}. Anal. Calcd: C, 81.95; H, 6.18; N, 2.28. Found: C, 80.35; H, 6.34; N, 2.04.

$[Cp_2TiMe(NC\text{-}t\text{-}Bu)]BPh_4$ (5): yield 73%; mp 93 °C; IR 3122 (w), 3070 (m), 3050 (w), 2985 (m), 2270 (s), 1595 (w), 1583 (m), 1482 (s), 1433 (s), 1373 (m), 1240 (s), 1070 (w) cm^{-1}. Anal. Calcd: C, 80.7; H, 7.06; N, 2.35. Found: C, 79.9; H, 7.14; N, 1.93.

$[Cp_2TiMe(NC_5H_5)]BPh_4$ (6). This complex was obtained similarly from 2.0 g of $Cp_2TiMeCl$ (8.8 mmol), 3.0 g of $NaBPh_4$ (8.8 mmol), and a mixture of pyridine (5 mL) and dichloromethane (10 mL), as pale brown crystals: yield 3.7 g (6.7 mmol, 76%); mp 105 °C; IR (Nujol mull) 3110 (w), 3050 (w), 1605 (m), 1580 (m), 1490 (m), 1442 (m), 1265 (w), 1220 (w), 1010 (m), 835 (s) cm^{-1}. Anal. Calcd: C, 81.2; H, 6.43; N, 2.37. Found: C, 81.0; H, 6.52; N, 2.41.

$[Cp_2TiMe(PMe_3)]BPh_4$ (7). A solution of 2.0 g (8.8 mmol) of $Cp_2TiMeCl$ in 20 mL of THF was stirred with 3.0 g (8.8 mmol) of $NaBPh_4$ at room temperature. A small excess of trimethylphosphine (750 mg, 9.8 mmol) was added slowly. After ca. 10 min the red-brown crystals of the product began to appear. Crystallization was completed by cooling to −10 °C overnight: yield 4.06 g (6.2 mmol, 78%); decomp pt 140–142 °C; IR (Nujol mull) 3120 (w), 3100 (w), 3060 (m), 1580 (m), 1470 (vs), 1425 (s), 1292 (m), 1135 (m), 1028 (m), 1015 (s), 950 (vs), 850 (s), 830 (vs), 760 (m), 742 (m), 730 (m), 715 (m), 700 (m), 612 (m) cm^{-1}. Anal. Calcd: C, 77.5; H, 7.10. Found: C, 77.2; H, 6.75.

This standard procedure is applicable to the preparation of the phosphine complexes **8**, **9**, and **10** and the indenyl complexes **14** and **15**.

$[Cp_2TiMe(PMe_2Ph)]BPh_4$ (8): yield 4.06 g (6.2 mmol, 71%); decomp pt 138 °C; IR (CCl_4 mull) 3125 (w), 3100 (w), 3060 (m), 3005 (m), 2995 (w), 2940 (m), 1585 (m), 1485 (s), 1445 (s), 1435 (s), 1295 (m), 1190 (w), 1155 (m), 1120 (m), 950 (w), 937 (m), 915 (m) cm^{-1}. Anal. Calcd: C, 79.4; H, 6.77. Found: C, 79.3; H, 6.69.

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[Cp$_2$TiMe(PMePh$_2$)]BPh$_4$ (9): yield 4.34 g (6.25 mmol, 71%); mp 132 °C; IR (CCl$_4$ mull) 3140 (m), 3060 (m), 3040 (m), 3000 (m), 2932 (m), 1585 (m), 1485 (s), 1445 (s), 1432 (m), 1270 (m), 1150 (m), 1105 (m), 1030 (m), 897 (m), 850 (m) cm^{-1}. Anal. Calcd: C, 80.9; H, 6.49. Found: C, 79.9; H, 6.56.

[Cp$_2$TiMe(P-*n*-Bu$_3$)]BPh$_4$ (10): yield 4.4 g (6.16 mmol, 70%); mp 109 °C; IR (CCl$_4$ mull): 1305 (m), 1140 (sh), 845 (w) cm^{-1}. Anal. Calcd: C, 79.0; H, 8.40. Found: C, 78.8; H, 8.0.

[Ind$_2$TiMe(NCMe)]BPh$_4$ (11): yield 3.75 g (5.8 mmol, 66%); mp 113 °C; IR (CCl$_4$ mull) 3120 (w), 2310 (m), 2282 (w), 1450 (m), 1410 (w), 1350 (w), 1340 (m), 1220 (m), 830 (m), cm^{-1}. Anal. Calcd: C, 82.7; H, 6.12; N, 2.14. Found: C, 82.3; H, 6.25; N, 2.10.

[Ind$_2$TiMe(NCPh)]BPh$_4$ (12): yield 4.47 g (6.24 mmol, 71%); mp 92 °C; IR (CCl$_4$ mull) 3120 (w), 2260 (m), 1480 (m), 1450 (m), 1430 (w), 1380 (m), 1350 (w), 1260 (m), 1220 (w), 825 (s) cm^{-1}. Anal. Calcd: C, 83.9; H, 5.87; N, 1.96. Found: C, 83.3; H, 5.66; N, 1.89.

[Ind$_2$TiMe(NC-*t*-Bu)]BPh$_4$ (13): yield 4.3 g (6.15 mmol, 70%); mp 85 °C; IR (Nujol mull) 3120 (w), 3100 (w), 3060 (m), 2275 (m), 1583 (m), 1430 (m), 1355 (m), 1345 (m), 1155 (m), 1032 (m), 840 (s), 745 (vs), 735 (sh), 710 (vs), 630 (w), 608 (m) cm^{-1}. Anal. Calcd: C, 82.9; H, 6.62; N, 2.01. Found: C, 82.6; H, 6.65; N, 2.00.

[Ind$_2$TiMe(PMe$_3$)]BPh$_4$ (14): yield 4.07 g (6 mmol, 68%); decomp pt 144–146 °C; IR (CCl$_4$ mull) 2920 (m), 1300 (m), 950 (w), 850 (w) cm^{-1}. Anal. Calcd: C, 80.2; H, 6.7. Found: C, 79.8; H, 6.8.

[Ind$_2$TiMe(PMe$_2$Ph)]BPh$_4$ (15): yield 4.49 g (6.2 mmol, 70%); mp 108 °C; IR (CCl$_4$ mull) 2920 (m), 1295 (m), 950 (w) cm^{-1}. Anal. Calcd: C, 81.6; H, 6.40. Found: C, 81.4; H, 6.38.

[Cp$_2$Ti(η^2-COMe)(NCMe)]BPh$_4$ (16): A solution of 1.0 g (1.7 mmol) of 2 in 15 mL of acetonitrile was treated at room temperature with a slow stream of carbon monoxide for 30 min. The dark brown solution became paler, and after removal of the solvent in vacuo, the residue was extracted with 2 × 10 mL of dichloromethane. The filtrate was concentrated and cooled to −10 °C to give **16** as pale brown crystals: yield 650 mg (1.1 mmol, 65%); mp 100 °C; IR (CCl$_4$ mull) 3110 (w), 3060 (m), 3045 (m), 3005 (w), 2995 (w), 2920 (w), 2315 (w), 2290 (m), 1630 (s), 1595 (w), 1580 (w), 1482 (s), 1430 (s), 1138 (m), 1275 (m), 1245 (m), 1123 (s) cm^{-1}. Anal. Calcd: C, 78.5; H, 6.19; N, 2.41. Found: C, 78.4; H, 6.45; N, 2.24.

[Cp$_2$Ti(COMe)(PMe$_2$Ph)]BPh$_4$ (17). The complex was obtained by reacting 2.0 g (3.4 mmol) of **16** with a small excess of PMe$_2$Ph in CH$_2$Cl$_2$: yield 1.8 g (2.7 mmol, 80%); decomp pt 150 °C; IR (CCl$_4$ mull) 3220 (w), 3060 (m), 2995 (m), 2920 (w), 1610 (m), 1585 (m), 1485 (m), 1440 (m), 1430 (m), 1120 (s), 935 (m), 910 (m) cm^{-1}. Anal. Calcd: C, 77.9; H, 6.49. Found: C, 77.2; H, 6.43.

[Cp$_2$Ti{η^2-C(Me)N-*t*-Bu}(CN-*t*-Bu)]BPh$_4$·MeCN (18). Compound **2** (2.0 g, 3.4 mmol) was dissolved at room temperature in 15 mL of acetonitrile and stirred while 0.3 g (6.8 mmol) of *tert*-butyl isocyanide was added. The color changed quickly from dark brown to pale yellow. The solution was concentrated, and ca. 5 mL of diethyl ether was added to the point of precipitation. Any precipitate was redissolved by warming, and the mixture was then cooled to allow crystallization. The product **18** was obtained as pale yellow air-stable prisms: yield 2.13 g (2.96 mmol, 87%); decomp pt 139–141 °C; IR (Nujol mull) 3110 (w), 3060 (m), 2290 (w), 2245 (w), 2190 (s), 1740 (s), 1585 (w), 1480 (m), 1430 (m), 1370 (m), 840 (m), 820 (s), 740 (s), 710 (s), 625 (w), 615 (w), 605 (m) cm^{-1}. Anal. Calcd: C, 78.4; H, 7.51; N, 5.84. Found: C, 78.4; H, 7.68; N, 5.87.

[Cp$_2$Ti{η^2-C(N-*t*-Bu)Me}(CN-*t*-Bu)]BPh$_4$ (19) was obtained from complex **3** and *t*-BuNC in THF: yield 2.20 g (90%); decomp pt 164–166 °C. IR (CCl$_4$ mull) 3120 (w), 2190 (vs), 1745 (s), 1586 (s), 1485 (s), 1460 (s), 1430 (s), 1375 (s), 1243 (m), 1190 (s), 1133 (m), 1070 (m) cm^{-1}. Anal. Calcd: C, 79.6; H, 7.52; N, 4.13. Found: C, 79.4; H, 7.53; N, 4.10.

X-ray Structure Determination of 18. The crystals grown from acetonitrile–diethyl ether are obtained as pale yellow prisms. The specimen used for the X-ray work had the dimensions 0.2 × 0.3 × 0.5 mm. The orientation matrix and cell dimensions were obtained by using standard SEARCH and INDEX routines on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and refined by using setting angles for 25 well-spaced reflections with $12 \leqslant \theta \leqslant 14°$. The crystal system was found to be monoclinic with space group P2$_1$/*c* and cell dimensions *a* = 13.212 (10) Å, *b* = 9.354 (2) Å, *c* = 33.95 (4) Å, β = 91.87 (4)°, *V* = 4193.3 Å^3, *Z* = 4, D_{calcd} = 1.14 g cm^{-3}, μ(Mo Kα) = 1.91 cm^{-1}, *F*(000) = 1536, and *T* = 291 K.

Table V. Fractional Atomic Coordinates (×10^4) for [Cp$_2$Ti(CN-*t*-Bu){C(Me)N-*t*-Bu}]BPh$_4$•MeCN

	x	*y*	*z*
Ti(1)	172 (1)	5112 (1)	1102 (1)
C(1)	615 (3)	3233 (4)	828 (1)
C(2)	460 (4)	2171 (5)	502 (1)
N(3)	1231 (2)	3402 (3)	1108 (1)
C(4)	2133 (3)	2614 (4)	1270 (1)
C(5)	2246 (4)	1164 (5)	1078 (2)
C(6)	1969 (4)	2430 (5)	1712 (1)
C(7)	3050 (3)	3550 (5)	1203 (2)
C(8)	1125 (3)	5922 (4)	1593 (1)
N(9)	1649 (3)	6436 (4)	1830 (1)
C(10)	2359 (4)	7098 (5)	2114 (1)
C(11)	3050 (6)	6081 (7)	2254 (3)
C(12)	2758 (7)	8323 (8)	1936 (2)
C(13)	1774 (5)	7540 (11)	2460 (2)
C(14)	−727 (4)	3556 (5)	1526 (2)
C(15)	−834 (4)	4936 (6)	1678 (1)
C(16)	−1364 (4)	5739 (6)	1398 (2)
C(17)	−1606 (4)	4868 (6)	1077 (2)
C(18)	−1210 (4)	3514 (6)	1156 (2)
C(19)	953 (8)	5861 (7)	509 (2)
C(20)	1291 (5)	6802 (11)	807 (3)
C(21)	412 (10)	7526 (6)	917 (2)
C(22)	−359 (6)	7038 (10)	698 (3)
C(23)	−45 (7)	6061 (9)	465 (2)
B(1)	−3565 (3)	10005 (5)	1336 (1)
C(30)	−4365 (3)	8788 (4)	1168 (1)
C(31)	−5295 (3)	9206 (5)	994 (1)
C(32)	−5965 (4)	8249 (6)	807 (1)
C(33)	−5724 (4)	6830 (6)	788 (2)
C(34)	−4826 (5)	6372 (5)	957 (2)
C(35)	−4156 (4)	7329 (5)	1142 (2)
C(40)	−2685 (3)	9325 (4)	1630 (1)
C(41)	−1678 (4)	9763 (5)	1639 (2)
C(42)	−957 (4)	9245 (6)	1913 (2)
C(43)	−1223 (4)	8255 (6)	2188 (2)
C(44)	−2202 (4)	7798 (5)	2192 (1)
C(45)	−2920 (4)	8326 (5)	1923 (1)
C(50)	−4117 (3)	11202 (4)	1608 (1)
C(51)	−4913 (3)	10846 (5)	1849 (1)
C(52)	−5322 (4)	11794 (7)	2116 (2)
C(53)	−4966 (5)	13154 (7)	2142 (2)
C(54)	−4187 (5)	13562 (5)	1912 (2)
C(55)	−3764 (4)	12600 (5)	1650 (1)
C(60)	−3106 (3)	10671 (5)	931 (1)
C(61)	−2362 (4)	9954 (6)	729 (1)
C(62)	−1994 (5)	10396 (8)	374 (2)
C(63)	−2360 (6)	11602 (9)	203 (2)
C(64)	−3114 (5)	12360 (7)	378 (2)
C(65)	−3484 (4)	11886 (5)	740 (1)
N(100)	2676 (5)	3584 (7)	11 (2)
C(101)	3312 (5)	2776 (7)	−5 (2)
C(102)	4115 (4)	1712 (7)	−20 (2)

Intensity data were recorded by using an $\omega/2\theta$ scan technique with $1.0 \leqslant \theta \leqslant 24.0°$, $\pm h,+k,+l$, ω scan width (ω = 0.70 + 0.35 tan θ), and variable scan speed (1.56 − 5.09 deg min^{-1}) to achieve $I \geqslant 33\sigma(I)$ subject to $t_{\max}$ = 60 s. A total of 6304 data were measured, of which 5760 were unique and 4346 observed [$I > 1.5\sigma(I)$]. The data were corrected for absorption empirically; relative maximum and minimum transmission factors were 1.0 and 0.982, respectively. The structure was solved via the application of direct methods (SHELXS 86),[48] the first *E* map giving the positions of all nonhydrogen atoms. Refinement was by blocked full-matrix least squares, with the atoms of the cation forming one block and those of the anion and the solvent molecule the other. All non-hydrogen atoms were assigned anisotropic displacement factor coefficients; hydrogen atoms were included

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(48) SHELXS86, G. M. Sheldrick, University of Göttingen, FRG, 1986.

in idealized postions with group isotropic dfc's. The final R and R_w values were 0.064 and 0.059, respectively, with 386 parameters and weights $= 1/[\sigma^2(F_o) + 0.0005F_o^2]$. The maximum and minimum values on the final difference electron density map were +0.6 and −0.4 e Å^{-3}, respectively. The non-hydrogen atom coordinates are listed in Table V.

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Registry No. **1**, 109630-83-3; **2**, 109630-95-7; **3**, 110613-17-7; **4**, 109631-03-0; **5**, 109631-01-8; **6**, 109631-07-4; **7**, 109631-05-2; **8**, 110589-64-5; **9**, 110589-66-7; **10**, 110589-68-9; **11**, 110589-70-3; **12**, 109631-37-0; **13**, 109631-09-6; **14**, 110589-72-5; **15**, 110589-74-7; **16**, 109630-97-9; **17**, 110589-76-9; **18**, 110589-79-2; $[Cp_2Ti\{\eta^2\text{-}C(Me)N\text{-}t\text{-}Bu\}(CN\text{-}t\text{-}Bu)]BPh_4$, 110589-78-1; Cp_2TiMe_2, 1271-66-5; $Cp_2TiMeCl$, 1278-83-7; $Ind_2TiMeCl$, 109630-87-7; $[Cp_2TiMe(NH_3)]ClO_4$, 109630-84-4; Cp_2TiCl_2, 1271-19-8; t-BuNC, 7188-38-7; carbon monoxide, 630-08-0.

Supplementary Material Available: Tables of fractional coordinates of hydrogen atoms, U_{ij} values for non-hydrogen atoms, bond lengths and angles (4 pages); lists of F_o/F_c values (26 pages). Ordering information is given on any current masthead page.

Michael-Type Addition Reactions of Bis(μ-phenylphosphido)bis(tricarbonyliron) with Olefinic α,β-Unsaturated Carbonyl Compounds. Construction of Chelating Bis(phosphido) Ligands

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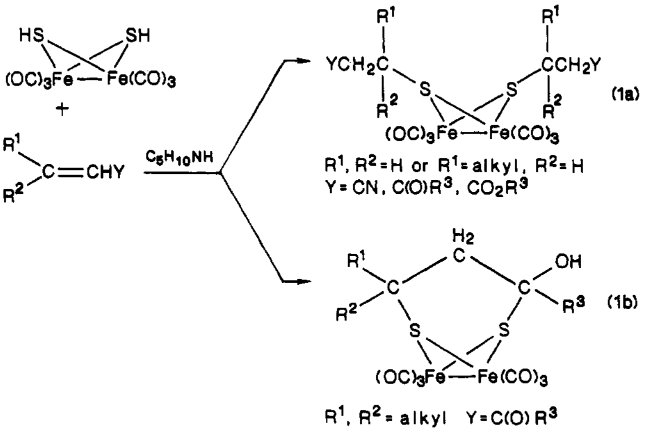
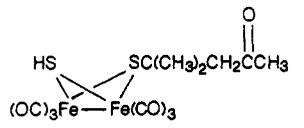
The piperidine-catalyzed addition of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ to olefinic α,β-unsaturated esters and ketones has been studied. With esters, 1:1 and 2:1 adducts were obtained. With terminally unsubstituted or monosubstituted ketones, two types of products were obtained in 1:1 reactions: the simple 1:1 addition product of a PH unit to the C═C bond and a bridged product in which one PH unit had added to the C═C bond and the other to the C═O bond of the α,β-unsaturated ketone. In the case of mesityl oxide, a terminally disubstituted α,β-unsaturated ketone, only the product of PH addition to the C═C bond was formed.

Introduction

In earlier studies, we investigated base-catalyzed addition of the SH units of $(\mu\text{-HS})_2Fe_2(CO)_6$ to α,β-unsaturated carbonyl compounds and nitriles.[1] In the case of olefinic α,β-unsaturated substrates, two types of behavior were encountered: independent addition of the two SH units to two molecules of the α,β-unsaturated compound (eq 1a) and addition of both SH units to one molecule of the olefin, one SH to the C═C bond and the other to the C═O bond (eq 1b). The reactions encompassed by eq 1a are an organometallic version of the Michael addition reaction. In eq 1b we have those cases where steric hindrance must be operative. The initial 1:1 adduct (e.g., 1 in the case of mesityl oxide) is too hindered to permit attack on a second $(CH_3)_2C{=}CHC(O)CH_3$ molecule. (Most likely, both isomers in which the $SC(CH_3)_2CH_2C(O)CH_3$ group is axial or equatorial are present.[1] As a consequence, the second SH adds to the C═O bond of the newly introduced organic group, giving a chelating 1,3-propanedithiolato unit, which contains an alcohol function. Similar base-catalyzed addition reactions of $(\mu\text{-HS})_2Fe_2(CO)_6$ to acetylenic α,β-unsaturated carbonyl compounds were observed. In parallel studies we have been investigating the chemistry of a phosphorus analogue of $(\mu\text{-HS})_2Fe_2(CO)_6$ and its derived dianion, $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$, the bridging phosphido complexes 2 and 3[2] and it was of interest to see if the base-catalyzed additions of 2 to α,β-unsaturated substrates would proceed similarly to such reactions of $(\mu\text{-HS})_2Fe_2(CO)_6$. In the present paper we report our results of





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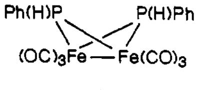

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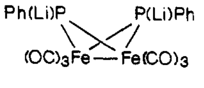

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[1] (1) Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* **1986**, *5*, 1568.

[2] (2) (a) Seyferth, D.; Wood, T. G.; Henderson, R. S. *J. Organomet. Chem.*, in press. (b) Seyferth, D.; Henderson, R. S.; Wood, T. G. *Red. J. R. Neth. Chem. Soc.*, in press.

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