it does not react with amines. This latter result makes it a particularly good drying agent for amines.
(55) This has been confirmed by mass spectrographic analyses. If only D_2 was produced in the reaction, it would be expected to undergo rapid H–D exchange with any unreacted starting material (ref 17).
(56) The formulation of the complexes through a definite Ti–N linkage is based on the amount of H_2 evolved. Since the IR spectrum of monodentate ureylene complexes has not been reported, we can only suggest that the shifts in the N–H and CO frequencies which we observe are consistent with the proposed formulation.
(57) A. N. Nesmeyanov, O. V. Nogina, and V. A. Dubovitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 527 (1968); J. A. J. Jarvis, B. E. Job, B. T. Kilbown, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Commun.*, 1149 (1967).
(58) R. J. Doedens, *Inorg. Chem.*, **11**, 2323 (1968); M. Dekker and G. Knox, *Chem. Commun.*, 1243 (1967).
(59) G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 33 (1963); G. W. A. Fowles, T. E. Lester, and R. A. Walton, *J. Chem. Soc. A*, 1081 (1968).
(60) W. C. Schumb and R. F. Sundström, *J. Am. Chem. Soc.*, **55**, 596 (1933); F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972.
(61) W. H. Knoth, *J. Am. Chem. Soc.*, **90**, 7172 (1968).
(62) R. T. Cowdell, G. W. A. Fowles, and R. A. Walton, *J. Less-Common Met.*, **5**, 386 (1963).
(63) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 980 (1969).
(64) M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, 874 (1971); G. Lucazean, L. Guemas, and A. Novak, *Inorg. Chim. Acta*, **20**, 11 (1976).
(65) P. S. Skell and J. E. Girard, *J. Am. Chem. Soc.*, **94**, 5518 (1972).
(66) D. O. Hayward and B. M. W. Trapnell, "Chemisorption", 2nd ed, Butterworths, London, 1964, p 247; M. Whaba and C. Kemball, *Trans. Faraday Soc.*, **49**, 1351 (1963).
(67) C. L. Thomas, "Catalytic Processes and Proven Catalysts", Academic Press, New York, N.Y., 1970, pp 52–53, 146–151.
(68) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 3911 (1971); J. I. Brauman and L. K. Blair, *ibid.*, **92**, 5986 (1970). Based on discussions with Professor Brauman, Stanford University, we would estimate that the acidities of NH_3 and primary and secondary amines in solution should be comparable and perhaps even in the reverse order observed for the corresponding gas-phase acidities.
(69) S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98**, 5850 (1976).
(70) M. J. Bennett and K. A. Simpson, *J. Am. Chem. Soc.*, **93**, 7156 (1971).
(71) M. Elder, *Inorg. Chem.*, **9**, 762 (1970).
(72) J. K. Hoyano, M. Elder, and W. G. Graham, *J. Am. Chem. Soc.*, **91**, 4568 (1969).
(73) Vacuum Atmospheres Corp., North Hollywood, Calif. 91605.
(74) Hoke Inc., Cresskill, N.J., 1-L spun-steel cylinders may be purchased from this company.
(75) All microanalyses were performed by Rita Hogan or Jane Heins, Allied Chemical Corp., Chemical Physics Department.
(76) W. P. Griffith, *Coord. Chem. Rev.*, **8**, 369 (1972); L. P. Morganthaler and R. P. Menichelli, *Anal. Chem.*, **37**, 570 (1965). Titanium nitrides are extremely stable compounds.
(77) M. L. H. Green and C. R. Lucas, *J. Chem. Soc., Dalton Trans.*, 1000 (1972).
(78) See supplementary data.

Contribution from the Chemical Research Center, Allied Chemical Corporation,
Morristown, New Jersey 07060

Reactions of an Imidohydridobis(dicyclopentadienyltitanium) with N_2, CO, and CO_2 and Olefins[1]

JOHN N. ARMOR

Received June 16, 1977

The chemical reactivity of the new, red, crystalline complex isolated from the reaction of NH_3 with $(C_5H_5)Ti(C_5H_4)Ti(C_5H_5)_2$ (I) has been investigated. The original interest in I was in its demonstrated ability to activate molecular nitrogen; however, compound I is so reactive that it readily reacts with many of the very same organonitrogen products which we sought to synthesize. Surprisingly, the product of the NH_3 reaction above, $[TiCp_2NH]_2H$ (II), is itself quite reactive. Carbon monoxide or CO_2 react with compound II to yield an isocyanate or carbamate complex, respectively. Despite the formal oxidation of I by NH_3, the product II is still capable of coordinating N_2. This latter N_2 complex can also be reduced further by potassium naphthalene to NH_3 (after addition of HCl). Further, compound II is an effective, low-pressure, homogeneous catalyst for the hydrogenation of olefins.

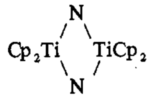
Introduction

Over the last few years, experiments have been conducted in these laboratories to determine if it might be possible to catalytically generate organonitrogen compounds (especially primary amines) directly from dinitrogen (or alternatively from NH_3). Extensive studies have been focused on the preparation and properties of a new, low-valent, coordinatively unsaturated titanium[2,3] metallocene, $(C_5H_5)_2\overline{TiC_5H_4}Ti(C_5H_5)$ (I). One feature of this complex[4] is its unusual η^1:η^5-bonded C_5H_4 group; another is its high reactivity toward small, unsaturated molecules such as N_2. Treatment of I with N_2 in the presence of potassium naphthalene followed by acid hydrolysis results in the transformation of most of the N_2 to NH_3. However, compound I is so reactive that it readily reacts with many of the very same organonitrogen products which we sought to synthesize. For example, compound I readily reacts with ammonia[5,6] and aliphatic and aromatic amines as well as ureas[7,8] to yield H_2. In the case of ammonia, the stoichiometry is

$$\underset{\text{I}}{Cp_2TiC_5H_4TiCp} + 2.0NH_3 \rightarrow \underset{\text{II}}{(Cp_2TiNH)_2H} + H_2 \qquad (1)$$

$$Cp = \eta\text{-}C_5H_5$$

While the precise location of the H atoms in II is based upon indirect arguments, the framework structure



incorporating a planar array of the titanium and nitrogen atoms, has been defined by x-ray crystallography.[5] We now report that II, prepared by the spontaneous reaction of I with NH_3, is still capable of coordinating N_2. Surprisingly, we also find that II is an olefin hydrogenation catalyst which is still active in the presence of free NH_3 or $C_2H_5NH_2$. Further, the reactivity of II with CO and CO_2 is described.

Results and Discussion

Reaction with Dinitrogen. Pressurizing a toluene solution of II with 150 psi of N_2 results in an immediate deepening in the color of the red solution. Evaporation of the solvent to dryness at 0 °C followed by washing with *n*-octane leaves a dark red solid, III, which analyzes for 10.3% N (~3 N/Ti). (The parent compound (II) contains 7.3% N, using the same Dumas method). The product slowly loses N_2 while stored in the cold or with exhaustive pumping. Attempts to determine the actual amount of coordinated N_2 using HCl, ICl, or KIO_3 to oxidize the complex resulted in an incomplete accounting of the total nitrogen originally present (probably due to the formation of stable titanium nitrides). Debye–Scherrer x-ray powder photographs (Vanadium-filtered Cr radiation) of this

0020-1669/78/1317-0213$01.00/0

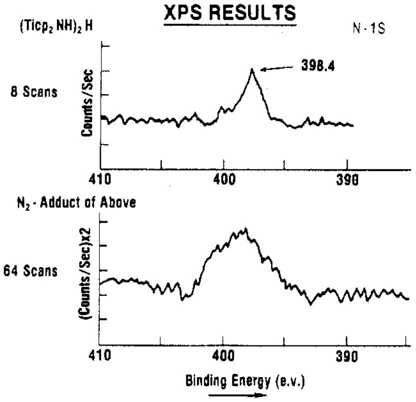


Figure 1. X-ray photoelectron spectra of $(TiCp_2NH)_2H$ and the corresponding N_2 complex.

N_2 adduct indicated that only four major lines[5] of the parent compound, II, remain. Additional lines were not observed due to disorder in the material.

The x-ray photoelectron spectrum (XPS) of II and III are illustrated in Figure 1. For the parent imide compound, II, a single band (width at half-height = 2.2 eV) is observed at 398.0 eV corresponding to the N 1s transition.[9] However, the N_2 adduct (recorded immediately after pumping the reaction chamber to 10^{-7} Torr) displays a much broader band centered at 398 eV with a bandwidth of 5.5 eV (at half-peak height). The intensity of the 398-eV band for III corresponds to more nitrogen[10] than is present in the parent imide complex. These XPS measurements support the presence of a different form(s) of nitrogen in III than is present in II.

It is possible to stoichiometrically reduce N_2 over solutions of II with potassium naphthalene (KNp). This was established by pressurizing a diethyl ether solution of II to 110 psi of N_2. The excess N_2 was removed, and KNp was added at −80 °C in vacuo. Hydrolysis of the product with HCl and Kjeldahl distillation of the ammonia gave NH_4Cl[11] (confirmed via mass spectrometry). Analysis of the total ammoniacal nitrogen in the hydrolyzed product shows ~2 mol of ammonia/mol sample of II treated in the above manner. In the absence of N_2, the same procedure only yields ~0.8 mol of NH_3/mol of II.[12] Use of $^{30}N_2$ in place of $^{28}N_2$ in the above procedure leads to substantial amounts of $^{15}NH_4Cl$ which was detected by mass spectroscopy. While some ammonia is expected from the parent compound, the appearance of $^{15}NH_3$ (when the only source of ^{15}N was $^{30}N_2$) provides a strong argument for the complexation of N_2 by II.

It is apparent that the combined experimental results (total N analysis, x-ray powder pattern, $^{30}N_2$ reduction by KNp, and the XPS results) suggest that N_2 is complexed by compound II and that this coordinated N_2 is sufficiently activated for reduction of KNp. There may be several different types of N_2 complexes that are formed; however, the N_2 seems to be more weakly coordinated to the titanium in this case than for the corresponding N_2 complexes of compound I. This latter result may arise from the higher formal oxidation state of the metal due to reaction of I with NH_3.

Hydrogenation of Olefins. Compound I is an active homogeneous catalyst[4] for the hydrogenation of olefins. Further studies have revealed that the hydrogenation of olefins proceeds even in the presence of ammonia and compound I. Since NH_3 (and organic amines) readily reacts with $Cp_2TiC_5H_4TiCp$ to yield the "imide" complex,[1] $(TiCp_2NH)_2H$ (II), the latter compound was also tested as a catalyst for the reduction of C_2H_4 and C_6H_{10} by H_2. Compound II (0.23 mmol) was dissolved in ~5 mL of toluene (contained in a heavy-wall, glass pressure tube) and pressurized to 136 psi with a 1:1 mixture of C_2H_4 and H_2. The generation of C_2H_6 was complete in less than 20 h at room temperature. Even in the presence of 1% NH_3 (in C_2H_4/H_2 mixtures) or 1–3% $EtNH_2$, the catalytic hydrogenation of C_2H_4 to C_2H_6 proceeded, although not as rapidly. In addition, compound II effected the catalytic hydrogenation of C_2H_4 in the absence of any solvent (P_0 = 150 psi of 1:1 C_2H_4:H_2 at room temperature). Further, cyclohexene (~8 mL) was catalytically hydrogenated by H_2 (at 116 psi, room temperature) to cyclohexane (>150 turnovers in 6 h), and the catalyst continued to be effective for several days. Preliminary kinetic data for the hydrogenation of cyclohexene by H_2 (P_0 ~ 700 Torr, 20 °C) revealed a pseudo-first-order rate behavior for the drop in pressure of hydrogen above the cyclohexene solution ($k = 2.8 \times 10^{-4}\ s^{-1}$ at 5.5×10^{-3} M $(TiCp_2NH)_2H$ in neat cyclohexene).

In retrospect, the ability of II to function as a hydrogenation catalyst is not too surprising in view of its hydridic behavior.[5] However, the close similarity in the rates of hydrogenation to that observed for the parent compound, I, is quite startling.[4] It was expected that the addition of NH_3 to I and the resulting evolution of H_2 (corresponding to a formal oxidation of the titanium centers) would result in a greatly diminished activity of the imide product, II, as an olefin hydrogenation catalyst. Perhaps, part of the reason that II is such an active hydrogenation catalyst is its ability to exist as a monomer[5] in solution, and, as such, it is coordinatively unsaturated.

The homogeneous, mild hydrogenation of olefins by H_2 in the presence of amines is significant since amines react degradatively with I to yield H_2. In addition, amines sometimes act as poisons for olefin hydrogenation catalysts[13] or force investigators to use more extreme temperatures and pressures. The present industrial hydrogenation of some olefins requires pretreatment of the olefin stream (with hydrodesulfurization catalysts)[14] to remove amines and mercaptans.

Reaction with Olefins. Addition of 1-hexene to $(TiCp_2NH)_2H$ in the absence of H_2 does not generate any significant amounts of hexane or isomerized hexenes over a period of 3 days at 40 °C. Further, while compound I has been reported[3] to catalyze the generation of butadiene and ethane from C_2H_4, compound II only assists in this reaction to produce a few percent of butadiene and ethane under the optimum conditions used for compound I. Therefore, the addition of ammonia to I results in a compound which does not promote the isomerization or dimerization of olefins, although this new compound, II (in the presence of H_2), is capable of hydrogenating olefins with rates comparable to those observed for the parent compound, I.

Reaction with Water and Amines. The addition of an excess of water (based on Ti) to II leads to an immediate and vigorous evolution of gas with the production of a blue-gray solution after 24 h. The gas corresponds to H_2 (~1.5 mol of H_2 per mol of Ti_2). Pressurizing a toluene solution of II with a large excess of NH_3 (at 110 psi) yields a product which displays several bands in the IR spectrum above 3200 cm^{-1} indicative of N–H vibrations (Dumas N analysis indicates ~3 N/Ti_2). This product probably corresponds to a solvated or coordinated ammonia complex of II. In a similar manner, compound II (in toluene) also seems to consume some $C_2H_5NH_2$ (in the presence of a large excess of the amine) without the evolution of H_2. Thus, the addition of NH_3 to I does not inhibit its ability to reduce H_2O to H_2, but it does inhibit the further dehydrogenation of organic amines as observed for compound I.[7] Again, it appears that the addition of NH_3 to I moderates its activity, but very selectively. These results suggest an interesting, although specialized use for II, namely, its use as an effective, exhaustive drying agent for laboratory preparation of extremely dry organic amines. We have since used compound II very effectively in this way. Even the amount of water originally present in the amine can be determined by measuring the amount of H_2 evolved.

Ammination of Olefins. The ability of compound II to function as an effective hydrogenation catalyst even in the presence of amines suggested that compounds I or II might be effective catalysts for the preparation of organonitrogen compounds from NH_3. The efficient, catalytic ammination of olefins selectively to primary amines has not been achieved, although the reaction is exoergic:

$$NH_3 + C_2H_4 \rightarrow C_2H_5NH_2 \quad \Delta G^\circ = -2.3 \text{ kcal/mol, } 25\ ^\circ\text{C} \tag{2}$$

While mixtures of amines have been observed under extreme reaction[15] conditions (using NH_3 as the starting material), no low-pressure, homogeneous catalysts have been developed for the specific amination of olefins by ammonia to primary amines. The stoichiometric addition of NH_3 to C_2H_4 has been observed using a platinum catalyst,[16] and a variety of reactions of olefins with secondary amines have been observed.[17]

Using a variety of C_2H_4 and NH_3 mixtures (2:1 to 1:2.5) at a total of ~150 psi over toluene solutions of I or II (20–95 °C), the catalytic consumption of C_2H_4 was not observed. Even using pressures of C_2H_4 as high as 2000 psi with the addition of a few milliliters of liquid ammonia did not enhance the reaction. The addition of hydrogen to the olefin and ammonia gas mixtures did not promote reaction 2. The IR spectrum of the titanium products obtained by evaporating the solution to dryness invariably displayed several bands above 3200 cm^{-1}. The GLC of the volatiles as well as the solvent from the reaction revealed a mixture of small amounts of $C_2H_5NH_2$, $(C_2H_5)_2NH$, and $(C_2H_5)_3N$. Addition of HCl followed by treatment with LiOMe in dioxane yielded only traces of $(C_2H_5)_2NH$ and $(C_2H_5)_3N$. The $(C_2H_5)_2NH$ was also confirmed by GLC/mass spectroscopy. However, the absence of any significant pressure drop during the reaction and the quantitative GLC results indicate that the yields of organic amines from the ethylene and ammonia are less than stoichiometric.

The assisted amination of ethylene by ammonia using compound I is probably regulated by the initial attack of NH_3 upon the titanium center. One can envision an oxidative addition of NH_3 upon the titanium center in compound I to yield an amide, hydride of titanium. Ideally, this hydride would reduce the olefin followed by the transfer of the alkyl function to the amide ligand to yield the organic amine. Unfortunately, we know that the first step is accompanied by the evolution of H_2, and this reaction probably prevents the reaction from being catalytic. The initial attempts at minimizing the loss of H_2 by adding H_2 to the reactants were complicated by the resulting hydrogenation of the olefin. Therefore, it is apparent that the addition of ammonia does markedly affect the catalytic activity of I. That is, while the reactivity of NH_3 with I is unique, the further elimination of H_2 (perhaps via reaction with another ammonia molecule) seems to inactivate the catalyst toward the catalytic amination of olefins.

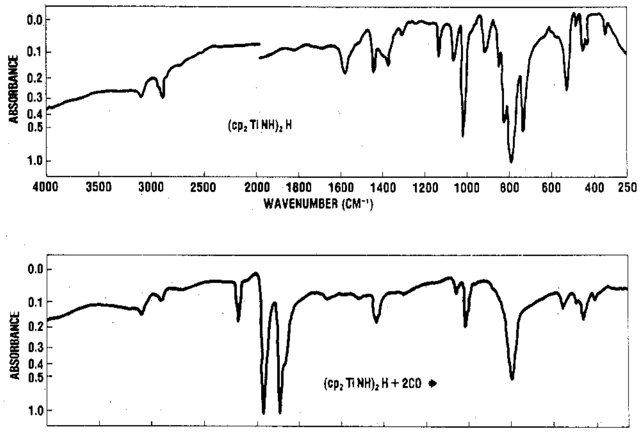


Figure 2. Comparison of IR spectra of $(TiCp_2NH)_2H$ and the same material treated with CO. The spectra have been corrected for solvent absorptions.

Reaction with CO. Toluene, THF, or diglyme solutions of II react readily with even traces of CO to generate a new product(s), IV. The IR spectrum of IV displays a new band at 2195 cm^{-1}, as well as numerous Ti–CO vibrations at 1975–1800 cm^{-1} (Figure 2). The main carbonyl vibrations are located exactly where $TiCp_2(CO)_2$ absorbs,[18] and the latter compound can be obtained from IV by sublimation at 80 °C (10^{-3} Torr).[19,20] The residue from the sublimation contains only traces of a titanium carbonyl complex while most of the 2195-cm^{-1} (2198 cm^{-1} in KBr) band remains. Treating $(TiCp_2{}^{15}NH)_2H$ with CO results in a shift of the 2195-cm^{-1} band to 2182 ± 1 cm^{-1}. With ^{13}CO and $(TiCp_2NH)_2H$, a shoulder appears at 2152 cm^{-1} on a main band at 2124 cm^{-1}. The relative magnitudes of the shifts[21] in the band originally at 2195 cm^{-1} upon ^{15}N or ^{13}CO substitution are consistent with an isocyanate complex ($TiCp_2(NCO)_2$ at 2220, 2170 cm^{-1}; $TiCp_2NCO$ at 2175 cm^{-1}).[22,23] Upon exposure of IV to air, the isocyanate band is shifted to 2196 cm^{-1} (shoulder at 2209 cm^{-1}) while the carbonyl vibrations are considerably reduced in intensity. Attempts to react the isocyanate product with amines (to yield ureas)[24] or with CH_3I (to yield CH_3NCO) were unsuccessful. The stoichiometry of the reaction is

$$(TiCp_2NH)_2H + 2.0CO \rightarrow IV + 0.25H_2 \tag{3}$$

$$IV + HCl \rightarrow 1H_2 + 1.6CO + 0.1CO_2 \tag{4}$$

$$IV + CH_3I \rightarrow 0.3CH_4 + 1.0CO \tag{5}$$

[Separate experiments using crystalline $TiCp_2(CO)_2$ dissolved in toluene and treated with excess, anhydrous HCl yielded 1.7 CO/Ti and 0.8 H_2/Ti and little or no CO_2. Treatment of $TiCp_2(CO)_2$ with CH_3I yields 0.95 CO/Ti and an acyl complex.[25]] The product, IV, behaves very similarly to a sample of $TiCp_2(CO)_2$. However, if one assumes that most of the CO has reacted with II to yield $TiCp_2(CO)_2$, then what is the remaining product with respect to the initial nitrogen atoms present in compound II? Clearly, an isocyanate complex has been formed, and this would also explain the initial evolution of hydrogen from reaction 4. However, a coordinated isocyanate would not be expected to yield CO upon treatment with CH_3I or HCl. The generation of CO_2 from the addition of HCl to IV would be consistent with the presence of an isocyanate complex.[26] This suggests that at least 5% of the CO absorbed by II generates an isocyanate complex; however, the residue must also contain the remaining nitrogen from the original sample. The $TiCp_2(CO)_2$ obtained by sublimation of IV could result from the thermal decomposition of IV or it may be a by-product of the reaction. It is apparent that IV is not a pure material. No single dimeric structure can be drawn which satisfactorily explains all the results (a tetrameric complex is possible, but such speculation is unwarranted at this stage). However, it is apparent that CO has reacted with the nitrogen in compound II to form the isocyanate. With this in mind, the following exoergic reactions for the catalytic[27,28] generation of organic isocyanates or ureas might be possible:

$$RNH_2 + CO \rightarrow RNCO + H_2 \tag{6}$$

$$2RNH_2 + CO \rightarrow (CO)(NHR)_2 + H_2 \tag{7}$$

However, the fact that the isocyanate ligand is not eliminated by treatment with CO, CH_3I, water, amines, or air certainly restricts its use as a catalytic intermediate for the formation of organic isocyanates or ureas according to eq 6 or 7. In our systems, the key step would be the cleavage of the Ti–NCO (or Ti–OCN) bond with the capability of regenerating the original catalyst. Because the Ti–N or Ti–O bonds are so strong,[38] the catalyst cannot be regenerated.

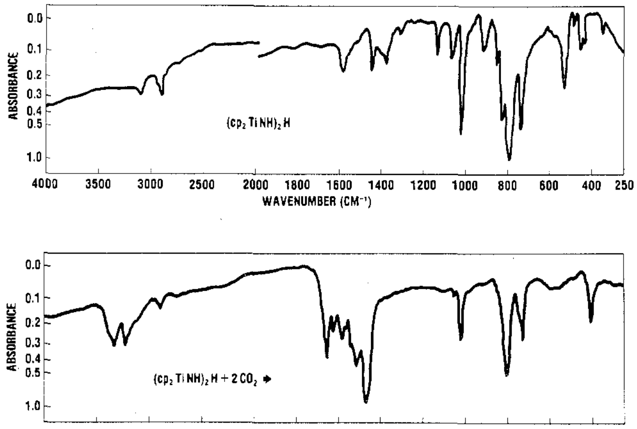


Figure 3. Comparison of IR spectra of $(TiCp_2NH)_2H$ and the same material treated with CO_2. The spectra have been corrected for solvent absorptions.

Reaction with CO_2. The red toluene solution of II slowly (hours) turns blue on exposure to an excess of CO_2. The stoichiometry corresponds to 2.0 mol of CO_2 consumed/mol of Ti_2 with no H_2 evolution. Evaporation of the toluene yields a sky blue solid (V) which is still very sensitive to air and moisture. The IR spectrum of V is given in Figure 3. Several new, strong bands are apparent at 3340, 3230, 1668, and 1510 cm^{-1} which were not present in the starting material. The first three bands are shifted when $^{15}NH_3$ is used to prepare II. Treatment of I with ND_3 (which should yield $(TiCp_2ND)_2D)$[5] followed by the addition of excess CO_2 ultimately yields a product having the expected N–D vibrations at 2540 and 2430 cm^{-1}. Addition of anhydrous HCl to V (in toluene) liberated[30] >80% of the initial CO_2 absorbed by II, and the IR spectrum of this latter product was consistent with a mixture of NH_4Cl and $TiCp_2Cl_2$. Exposure of a toluene solution of V to O_2 resulted in a vigorous reaction with the release of 67% of the original CO_2. The IR spectrum of the O_2 exposed product shows several bands indicative of either amines or metal carbonates. Addition of excess PPh_3 or CO to V yields no CO_2 while excess CH_3I yields most of the original CO_2.

Although V may not be a pure material, it is apparent that the nitrogen centers in II have reacted with CO_2 to form a carbamate complex. Recently, $[RuH(PMe_2Ph)_5]PF_6$ in $HNMe_2$ was reported[31] to react with CO_2 to yield a carbamate complex, $[Ru(O_2CNMe_2)(PMe_2Ph)_4]PF_6$. Addition of HCl to this ruthenium carbamate yields CO_2 and the amine hydrochloride. The Ru–carbamate complex has IR bands at 1565 and 1465 cm^{-1} while various Nb, W, and Zr carbamates reported by Chisholm[32,33,34] have bands ranging from 1685 to 1594 cm^{-1}. The observation that II reacts with CO to yield an isocyanate leads one to suggest that CO_2 also ought to be able to react with the Ti–N moiety in II to yield a carbamate complex. The elimination of CO_2 upon treatment of V with HCl, CH_3I, or O_2 may arise because these reagents effectively oxidize the center. Oxidation of the metal center would eliminate the carbamate ligand leaving it prone to decomposition into CO_2. The absence of any CO_2 upon treatment of V with CO strongly rules out a CO_2 complex.[35,36]

Besides the reactivity of II with CO_2, another interesting feature is the apparent ability of CO_2 to bring out the previously hidden N–H vibrations above 3200 cm^{-1} in II. The addition of ND_3 to I yields D_2 and a compound which, if used immediately, must still contain N–D bridges and no C–D vibrations.[5] The appearance of N–D vibration when CO_2 is added to this deuterated complex proves that the bridging nitrogen atoms of II contain N–H bonds. This suggests that the addition of CO_2 may serve as a useful probe for identifying compounds having features similar to II. Other Lewis bases such as PPh_3 or NH_3 may function in a similar manner by disturbing the symmetry of compound II, but the result is much more definitive when CO_2 is used.

Conclusion

A variety of reactions of II with N_2, olefins, mixtures of olefins and hydrogen, CO, CO_2, and H_2O have been described. Except for olefins, the imide complex, II, reacts quite readily with all these materials despite the formally oxidized titanium center. Compound II reacts with CO to yield both a carbonyl complex and small amounts of an isocyanate species; with CO_2 it yields a carbamate complex. In spite of the quantitative uptake of exactly 2 mol of CO by II, a mixture of products is formed. These mixtures may result from the existence of two competitive pathways with one complex or the reaction of two different complexes. (It should be recalled that II appears to dissociate into two different monomeric species in solution.) In any event, it appears that either CO or CO_2 reacts with compound II to generate N–C bonded products. However, these products cannot be liberated intact from the titanium center(s), and this limits the application of the complex to catalytic systems incorporating CO or CO_2 as reagents.

While NH_3 appears to react degradatively with I (by the evolution of H_2 and the formal oxidation of the titanium center), a new catalyst is still generated. The latter complex, II, is as active a hydrogenation catalyst for olefins as is "bis(titanocene)", I. The actual catalyst for this reaction may be the same as, or very similar to, that in the "bis(titanocene)" system (I). (Alternatively, it may be that the mononuclear form of complex II is an active hydrogenation catalyst because it is coordinatively unsaturated.) Further, this ammine derivative of "bis(titanocene)" is an effective room temperature, low-pressure, homogeneous catalyst for the hydrogenation of olefins in the presence of amines. In addition, compound II has been demonstrated to bind N_2. This coordinated N_2 can be reduced by KNp to NH_3 (after addition of HCl). It is apparent that while NH_3 does affect the catalytic activity of I, it does so very selectively. While reaction with NH_3 inactivates I toward olefin isomerization, it does not inhibit it as a catalyst for the hydrogenation of olefins or the activation of N_2. Thus, the addition of NH_3 to I generates a new compound which has acquired some selectivity in its catalytic properties. Despite the facile reaction of I with NH_3, the product II is still very reactive as evidenced by its reaction with CO, CO_2, and even N_2.

Experimental Section

Apparatus and Reagents. All chemicals used were of the highest purity available. The extremely air-sensitive nature of the metallocenes used throughout this work requires the rigorous exclusion of air and water. All solids were transferred or handled in a Vacuum Atmospheres drybox filled with argon containing <5 ppm O_2 or H_2O. The titanium complexes were dissolved in solvents using glassware fitted with Kontes Teflon, vacuum valves. The solvents were transferred using standard vacuum line (10^{-4} Torr) techniques. The solvents and gases were dried and purified as described in our earlier publication which also gave the details regarding the syntheses of I and II. The physical measurements and techniques were the same as those reported earlier.[2,5] KBr pellets for the IR spectra were prepared (using dried spectroquality KBr) in the drybox using a mini-KBr press. Carbon dioxide was purified by drying over P_2O_5 and outgassing at −196 °C. All experiments using compound II were performed with the crystalline material.

$TiCp_2(CO)_2$. The dicarbonyl complex was prepared by the Al(Hg) reduction of $TiCp_2Cl_2$ in the presence of CO.[37] The crude brown residue, obtained after evaporating the filtrate to dryness, could be purified by sublimation at 80 °C at <10^{-3} Torr. The deep red crystals of $TiCp_2(CO)_2$ were used immediately after sublimation.

Catalytic Hydrogenation of Olefins. Crystals of II were weighed under argon and transferred to the 200-mL flask into which the cyclohexene was distilled. The rates for the hydrogenation of cyclohexene were obtained by monitoring the drop in the pressure of H_2 over a known weight of a cyclohexene solution at 20 °C. When the H_2 pressure had fallen to 100 Torr, additional hydrogen was added to 740 Torr. Plots of log P vs. time were linear over >4 half-lives. Repressurizing the reactor with H_2 did not yield different rate constants. For the high-pressure experiments with C_2H_4 and H_2 (150 psi), the extent of hydrogenation was monitored by measuring the pressure of H_2 remaining at various time intervals (by freezing the contents of the glass tube with liquid N_2). The ratio of C_2H_4 to C_2H_6 was confirmed by GLC analysis using a 3-ft Carbosieve (45/60 mesh) column at 140 °C (He flow) and also by GLC–mass spectroscopy.

Isomerization of Olefins. A solution of 1-hexene (dried over molecular sieves) was distilled into a solution of II (0.2 mmol). Both the gas and liquid phases were sampled after 3 days. Even with additional heating at 40 °C, no significant isomerization was observed. The absence of 2- and 3-hexenes was confirmed by GLC techniques (15% sulfolane on Chromosorb W, 25 °C, He flow). The dimerization of C_2H_4 to butadiene was followed by GLC using an *n*-octane on porasil column (25 °C) to detect C_4H_6 and a 5-ft Chromosorb 103 column (218 °C) to detect C_2H_6. The gas and liquid phases were sampled (after 24 h) after treatment of a THF solution of II (0.3 mmol) with 136 psi of C_2H_4 (98 °C).

CH_3I Experiments. Methyl iodide was dried over molecular sieves (Linde, 5A). After 4 days, it was then partially distilled from the sieves into a tube containing "bis(titanocene)", I. The CH_3I was distilled as needed from this solution being careful to outgas the CH_3I thoroghly prior to reaction with the titanium compounds. Reaction of neat CH_3I with the isocyanate compound (IV) at 95 °C for 40 h did not yield significant amounts of CH_3NCO. The latter compound can be identified by its distinctive NCO vibration at 2200 cm^{-1} in the IR spectrum (using a solution IR cell containing CH_3I in the reference beam).

Reduction of N_2. A heavy-walled pressure tube was provided with a side arm into which KNp could be added and stored until needed. The tube was also loaded with 0.39 mmol of II. Diethyl ether was distilled onto the red $(TiCp_2NH)_2H$ and the solution pressurized with $^{28}N_2$ (or $^{30}N_2$) to 110 psi. After 24 h, the ether solution was cooled to −80 °C, the N_2 vented to 1 atm, and the solution then quickly evacuated to 10^{-3} Torr. The KNp (1.5 mmol) was then tipped into the dark red solution and allowed to stir for 8 h at −80 °C. The solution was then warmed to room temperature for 24 h, after which a large excess of anhydrous HCl was condensed into the pressure tube. The reaction was allowed to stir for 24 h before evaporating the mixture to dryness. The residue was than analyzed for nitrogen by an exhaustive Kjeldahl method. The mass spectrum of the reduced nitrogen product was obtained by treating the NH_3 from the Kjeldahl distillate with excess HCl and evaporating the solution to dryness.

XPS Measurements. X-ray photoelectron spectra were recorded on an AEI-ES 200b spectrometer fitted with an x-ray monochromator (using Mg Kα source (1253.6 eV)). A special probe was designed so that the extremely air-sensitive samples could be mounted in the drybox, sealed under argon, transported to the XPS lab, and then opened in the high-vacuum chamber of the spectrometer. No discoloration of the red solid (indicative of exposure to O_2) or intense oxygen XPS bands where detected in the sample. Because of the instability of the N_2 adduct, all the XPS data were collected within 3 min of the initial exposure of the sample to the x-ray beam.

CO_2 Analysis. The amount of CO_2 consumed by II was determined volumetrically using a Toepler pump. The solution of II was frozen and a known amount of CO_2 was condensed into the reactor. The reaction was allowed to proceed to completion (<24 h) and frozen with liquid nitrogen. The gas phase was sampled for N_2 and H_2 using a Toepler pump. The reactor was then removed from the liquid N_2 and immersed in a bath at −80 °C. The gas phase was again collected using a Toepler pump, and the gaseous products were then analyzed by GLC or GLC/MS.

CO Analysis. A toluene solution of II (weighed as crystals) was exposed to a known amount of CO and the reaction was carried to completion. The solution was frozen with liquid N_2, and the resulting H_2 (confirmed by mass spectroscopy) and CO were collected using the Toepler pump. The gases were then recycled over Cu–O heated to 400 °C (with liquid N_2 traps before and after the furnace). The liquid N_2 traps were removed and replaced with −80 °C baths, and the CO_2 was collected using the Toepler pump.

Analysis of Amines. The presence of organic amines can be easily demonstrated using GLC techniques. Our Varian 90P-3 chromatograph was equipped with a 10-ft Pennwalt 221 column (175 °C, He flow) which readily separates primary, secondary, and tertiary amines. In order to remove any catalyst decomposition products, which might elute off the GLC column where the amines also appear, the reaction products were digested with NaOH. The gases were distilled onto aqueous HCl. After 24 h, the aqueous HCl was evaporated to dryness. A minimum amount of dioxane was added to the white residue, followed by the addition of an excess of LiOMe. The gas phase of the reaction tube was then sampled by means of a vacuum/gas-inlet system appended to the GLC.

Acknowledgment. I wish to thank Mr. Robert Leming for his technical assistance throughout the course of this work. In addition, I would also like to acknowledge my colleagues Drs. Guido Pez and L. Ray Anderson for their many useful comments, assistance, and support. Thanks are also given to Drs. R. Grey, M. Novotny, A. Signorelli (XPS), Paul Harget (x-ray), Peter Apgar (x-ray), Rita Hogan (nitrogen analyses), and Ed McCarthy (mass spectroscopy).

Registry No. II, 64611-27-4; $TiCp_2(CO)_2$, 12129-51-0; $TiCp_2(NCO)_2$, 12109-61-4; N_2, 7727-37-9; C_2H_4, 74-85-1; C_2H_6, 74-84-0; C_6H_{10}, 110-33-8; C_6H_{12}, 110-82-7; H_2O, 7732-18-5; CO, 630-08-0; CO_2, 124-38-9; NH_3, 7664-41-7.

References and Notes

(1) This is the name used to refer to the crystalline product isolated from the reaction of NH_3 with $(C_5H_5)_2\overline{\mathrm{Ti}(C_5H_4)\mathrm{Ti}}(C_5H_5)$. While the positions of the H atoms for the imide complex are based upon indirect arguments, the x-ray data are conclusive on the presence of two bridging, non-"nitridic" nitrogen atoms.

(2) G. Pez, *J. Am. Chem. Soc.*, **98**, 8072 (1976); G. Pez, U.S. Patent No. 3 776 932 (1973).

(3) G. Pez, *J. Chem. Soc., Chem. Comm.*, 560 (1977).

(4) G. Pez and S. Kwan, *J. Am. Chem. Soc.*, **98**, 8072 (1976).

(5) J. Armor, submitted for publication to *Inorg. Chem.*

(6) J. Armor, Abstracts of the 174th Meeting of the American Chemical Society held jointly with the CIC, May 1977.

(7) J. Armor and G. Pez, U.S. Patent No. 4 046 790.

(8) J. Armor, Abstracts of the Inorganic Division, 175th National Meeting of the American Chemical Society, Aug 1977.

(9) Other metal ammine complexes display XPS bands in a similar location: D. N. Hendrickson, J. M. Hollander and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

(10) Other N_2 complexes also absorb in this region: D. Sellman, *Agnew. Chem., Int. Ed. Engl.*, **13**, 639 (1974); H. Binder and D. Sellman, *ibid.*, 1017 (1973).

(11) The ammonia was distilled into an excess of HCl without any indicator present. This aqueous solution was evaporated to dryness yielding a white solid. The presence of ^{15}N and its relative concentration over ^{14}N were determined using a high-resolution, ratio mass spectrometer.

(12) The Kjeldahl method of analysis on the crystalline samples of compound II yields only half of the theoretical amount of nitrogen. However, the modified Dumas method (ref 5) gives the correct amount of nitrogen as confirmed by the x-ray data. The discrepancy is probably due to the formation of the extremely stable titanium nitride during the Kjeldahl analysis.

(13) R. Baltzly, *J. Org. Chem.*, **41**, 928 (1976).

(14) For a review of hydrotreating see SRI report No. 47, "Process Economics Program report on Petroleum Desulfurization", by S. Takaoka, Jan 1969.

(15) L. Uhlman, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **5**, 263, (1963); B. W. Howk, E. L. Little, S. L. Scott, and G. M. Whitman, *J. Am. Chem. Soc.*, **76**, 1899 (1954).

(16) A. DeRenzi, G. Paiaro, A. Panunzi, and L. Paulillo, *Gazz. Chim. Ital.*, **102**, 281 (1972); R. Palumbo, A. DeRenzi, A. Panunzi, and G. Paiaro, *J. Am. Chem. Soc.*, **91**, 3874 (1969).

(17) D. R. Coulson, *Tetrahedron Lett.*, **5**, 429 (1971); H. Lehmkuhl and D. Reinehr, *J. Organomet. Chem.*, **55**, 215 (1973); R. Baker, D. E. Holliday, and T. N. Smith, *Chem. Commun.*, 1583 (1971).

(18) H. P. Fritz and E. F. Paulus, *Z. Naturforsch. B*, **18**, 435 (1963).

(19) F. Calderazzo, J. J. Salzmann, and P. Mosimann, *Inorg. Chim. Acta*, **1**, 65 (1967).

(20) B. Demerseman, G. Bouquet, and M. Bigorne, *J. Organomet. Chem.*, **101**, C-24 (1975).

(21) A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959).

(22) J. L. Burmeister, E. A. Deardorff, A. Jensen, and V. H. Christiansen, *Inorg. Chem.*, **9**, 58 (1970).

(23) R. Coutts and P. C. Wailes, *Inorg. Nucl. Chem. Lett.*, **3**, 1 (1967).

(24) R. J. Angelici and L. Busetto, *J. Am. Chem. Soc.*, **91**, 3197 (1969).

(25) C. Floriani and G. Fachinetti, *J. Chem. Soc., Chem. Commun.*, 790 (1972).

(26) Isocyanate complexes are known to undergo acid hydrolysis to yield CO_2. For example see P. C. Ford, *Inorg. Chem.*, **10**, 2153 (1971).

(27) J. J. Byerley, G. L. Rempel, N. Takebe, and B. R. James, *Chem. Commun.*, 1982 (1971).

(28) F. Calderazzo, *Inorg. Chem.*, **4**, 293 (1965).

(29) The bridging N–H groups of compound II do not exchange with solvent or with the C_5H_5 ligands.

(30) This should be regarded as a lower limit. Since we had to analyze for CO_2 in the presence of HCl, $(C_2H_5)_3N$ was used to absorb the HCl. The CO_2 was then collected with the Toepler pump. It is very difficult to collect all the CO_2 because of the solubility of CO_2 in amines.

(31) T. V. Ashworth, M. Nolte, and E. Singleton, *J. Organomet. Chem.*, **121**, C57 (1976).

(32) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782 and 792 (1977).

(33) D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, **9**, 273 (1976).

(34) M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, **97**, 1623 (1975).

(35) M. E. Vol'pin and I. S. Kolomnikov, *Organomet. React.*, **5**, 313 (1975).

(36) M. E. Vol'pin and I. S. Kolomnikov, *Pure Appl. Chem.*, **30**, 567 (1973).

(37) B. Demerseman, G. Bouquet, and M. Bigorgne, *J. Organomet. Chem.*, **101**, C24 (1975).

Contribution from the Department of Chemistry,
University of Ife, Ile-Ife, Nigeria

Mechanisms of the Titanium(III) Reduction of Tris(1,10-phenanthroline)cobalt(III), Tris(oxalato)cobaltate(III), and Tris(1,10-phenanthroline)iron(III) in Aqueous Solutions

NIYI AKINYUGHA, JIDE IGE, J. FOLORUNSO OJO,* OLUSEGUN OLUBUYIDE, and R. SIMOYI

Received May 5, 1977

The reduction of tris(1,10-phenanthroline)cobalt(III), tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) by titanium(III) in aqueous solutions has been studied at 25 °C, $I = 1.0$ mol dm^{-3} (LiCl). The dependence of the second-order rate constants, k_{obsd}, on [H$^+$] has been investigated over the range 0.05–1.00 mol dm^{-3}, and the rate constant is of the form $k_{obsd} = k_0 + k_1[H^+]^{-1}$ for tris(1,10-phenanthroline)cobalt(III). The [H$^+$] dependence for tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) is of the form $1/k_{obsd} = a + b[H^+]$. The magnitudes of the parameters a and b for tris(oxalato)cobaltate(III) are indicative of precursor complex formation, attributed to chelation of $TiOH^{2+}$ by oxalate ligand. The magnitudes of a and b for tris(1,10-phenanthroline)iron(III) do not indicate precursor complex formation. Observed catalytic effects of added anions and calculations based on the Marcus equation on the reaction of tris(1,10-phenanthroline)cobalt(III) and tris(1,10-phenanthroline)iron(III) suggest that they react with titanium(III) by outer-sphere mechanisms.

Assignment of mechanism to redox reactions involving titanium(III) has been based on usual criteria applied to other reductants, viz., relative rates[1,2] (k_{N_3}/k_{NCS}), electron mediating ability of carboxylate groups[3a,3b] through conjugation and/or chelation, and log–log plots using Marcus linear free energy relationships.[4] Inverse hydrogen ion dependence[1–8] of observed second-order rate constants has dominated the kinetics of aqueous reactions of titanium(III), and the nature of this has been used recently in some cases to suggest precursor complex formation and hence inner-sphere mechanisms. The complex nature of the inverse hydrogen-ion dependence observed in certain cases makes alternative[2,8] or parallel reaction paths possible. Thus, while Orhanovic and Earley[8] were unable to assign a mechanism to the reactions of titanium(III) with $Co(NH_3)_5Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2^+$, Thompson and Sykes[4] were able to use log–log plot correlations to assign an outer-sphere mechanism to these reactions. We here report a study utilizing some of the above criteria, as well as current ideas on the characteristic hydrolytic behavior of titanium(III), to assign mechanisms to its reactions with tris(1,10-phenanthroline)cobalt(III), tris(oxalato)cobaltate(III), and tris(1,10-phenanthroline)iron(III).

Experimental Section

Materials. $LiClO_4$ was prepared and recrystallized several times by standard procedures.[9]

LiCl (Hopkin and Williams Reagent grade) was recrystallized twice. The hydrochloric acid was Analar grade reagent. Pure titanium(III) chloride (Koch-Light Laboratories, Ltd.) was used. Fresh Ti(III) solutions, prepared and stored at 0 °C each day before use, were standardized as described[2] previously.

The complexes $Co(phen)_3^{3+}$, $Co(C_2O_4)_3^{3-}$, and $Fe(phen)_3^{3+}$ were prepared and recrystallized as described in the literature.[10,11] Their UV–visible spectra were in good agreement with literature[12–14] values. $Co(C_2O_4)_3^{3-}$ was kept in a tube wrapped with aluminum foil to avoid photolysis. $Fe(phen)_3^{3+}$ solutions in 5 mol dm^{-3} perchloric acid were freshly prepared each day and kept in ice before use.

Kinetics. The fast reactions of Ti(III) with $Co(C_2O_4)_3^{3-}$ and $Fe(phen)_3^{3+}$ were monitored on a Durrum-Gibson stopped-flow spectrophotometer. Decreasing absorbance of $Co(C_2O_4)_3^{3-}$ was followed[13] at λ 605 nm (ε 175 dm^3 mol^{-1} cm^{-1}) for the Ti(III)–$Co(C_2O_4)_3^{3-}$ reaction; increasing absorbance of $Fe(phen)_3^{2+}$ produced in the Ti(III)–$Fe(phen)_3^{3+}$ reaction was followed[14] at λ 510 nm (ε 1.09 × 10^4 dm^3 mol^{-1} cm^{-1}). The slow Ti(III)–$Co(phen)_3^{3+}$ reaction was followed on an SP 500 spectrophotometer. The reductant was always in large excess (≥tenfold). All runs were performed at 25.0 ± 0.1 °C in chloride media, with $I = 1.0$ mol dm^{-3} (LiCl). The use of perchlorate was avoided due to complications arising from its reactions with Ti(III).[3a] However, where effects of chloride were investigated, $LiClO_4$ was used to maintain the ionic strength at 1.0 mol dm^{-3}. Perchlorate was introduced via the oxidant solution. Pseudo-first-order rate plots were linear to more than 85% reaction in all cases.

Results

Stoichiometry was checked for each of the reactions by recording the UV–visible spectra of the reaction mixtures before and after each reaction. The results were consistent with the reduction of 1 mol of oxidant by 1 mol of Ti(III). Each reaction could therefore be written as

$$\mathrm{Ti(III)} + \mathrm{M(III)} \rightarrow \mathrm{Ti(IV)} + \mathrm{M(II)} \tag{1}$$

where M = Co or Fe. The reactions obey the rate law

$$\mathrm{rate} = k_{\mathrm{obsd}}[\mathrm{Ti(III)}][\mathrm{M(III)}] \tag{2}$$

Second-order rate constants k_{obsd} are listed in the tables.

Ti(III)–Co(phen)$_3^{3+}$ Reaction. The dependence of k_{obsd} on [H$^+$] was investigated in the range 0.05–1.00 mol dm^{-3} (Table I) and is of the form

$$k_{\mathrm{obsd}} = k_0 + k_1[\mathrm{H}^+]^{-1} \tag{3}$$

with $k_0 = 0.038 \pm 0.009$ dm^3 mol^{-1} s^{-1} and $k_1 = 0.24 \pm 0.04$ s^{-1}.

Thompson and Sykes[4] have used the equation in the form

$$k_{\mathrm{obsd}} = k_1/(K_a + [\mathrm{H}^+]) \tag{4}$$

to make more precise evaluation of k_1, where K_a is the hydrolysis constant for Ti^{3+}:

$$\mathrm{Ti}^{3+} + \mathrm{H_2O} \overset{K_a}{\rightleftharpoons} \mathrm{TiOH}^{2+} + \mathrm{H}^+ \tag{5}$$

A good fit of their data to eq 4 was found for the Co(III)

0020-1669/78/1317-0218$01.00/0