

Lewis Base Behavior of Dinitrogen and Carbonyl Complexes of Rhenium toward Titanium Tetrachloride and Related Species

R. ROBSON¹

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Two previously reported products from $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ and titanium trichloride are shown here to be derived from titanium(IV). The preparation from titanium tetrachloride and characterization of the adducts $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4]$ and $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{thf})]$ are described. The former is the first fully characterized example of a trinuclear complex containing two bridging dinitrogen ligands. $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ is a much more powerful donor for titanium tetrachloride than is thf, the strongest neutral donor for this Lewis acid hitherto reported. Titanium tetrachloride, in excess, reacts with $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ in the presence of diethyl ether to yield $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$, which shows a very low $\nu(\text{N}_2)$ at 1622 cm^{-1} . $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ with a deficiency of titanium tetrachloride yields $[\{\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4]$ but with an excess of titanium tetrachloride suffers oxidation to $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$.

Introduction

A number of products, generally but not always simple adducts, from the complex *trans*- $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (hereafter abbreviated to $[\text{ReN}_2]$) and various Lewis acids have been reported.²⁻⁵ However, these products generally have been incompletely characterized, with the exception of those derived from some aluminum acceptor molecules⁵ and from $[\text{CrCl}_3(\text{thf})_3]$.⁴ The results presented here arose out of a re-examination of two previously reported ill-defined products presumed to be derived from titanium trichloride, namely, a blue product obtained from reaction mixtures containing 1:1 proportions of $[\text{ReN}_2]$ and either TiCl_3 , $[\text{TiCl}_3(\text{thf})_3]$, or $[\text{TiCl}_3(\text{MeCN})_3]$ and a red product from mixtures containing an excess of TiCl_3 or $[\text{TiCl}_3(\text{MeCN})_3]$.³

Results and Discussion

Under carefully controlled anhydrous and dioxygen-free conditions, no blue product comparable to that previously reported can be isolated from the mauve solutions containing $[\text{ReN}_2]$ and $[\text{TiCl}_3(\text{thf})_3]$ in 1:1 proportions in dichloromethane. However, admission of dioxygen to this reaction mixture allows the subsequent isolation of a deep blue crystalline product derived from titanium tetrachloride with composition $[(\text{ReN}_2)_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$ ($\nu(\text{N}_2)$ 1812 cm^{-1} (Nujol)), which is virtually identical with the previously reported blue product.³ That this product was derived from TiCl_4 was suggested by its diamagnetism and was proven by its isolation from dichloromethane solutions of $[\text{ReN}_2]$ and TiCl_4 in 2:1 proportions. At 50° under high vacuum the material could be desolvated to a residue of composition $[(\text{ReN}_2)_2\text{TiCl}_4]$. An analogous crystalline product, $[(\text{ReN}_2)_2\text{TiCl}_4(\text{C}_6\text{H}_5)_1.5]$, with a much sharper $\nu(\text{N}_2)$ band at 1814 cm^{-1} (Nujol) was obtained from benzene, but in this case the solvent molecules were tenaciously held, even at 60° under high vacuum. These adducts degenerated in the atmosphere only slowly in the solid state, but solutions were very moisture sensitive. $[\text{ReN}_2]$ was isolated in virtually quantitative yield upon destruction of the adduct with ethanol, which indicates the retention of the $[\text{ReN}_2]$ structural unit in the adduct. Con-

trary to the earlier report,³ TiCl_4 , even in large excess, does not oxidize $[\text{ReN}_2]$ to $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]^+$. Clearly, in the earlier work Ti(III) was oxidized to Ti(IV), very probably as a result of the inadvertent admission of dioxygen.

A strong band at 1815 cm^{-1} in the ir spectrum of the purple solution of $[(\text{ReN}_2)_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$ in anhydrous tetrahydrofuran indicates that the $[(\text{ReN}_2)_2\text{TiCl}_4]$ unit survives. Additional bands at 1925 cm^{-1} , due to $[\text{ReN}_2]$, and at 1755 cm^{-1} , due to $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ (see below), indicate equilibria in which $[\text{ReN}_2]$ and thf compete as ligands for coordination to titanium. The species $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ could be isolated, as an air-sensitive deep red crystalline solid, from tetrahydrofuran solutions of $[\text{ReN}_2]$ and TiCl_4 in 1:1 proportions. Solutions of this product were particularly air sensitive. $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ was recrystallized from dichloromethane-pentane solution without loss of tetrahydrofuran, but variable amounts of dichloromethane were occluded, the last traces of which were difficult to remove. The shape and precise position of the $\nu(\text{N}_2)$ band were dependent on the amount of dichloromethane present (range $1720\text{--}1740\text{ cm}^{-1}$), but after several hours at 50° under high vacuum a dichloromethane-free residue was obtained with $\nu(\text{N}_2)$ 1740 cm^{-1} (Nujol).

The ir spectrum of red-brown dichloromethane solutions of $[\text{ReN}_2]$, in the presence of an excess of TiCl_4 , showed only a weak broad $\nu(\text{N}_2)$ band at 1635 cm^{-1} . As the spectroscopic sample was allowed progressively to hydrolyze by influx of atmospheric moisture, new and much more intense peaks grew, first at 1800 cm^{-1} ($[(\text{ReN}_2)_2\text{TiCl}_4]$) and then at 1925 cm^{-1} ($[\text{ReN}_2]$), at the expense of the 1635 cm^{-1} peak. Great difficulty was experienced in attempts to isolate the species with $\nu(\text{N}_2)$ at 1635 cm^{-1} in pure form, for it was extremely moisture sensitive and tended to separate from solution in a gummy form. The only effective means discovered for obtaining solid products with reproducible properties was to use diethyl ether for precipitation purposes when the product had the formulation $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$. On one occasion a crystalline specimen of composition $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{CH}_2\text{Cl}_2)]$ was obtained from dichloromethane-pentane, in which the partial hydrolysis of the TiCl_4 had presumably been caused by the fortuitous admission of traces of moisture in just the correct quantity, but many further attempts to repeat this, in which water vapor was either scrupulously avoided or deliberately introduced, yielded nothing but gummy products. Possibly the diethyl ether plays a crucial role in providing the oxide ion present in the product and, indeed, TiCl_4 is known to promote C-O fission in

(1) Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Victoria, Australia.

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Table I. Conductance and Uv-Visible and Ir Spectral Data^a

	$\nu(\text{N}_2)$, cm^{-1}		Uv-visible spectrum ^b		Molar conductance, ^c $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
	Nujol	CH_2Cl_2	ν , $\text{cm}^{-1} \times 10^{-3}$	ϵ	
$[(\text{ReN}_2)_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$	1812 (s)	1800 (s)	19.8 15.7	4,200 5,500	3 (2.5)
$[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$	1740 (s)	1726 (s)	19.8	21,100	2 (2.8)
$[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$	1622 (w)	1635 (w)	21.6	23,100	8 (5.0)
$[(\text{ReCO})_2\text{TiCl}_4]$	1622 (s)	1610 (s)	18.2	6,060	2 (2.3)
	1628 (s)				

^a Key: s = strong, w = weak. ^b In CH_2Cl_2 solution. Range 12000–33000 cm^{-1} . ^c In CH_2Cl_2 solution at ca. 20°. Ca. 60 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ expected for 1:1 electrolyte: R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **9**, 2048 (1970). Molarities $\times 10^3$ in parentheses.

ethers.⁶ $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$ was found to be virtually identical, on the basis of its ir spectrum, with the previously reported³ ill-defined red product presumed to be derived from titanium trichloride.

Some physical properties of the products are presented in Table I.

All the available evidence concerning adducts of Lewis acids with $[\text{ReN}_2]$ and related dinitrogen complexes suggests that the acceptor, M, is attached to the terminal nitrogen atom. The lowered $\nu(\text{N}_2)$ compared with free $[\text{ReN}_2]$ can be understood in terms of transfer of electron density from the formally filled $d\pi$ orbitals of Re to the empty $d\pi$ orbitals of the acceptor, M, which can be seen to lead to a weakening of the NN bond either in terms of the valence bond structures $\text{Re} \leftarrow \text{N} \equiv \text{N} \rightarrow \text{M} \leftrightarrow \text{Re} \rightleftharpoons \text{N} = \text{N} \rightleftharpoons \text{M}$ or in terms of four-center π molecular orbitals as has been discussed previously.⁴ The lower $\nu(\text{N}_2)$ observed for $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ compared with the $[(\text{ReN}_2)_2\text{TiCl}_4]$ derivatives is consistent with this view, for, in the latter, two $[\text{ReN}_2]$ units are available to satisfy the electron deficiency of the Ti(IV) center, while in the former the Ti(IV) exerts a greater demand on the π electrons of the single $[\text{ReN}_2]$ unit.

The formation of $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ (virtually in 100% yield judging from the ir spectrum) directly from the components in dilute solution in tetrahydrofuran and the above-mentioned persistence of $[(\text{ReN}_2)_2\text{TiCl}_4]$ in this solvent indicate a striking preference of TiCl_4 for $[\text{ReN}_2]$ over thf, hitherto the strongest neutral donor for TiCl_4 reported.⁷ Indeed, it would appear that $[\text{ReN}_2]$, being able to donate electronic charge to an acceptor in both the σ and π systems, is uniquely suited for coordination to d^0 cations in which the d orbitals are energetically accessible. By comparison, $[\text{ReN}_2]$ competes unsuccessfully with thf for coordination to AlMe_3 even when the thf is present in dilute solution (in benzene) at molar concentrations comparable with that of $[\text{ReN}_2]$.⁵ This difference arises no doubt from the energetic inaccessibility of the empty d orbitals on aluminum.

In view of the marked affinity of $[\text{ReN}_2]$ for TiCl_4 , attempts were made to attach more than two $[\text{ReN}_2]$ units to the same titanium center. However, ir spectra of mixtures containing more than 3 mol of $[\text{ReN}_2]$ per TiCl_4 showed no evidence for species other than $[(\text{ReN}_2)_2\text{TiCl}_4]$ and $[\text{ReN}_2]$. Presumably the $[\text{ReN}_2]$ ligand is too bulky⁸ to allow attachment of more than two to the same center, but related rhenium-dinitrogen complexes with less bulky phosphine ligands may well behave otherwise.

All the products are diamagnetic and the ^1H nmr spectra are very similar (except for easily identifiable additional res-

onances due to thf or Et_2O) to that of $[\text{ReN}_2]$ itself; in particular, the single resonance of the methyl protons of the phosphine ligands is insignificantly affected by adduct formation, confirming that the $[\text{ReN}_2]$ retains its integrity in the adducts. Comparison of the ^1H nmr spectra in CD_2Cl_2 of $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ and thf itself clearly indicates that the thf is coordinated for the multiplets centered at 1.66 (4 protons adjacent to oxygen) and 3.54 ppm (4 protons remote from oxygen) upfield of CH_2Cl_2 in free thf, are shifted 0.91 and 0.25 ppm downfield, respectively, in $[(\text{ReN}_2)_2\text{TiCl}_4(\text{thf})]$. By contrast the resonances originating in the Et_2O of $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$ are identical with those of free Et_2O indicating that the ether is not coordinated in this case.

As indicated in Table I, the adducts behaved effectively as nonelectrolytes in dichloromethane.

The available evidence concerning the $[(\text{ReN}_2)_2\text{TiCl}_4]$ derivatives and $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ supports six-coordinate, probably basically octahedral, geometry around titanium in both cases. The lack of any splitting of $\nu(\text{N}_2)$ in the former suggests a trans arrangement of the $[\text{ReN}_2]$ donors, as would be expected of a ligand so bulky.⁸ The $[(\text{ReN}_2)_2\text{TiCl}_4]$ derivatives are, to our knowledge, the first fully characterized examples of a trinuclear complex containing two bridging dinitrogen ligands.

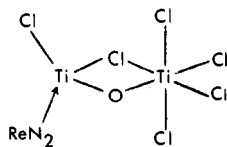
The adducts show intense absorptions in the visible region where neither yellow $[\text{ReN}_2]$ nor colorless TiCl_4 absorb. The electronic spectrum of $[(\text{ReN}_2)\text{TiCl}_4(\text{thf})]$ can be understood qualitatively in terms of the four-center π molecular orbital scheme proposed previously for $[(\text{ReN}_2)\text{CrCl}_3(\text{thf})_2]$.⁴ In the ground state the $1e$ (predominantly π_x and π_y on N_2 , z being the internuclear axis) and $2e$ (predominantly d_{xz} or d_{yz} on Re) orbitals are full and the observed intense visible band may be assigned to the allowed transition $2e \rightarrow 3e$, which involves charge transfer from rhenium to titanium. The two bands observed for $[(\text{ReN}_2)_2\text{TiCl}_4]$ no doubt have a related origin. In this case each of the two equivalent π systems mutually at right angles consists of seven molecular orbitals, the lowest four of which are filled in the ground state. The intense visible bands can now be assigned qualitatively to transitions from the highest filled π molecular orbital to one or more of the remaining three orbitals.

$[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$ with its unusually low $\nu(\text{N}_2)$ presents interesting structural possibilities, and it is unfortunate that crystals suitable for X-ray studies could not be obtained. The nonelectrolyte behavior eliminates any possibility such as $[(\text{ReN}_2)\text{TiCl}_3]^+[\text{TiOCl}_3]^-$ in which the positive charge at the acceptor site might very much enhance the transfer of π -electron density to titanium and thus account for the unusually low $\nu(\text{N}_2)$. However, related bridged arrangements in which the two titanium ions are unequally loaded with anions so that the titanium attached to ReN_2 effectively is positively charged are possible.

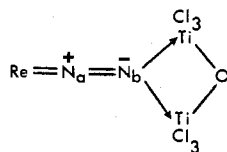
(6) P. M. Hamilton, R. McBeth, W. Bekebrede, and H. H. Sisler, *J. Amer. Chem. Soc.*, **75**, 2881 (1953).

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Alternatively both titanium atoms may be attached to the terminal nitrogen atom while the ReNN system remains linear.



In a structure of this type N_a would be sp hybridized and N_b sp^2 hybridized, and the N_2 unit would formally be represented as $\text{N}_a^+ = \text{N}_b^-$. The negatively charged N_b would then provide a good bridging site for two cations (two filled sp^2 hybrids on N_b would provide two $\text{N}-\text{Ti}$ σ bonds). N_a , on the other hand, formally having a filled sp hybrid and an empty p orbital in the same plane as the N_bTi_2 system, would participate in a strong double bond to the Re atom which has a compatible combination of an empty $d\sigma$ orbital and a filled $d\pi$ orbital; Re appears to be in general prone to formation of short strong multiple bonds to nitrogen. Seen in these terms dinitrogen appears well suited to coordination at one end to two strong Lewis acids and at the other end to one metal in a low oxidation state. By contrast, if the ten valence electrons of the isoelectronic CO are rearranged in this way the dipolar arrangement so important in the above mode of bridging is not generated.

$\text{N}(1s)$ and $\text{Ti}(2p)$ electron binding energies relative to $\text{C}(1s)$ estimated at 285 eV were measured for the series of adducts by esca, the sample introduction arrangement of the instrument having been modified so that air-sensitive materials could be handled apparently satisfactorily. The observed signals for all the adducts were identical within the limits of accuracy of the technique, consisting of two incompletely resolved $\text{N}(1s)$ bands at *ca.* 400.0 and 398.5 eV and two $\text{Ti}(2p)$ bands at *ca.* 464.5 (broad $\text{Ti}(2p_{1/2})$) and 458.5 eV ($\text{Ti}(2p_{3/2})$). No evidence for two sorts of titanium in the case of $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$ was obtained, which possibly supports the structure in which two titanium atoms are attached to the same nitrogen, but which may simply reflect the insensitivity of the technique. The $\text{N}(1s)$ binding energies were very similar to those of $[\text{ReN}_2]$ itself.⁹ In the case of $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$ the formal charge separation in $\text{N}^+ = \text{N}^-$, prior to attachment of one $\text{Re}(\text{I})$ and two titanium-(IV) ions as suggested above, would no doubt be very much reduced when the N -metal bonds are established, and possibly not very different binding energies would be expected for the two N atoms. It is possible that, despite elaborate precautions to prevent it, the thin surface layer under observation by esca was hydrolyzed in all cases to $[\text{ReN}_2]$. However, the samples did retain their characteristic colors after withdrawal from the spectrometer and this possibility is considered unlikely.

As might be expected of substances as complex as these the far-ir spectra were very complex and ill-resolved and of no diagnostic value.

Interaction of *trans*- $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ with TiCl_4 . Re -

cently a number of reports have appeared of adducts between metal carbonyls and Lewis acids in which the latter are attached to the carbonyl oxygen atoms.¹⁰ A marked lowering of $\nu(\text{CO})$ is observed in these cases. In view of the considerations outlined above concerning the potential relative capacities of N_2 and CO to bridge three metal ions, an investigation of the interaction of TiCl_4 with *trans*- $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ (hereafter abbreviated to $[\text{ReCO}]$) was undertaken.

Existing methods for the preparation of $[\text{ReCO}]$ give impure products in poor yields. An improved simpler procedure was devised affording pure $[\text{ReCO}]$ in fair yield by heating $[\text{Re}(\text{N}_2\text{COPh})\text{Cl}_2(\text{PPh}_3)_2]$ ¹¹ and $[\text{PMe}_2\text{Ph}]$ in benzyl alcohol at 190° and then introducing CO at atmospheric pressure to the resulting solution cooled to room temperature.

A crystalline deep blue adduct of composition $[(\text{ReCO})_2\text{TiCl}_4]$ was isolated from dichloromethane solutions of $[\text{ReCO}]$ and TiCl_4 in 2:1 proportions. Solutions of this adduct were markedly more sensitive to atmospheric moisture than those of $[(\text{ReN}_2)_2\text{TiCl}_4]$. Some physical properties of $[(\text{ReCO})_2\text{TiCl}_4]$ are given in Table I. The very low $\nu(\text{CO})$ is in accord with attachment of titanium to the carbonyl oxygen atom. There is some indication of splitting of $\nu(\text{CO})$ in solid $[(\text{ReCO})_2\text{TiCl}_4]$ (1622 and 1628 cm^{-1}) but only a single band is observed in dichloromethane solution (1610 cm^{-1}) and a *trans* arrangement of $[\text{ReCO}]$ units around titanium is proposed, the splitting in the Nujol spectrum being ascribed to a solid state effect. The adduct is a nonconductor in dichloromethane, and the ^1H nmr spectrum (CD_2Cl_2), which is virtually identical with that of $[\text{ReCO}]$, confirms the retention of intact $[\text{ReCO}]$ units. Crystalline $[(\text{ReN}_2)_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$ and $[(\text{ReCO})_2\text{TiCl}_4]$ could both be obtained under identical conditions from dichloromethane-pentane solution, and the failure to incorporate dichloromethane in the latter suggests significantly different geometries in the two cases. There appears to be a tendency for metal carbonyls to take on Lewis acids to form nonlinear adducts, bent at oxygen,¹⁰ and perhaps the difference arises in this way.

An ir study of the interaction of $[\text{ReCO}]$ with various proportions of TiCl_4 in dichloromethane solution indicated the formation of other species in addition to $[(\text{ReCO})_2\text{TiCl}_4]$, for broad complex $\nu(\text{CO})$ patterns in the range 1570–1610 cm^{-1} were observed when the components were in roughly equimolar proportions. No solid compounds corresponding to these solution species were isolated. At higher proportions of TiCl_4 new $\nu(\text{CO})$ bands appeared at 1870 and 1920 cm^{-1} . Solutions containing a threefold excess of TiCl_4 showed only a single $\nu(\text{CO})$ band at 1920 cm^{-1} . Alcoholysis of the latter solution yielded yellow crystalline $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$. Clearly, TiCl_4 in excess is capable of effecting the two-electron oxidation of $[\text{ReCO}]$. The new $\nu(\text{CO})$ band appearing at 1870 cm^{-1} in the ir spectrum of $[\text{ReCO}]-\text{TiCl}_4$ mixtures can be ascribed to free $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$ and that at 1920 cm^{-1} to an adduct of the latter with TiCl_4 as can be demonstrated by observing the ir spectrum of authentic $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$ before and after the introduction of TiCl_4 . The increased $\nu(\text{CO})$ upon adduct formation suggests TiCl_4 is attached to one or, more probably, two of the chloride ligands on rhenium, rather than to the carbonyl group. This mode of association would be expected to raise $\nu(\text{CO})$ since electron density would be withdrawn from the rhenium center which would then be less capable of back

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(11) J. Chatt, J. R. Dilworth, and G. J. Leigh, *Chem. Commun.*, 687 (1969).

donation to the carbonyl group. It has been observed that $[\text{ReN}_2]$ is generally more prone to one-electron oxidation than $[\text{ReCO}]$ which is to be contrasted with the behavior observed here, where $[\text{ReN}_2]$ is stable to large excess of TiCl_4 while $[\text{ReCO}]$ suffers facile two-electron oxidation to $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$.

Experimental Section

Solvents. All solvents were predried as indicated below and then, generally, were finally dried with the appropriate desiccant and transferred to reaction mixtures, etc., by distillation on the vacuum line. Benzene and petroleum ether solvents were shaken with concentrated sulfuric acid and distilled from calcium hydride under dry dinitrogen. Diethyl ether and tetrahydrofuran were distilled from sodium diphenylketyl under dry dinitrogen. Dichloromethane was distilled from phosphorus pentoxide.

Reagents. Chlorodinitrogen tetrakis[*dimethyl(phenyl)phosphine*]rhenium(I). $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ was prepared by the method of Chatt, *et al.*¹¹

Chlorocarbonyltetrakis[*dimethyl(phenyl)phosphine*]rhenium(I). To $[\text{ReCl}_2(\text{N}_2\text{COPh})(\text{PPh}_2)_2]$ ¹¹ (6.0 g) and benzyl alcohol (5 cm³) under dinitrogen was added *dimethyl(phenyl)phosphine* (9.3 g). The reaction flask was placed in an oil bath at 190° whereupon vigorous evolution of dinitrogen occurred. After 10 min the reaction mixture was cooled to room temperature and carbon monoxide was bubbled through the resulting yellow-brown solution for 1.5 hr. A mixture of methanol (50 cm³), ethanol (50 cm³), and hexane (50 cm³) was added to precipitate the crude product which was recrystallized from benzene-methanol to yield colorless crystalline chlorocarbonyltetrakis[*dimethyl(phenyl)phosphine*]rhenium(I) (2.5 g). *Anal.* Calcd for $\text{C}_{33}\text{H}_{44}\text{ClOP}_4\text{Re}$: C, 49.4; H, 5.5. Found: C, 49.6; H, 5.7. A single sharp $\nu(\text{CO})$ band at 1792 cm⁻¹ (CH_2Cl_2) was observed.

Titanium tetrachloride as supplied by Hopkin and Williams (120 cm³) was stirred under dry dinitrogen with Cu powder (5 g) for 20 min in a bath maintained at 95°. The mixture was filtered through a coarse sinter sealed onto the flask directly into a distillation apparatus. The liquid was distilled under dinitrogen through a fractionating column at atmospheric pressure. A forerun of ca. 20 cm³ was discarded and the completely colorless fraction boiling at 135° collected in a receiver fitted with a break-seal arm. The receiver was sealed off and the side arm with the break seal attached to the vacuum line for all further manipulations. The container was protected from light.

Manipulation of TiCl_4 . The TiCl_4 reservoir was connected to the high vacuum line *via* two Rotaflo PTFE taps arranged so that both the vacuum manifold and the TiCl_4 reservoir could be sealed off using the "better" seal provided by the end of the PTFE plunger. All other taps in the system were of the normal greased type and were cleaned and regreased after each operation involving TiCl_4 . Also attached to the line was a graduated tube of capacity 1 cm³. TiCl_4 , as required, was transferred to this liquid buret by distillation and then known volumes of liquid could be dispensed to reaction mixtures, etc., by distillation.

Manipulation of Adducts. All the adducts described here were air sensitive, especially in solution, and were handled either on the vacuum line or under dinitrogen dried with 1500 g of activated Linde molecular sieves (4A) packed into a tube ca. 1 m long.

$[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$. Dichloromethane (ca. 25 cm³) was distilled from P_2O_5 on the vacuum line to a reaction flask containing $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (0.97 g). TiCl_4 (0.066 cm³) was then transferred to the reaction flask which was allowed to warm up to room temperature yielding a deep blue solution. Pentane (45 cm³) was added under dinitrogen with stirring. The resulting solution was immediately filtered under dinitrogen and the filtrate upon standing at room temperature deposited $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$ as deep blue crystals with a red luster. The crystals were dried at room temperature under high vacuum for 6 hr, yield 0.90 g. *Anal.* Calcd for $\text{C}_{66}\text{H}_{92}\text{Cl}_{10}\text{N}_4\text{P}_8\text{Re}_2\text{Ti}$: C, 40.4; H, 4.7; Cl, 18.1; N, 2.9; P, 12.6; Ti, 2.4. Found: C, 40.8; H, 4.7; Cl, 18.2; N, 2.9; P, 12.8; Ti, 2.5. The material was desolvated at 60° under high vacuum for 5 hr. *Anal.* Calcd for $\text{C}_{64}\text{H}_{88}\text{Cl}_6\text{N}_4\text{P}_8\text{Re}_2\text{Ti}$: C, 42.8; H, 4.9; Cl, 11.8; N, 3.1; P, 13.8. Found: C, 42.6; H, 4.9; Cl, 11.6; N, 3.2; P, 13.4.

An identical product was obtained from $[\text{TiCl}_3(\text{thf})_3]$ as follows: A deep mauve solution of $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (0.62 g) and $[\text{TiCl}_3(\text{thf})_3]$ (0.29 g) in benzene (15 cm³) (distilled on a vacuum line from LiAlH_4) was exposed with stirring to dry air (18 hr). Addition of dry hexane precipitated the crude product which was recrystallized from dichloromethane-pentane. The ir spectrum (Nujol mull) was identical with that of the above analytically pure dichloromethane-

solvated product. *Anal.* Calcd for $\text{C}_{66}\text{H}_{92}\text{Cl}_{10}\text{N}_4\text{P}_8\text{Re}_2\text{Ti}$: C, 40.4; H, 4.7; Cl, 18.1; N, 2.9. Found: C, 40.0; H, 4.8; Cl, 17.3; N, 2.9.

$[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{C}_6\text{H}_6)_{1.5}]$. Benzene (15 cm³) was distilled on the vacuum line from LiAlH_4 onto TiCl_4 (0.041 cm³) and the resulting solution at room temperature was added under dinitrogen to a solution of $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (0.60 g) in benzene (7 cm³). Pentane (25 cm³) was added with stirring under dinitrogen and the solution was immediately filtered. The filtrate upon standing at room temperature deposited $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{C}_6\text{H}_6)_{1.5}]$ as deep blue crystals with a red luster. The solid was dried at room temperature under vacuum, yield 0.65 g. *Anal.* Calcd for $\text{C}_{73}\text{H}_{97}\text{Cl}_6\text{N}_4\text{P}_8\text{Re}_2\text{Ti}$: C, 45.9; H, 5.1; Cl, 11.1; N, 2.9. Found: C, 45.4; H, 5.1; Cl, 11.1; N, 3.0. No further benzene was lost after 5 hr at 60° under high vacuum for the elemental composition was unchanged.

$[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{thf})]$. TiCl_4 (0.076 cm³) was distilled on the vacuum line into thf (15 cm³) (which had been previously distilled from LiAlH_4 on the line) in a reaction vessel equipped with a rotatable side arm containing $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (0.57 g). The solution was allowed to warm to room temperature and the $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ introduced with stirring, yielding a deep red solution. Addition of pentane (20 cm³) under dinitrogen precipitated crude product which was redissolved in dichloromethane (10 cm³). Pentane (30 cm³) was added with stirring and the solution was immediately filtered. The filtrate upon standing at -10° deposited very deep red crystals which had a strong tendency to hold a fraction of a mole of dichloromethane. The solid was dried at 50° under vacuum for 5 hr yielding $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4(\text{thf})]$ (0.60 g). *Anal.* Calcd for $\text{C}_{36}\text{H}_{52}\text{Cl}_5\text{N}_2\text{OP}_4\text{ReTi}$: C, 40.6; H, 4.9; Cl, 16.7; N, 2.6; P, 11.6; Ti, 4.5. Found: C, 40.4; H, 4.9; Cl, 16.6; N, 2.7; P, 11.5; Ti, 4.6.

$[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$. A solution of TiCl_4 (0.242 cm³) in benzene (25 cm³) was added with stirring under dinitrogen to a solution of $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (0.59 g) in benzene (5 cm³) and diethyl ether (40 cm³). The red-brown solid which precipitated was collected and dried at 45° for 5 hr under vacuum, yield 0.69 g. The residue was dissolved in dichloromethane (1 cm³) and diethyl ether (20 cm³) was added yielding an amorphous red-brown precipitate of $[\{\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4\}_2(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$. The solid was dried at 45° under high vacuum for 5 hr, yield 0.47 g. *Anal.* Calcd for $\text{C}_{36}\text{H}_{54}\text{Cl}_7\text{N}_2\text{O}_2\text{P}_4\text{ReTi}_2$: C, 36.0; H, 4.5; Cl, 20.7; N, 2.3; P, 10.3; Ti, 8.0. Found: C, 35.8; H, 4.5; Cl, 21.7; N, 2.5; P, 10.6; Ti, 8.1.

$[\{\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4]$. TiCl_4 (0.046 cm³) was distilled on the vacuum line into dichloromethane (20 cm³) in a flask equipped with a rotatable side arm containing $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ (0.68 g). After the solution had warmed up to room temperature the $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ was introduced with stirring. Pentane (50 cm³) was added with stirring under dinitrogen and the resulting suspension was immediately filtered. The filtrate upon standing at -10° under dinitrogen yielded $[\{\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4\}_2\text{TiCl}_4]$ as deep blue crystals which were dried at 45° under high vacuum for 3 hr, yield 0.29 g. *Anal.* Calcd for $\text{C}_{66}\text{H}_{88}\text{Cl}_6\text{O}_2\text{P}_8\text{Re}_2\text{Ti}$: C, 44.2; H, 4.9; Cl, 11.9; P, 13.8; Ti, 2.7. Found: C, 43.9; H, 4.8; Cl, 11.6; P, 13.5; Ti, 2.9.

Reaction of $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ with Excess TiCl_4 . A solution of $[\text{ReCl}(\text{CO})(\text{PMe}_2\text{Ph})_4]$ in dichloromethane treated with 3 *M* proportions of TiCl_4 showed only a single $\nu(\text{CO})$ band at 1920 cm⁻¹. An equal volume of ethanol was added and the resulting yellow solution upon standing at room temperature deposited yellow crystals which showed an ir spectrum identical with that of authentic $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$ prepared by the method of Gunz.¹² Authentic $[\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$ in CH_2Cl_2 showed $\nu(\text{CO})$ at 1870 cm⁻¹ which was shifted to 1920 cm⁻¹ upon introduction of 1 molar equiv of TiCl_4 .

Microanalyses. Carbon, hydrogen, nitrogen, chlorine, and phosphorus were determined by Dr. A. Bernhardt, Hohenweg 17, West Germany. Titanium was determined by the spectrophotometric peroxide method after destruction of the complex with hot concentrated sulfuric-perchloric acid mixtures.

Physical Measurements. Ir spectra were recorded on Unicam 200G (1500-2000 cm⁻¹), Unicam SP 1200 (400-4000 cm⁻¹), and Grubb-Parsons D.M.4. (200-400 cm⁻¹) instruments. Visible-uv spectra were recorded on a Unicam SP 1800 instrument. ¹H nmr spectra were recorded on a Jeol PS-100 instrument using CD_2Cl_2 as solvent with CH_2Cl_2 as internal standard. The diamagnetism of $[(\text{ReN}_2)_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$ and $[(\text{ReCO})_2\text{TiCl}_4]$ was observed by the Faraday method but the diamagnetism of the other more air-sensitive adducts was inferred from the normal ¹H nmr spectra. Conductance measurements were made in anhydrous dichloromethane at ca. 20°

using a Portland Electronics conductivity bridge and an evacuable conductance cell which could be attached to the vacuum line for introduction of solvent by distillation. Esca measurements were made on an AEI E.S.-100 instrument modified so that air-sensitive samples could be introduced.

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Registry No. $[\text{ReCl}_2(\text{N}_2\text{COPh})(\text{PPh}_3)_2]$, 34347-22-3; $[\text{ReCO}]$, 25259-88-5; $[(\text{ReN}_2)_2\text{TiCl}_4(\text{CH}_2\text{Cl}_2)_2]$, 42934-19-0; $[\text{ReN}_2]$, 25263-89-2; $[\text{TiCl}_3(\text{thf})_3]$, 18039-90-2; $[(\text{ReN}_2)_2\text{TiCl}_4(\text{C}_6\text{H}_6)_{1.5}]$, 42934-20-3; $[(\text{ReN}_2)_2\text{TiCl}_4(\text{thf})]$, 42934-21-4; $[(\text{ReN}_2)(\text{Ti}_2\text{Cl}_6\text{O})(\text{Et}_2\text{O})]$, 39455-32-8; $[(\text{ReCO})_2\text{TiCl}_4]$, 43070-52-6.

Notes

Contribution from the Departments of Chemistry, Boston University, Boston, Massachusetts 02215, and Stanford University, Stanford, California 94305

Nitrogen-15-Labeled Complexes of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$

S. Pell, R. H. Mann, H. Taube, and J. N. Armor*

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Although the positions of the bands in the infrared spectrum of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$ have been reported in detail,¹ only brief references^{2,3} have been made to the exact positions of some of the dinitrogen-labeled complexes. Several years ago,⁴ we began to compile data on the dinitrogen-28 and -29 complexes. Only recently, we have developed an efficient method for preparing pure samples of the dinitrogen-29 complex.⁵ In the course of our work, we also prepared the dinitrogen-30 sample for another investigator. Quinby and Feltham⁶ recently published estimates for the dinitrogen bands in $\text{Ru-}^{14}\text{N-}^{15}\text{N}$ and $\text{Ru-}^{15}\text{N-}^{14}\text{N}$ based upon curve resolution of our earlier data. We now have a complete set of more accurate results. While their conclusions do not need to be altered, the actual positions of the bands are sufficiently shifted to warrant a further report. In addition, a complete description of the dinitrogen bands in the infrared spectrum of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$ (when N_2 is 28, 29, or 30) will be presented. We believe that such a compilation will prove useful for future investigators seeking to assess the exact origin of the transitions and pursuing the mechanistic details of other dinitrogen formation reactions

Experimental Section

$[\text{Ru}(\text{NH}_3)_5^{28}\text{N}_2]\text{Br}_2$ was prepared by any one of several synthetic procedures.^{1,5,7,8} $[\text{Ru}(\text{NH}_3)_5^{29}\text{N}_2]\text{Br}_2$ was prepared by reaction of Cr^{2+} with $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{O}^{2+}$ with the N_2O labeled in either the endo or exo positions ($^{15}\text{N-N-O}$ or $\text{N-}^{15}\text{N-O}$). Alternatively, the treatment of alkaline solutions of $\text{Ru}(\text{NH}_3)_6^{3+}$ with ^{15}NO also results in the formation of the $^{29}\text{N}_2$ complex.⁵ $[\text{Ru}(\text{NH}_3)_5^{30}\text{N}_2]\text{Br}_2$ was prepared by Cr^{2+} reduction of $[\text{Ru}(\text{NH}_3)_5^{15}\text{N-}^{15}\text{N-O}]^{2+}$. The latter was formed in solution upon the treatment of $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ with $^{15}\text{N-}^{15}\text{N-O}$.⁸ All compounds were checked for their purity using the λ_m at 221 nm,

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ϵ $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Of the compounds described above, only the $[\text{Ru}(\text{NH}_3)_5^{30}\text{N}_2]\text{Br}_2$ displayed a significant impurity (and it was the $[\text{Ru}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ complex (~17%).

Ir spectra in the range $4000\text{--}250 \text{ cm}^{-1}$ were recorded as Nujol mulls on KBr plates using a Perkin-Elmer 180 ir spectrometer. A few room-temperature spectra were recorded using KBr disks. The 2180-cm^{-1} region was calibrated using atmospheric CO_2 (2350 cm^{-1}). The 500-cm^{-1} region was calibrated using atmospheric water vapor.⁹ Low-temperature spectra were obtained by mounting the KBr plates (~30 mg of Ru complex, 2 drops Nujol) against a copper cold finger filled with liquid nitrogen. This unit was placed inside a glass sleeve through which cold, dry nitrogen was purged. The flow of cold nitrogen over the faces of the KBr disks prevented the formation of significant amounts of ice on the faces of the disk. The glass sleeve was clamped into position in the sample beam and encased within a large plastic sheet taped to the instrument. Reproducible low-temperature spectra were obtained within 3 min after pouring liquid nitrogen into the copper cold finger.

Results and Discussion

The data in Table I summarize the dinitrogen frequencies for the four possible isomers obtained using ^{14}N and ^{15}N sources of nitrogen. The values for $^{14}\text{N-}^{15}\text{N}$ and $^{15}\text{N-}^{14}\text{N}$ frequencies are based upon equilibrated samples of $^{14}\text{N-}^{15}\text{N}$ or $^{15}\text{N-}^{14}\text{N}$ (prepared *via* the appropriately labeled samples of the nitrous oxide complexes). In addition, the value for the $^{14}\text{N-}^{15}\text{N}$ frequency has been confirmed by the direct reaction of ^{15}NO with the coordinated ammine.⁵ While the definition of the bands varied as a function of the preparation, the apparent increase in intensity and sharpening of the bands at low temperature did provide an opportunity to assign the bands in Table I. On lowering the temperature, all the bands for $\delta_{\text{Ru-N}_2}$ were shifted $\sim 4 \text{ cm}^{-1}$ toward higher energy.

When one allows for the affect of counterion¹⁰ on the exact positions of dinitrogen frequencies in the ir spectrum, our values are found to be internally consistent with previously published values in the 2100-cm^{-1} region.^{2,3} Shifts on the order of $\Delta\nu \sim 70 \text{ cm}^{-1}$ for Ru^{28}N_2 vs. $\text{Ru-}^{30}\text{N}_2$ have been reported in the past.¹¹⁻¹³ However, one report² claims that $\text{Ru-}^{14}\text{N-}^{15}\text{N}$ absorbs at 2098 cm^{-1} (as the I^- salt), while $\text{Ru-}^{15}\text{N-}^{14}\text{N}$ absorbs at 2094 cm^{-1} . Within the resolution afforded by our instruments in this spectral region, we did not observe any splitting of equilibrated mixtures of the Br^- salts for $\text{Ru-}^{14}\text{N-}^{15}\text{N}$ or $\text{Ru-}^{15}\text{N-}^{14}\text{N}$ in Nujol mulls. In addition, KBr disks of our $\text{Ru-}^{29}\text{N}_2$ samples demonstrated no discernible

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