## Conversion of Molecular Nitrogen to Hydrazine

*Sir:*

We wish to report that molecular nitrogen, on successive treatment with a transition metal alkoxide–radical anion system[1] and proton source, generates hydrazine, apparently the first case of substantial transition metal catalyzed conversion of elemental

$$\mathrm{N_2 + 4e^- + 4H^+ \longrightarrow N_2H_4}$$

nitrogen to any compound other than ammonia.[2]

After addition during 15–90 min of titanium(IV) isopropoxide to a stirred THF solution of sodium naphthalide under nitrogen, all at room temperature and atmospheric pressure, immediately followed by hydrolysis,[1] there were liberated hydrazine and ammonia in proportions which were dependent upon the ratio of the fixing to the reducing agents. The yield of hydrazine rose with decreasing Ti(IV):NaNP molar ratios to a maximum of 15–19% (based on Ti) at a Ti(IV):NaNP ratio of 1:5–6, while the $\mathrm{2NH_3{:}N_2H_4}$ ratio varied within the range 3.3–5.0.

Initially, the presence of hydrazine in hydrolysates was indicated by a spot test method of Feigl.[3] Confirmatory identification was made by means of the *p*-dimethylaminobenzaldehyde azine,[4] prepared from the fixation–reduction hydrolysate after removal of ammonia, THF, and naphthalene, followed by acidification. Hydrazine was determined quantitatively by a known spectrophotometric method.[5]

When any one of the transition metal compounds $\mathrm{CoCl_2}$, $\mathrm{MoCl_5}$, $\mathrm{WCl_6}$, $\mathrm{CrCl_3}$, $\mathrm{NiBr_2}$, or $\mathrm{FeCl_3}$ was substituted for titanium(IV) isopropoxide in the experimental procedure described (6 molar equiv of NaNP used), no hydrazine could be detected as product.[6] Also, no hydrazine apparently was formed when a benzene solution of the previously described[1] $\mathrm{(C_5H_5)_2Ti\cdot N_2}$ dimer was exposed to water, alcohol, aqueous acid, aqueous base, or 2–4 molar equiv of NaNP in THF. Similarly, the $\mathrm{Ru^{II}(NH_3)_5N_2}$[7] ion did not generate hydrazine on treatment with limited amounts of NaNP.

Although a complete description of the reaction course is not possible at this time, various observations permit a tentative interpretation of the hydrazine–ammonia synthesis sequence. The titanian hydrazine progenitor is subject to further *in situ* reduction, as shown by the increase (to 22) in the $\mathrm{2NH_3{:}N_2H_4}$ ratio after a reaction mixture of the type described above is treated overnight with a large excess (12 equiv) of sodium naphthalide. The nitrogeneous unit, convertible in the protonation step to hydrazine, is capable of transferral from the titanium sphere, as shown by the absence of hydrazine formation after a fixation–reduction reaction, as described above, is carried out in the presence of Al(III), presumed to effect abstraction from titanium of hydrazine level nitrogen and then permit facile, subsequent reduction to the ammonia level.[8] Lack of appreciable molecular nitrogen liberation during the protonation step is consistent with the absence of diimide-level bound nitrogen, which normally would, on protonation, release free diimide, known to disproportionate rapidly to elemental nitrogen and hydrazine. If the foregoing is taken in conjunction with previously acquired knowledge of this system,[1] the relationships expressed in Chart I emerge.

**Chart I**

$$\begin{tikzcd}
\mathrm{Ti(OR)_4} \arrow[r, "\mathrm{NaNp}"] & \mathrm{[Ti(OR)_2]_{\mathit{x}}} \arrow[r, "\mathrm{N_2}"] & \mathrm{[Ti(OR)_2\cdot N_2]_{\mathit{x}}} \arrow[r, "\mathrm{4NaNp}"] & {} \\
 & & \mathrm{[Ti(OR)_2\cdot N_2]_{\mathit{x}}{}^{4-}} \arrow[r, "\mathrm{2NaNp}"] \arrow[d, "\mathrm{4H^+}"] & \mathrm{[Ti(OR)_2\cdot N_2]_{\mathit{x}}{}^{6-}} \arrow[d, "\mathrm{6H^+}"] \\
 & & \mathrm{N_2H_4} & \mathrm{2NH_3}
\end{tikzcd}$$

**Acknowledgment.** Financial support was provided by the National Institutes of Health (GM 13797).

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[1] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969), and references provided therein.

[2] M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, and L. A. Prodayko, *Chem. Commun.*, 1038 (1969), have described the formation of aniline in 3% yield by reaction of nitrogen with dicyclopentadienyltitanium dichloride and phenyllithium in ether.

[3] F. Feigl, "Spot Tests in Inorganic Analysis," Elsevier Publishing Co., New York, N. Y., 1958, p 240.

[4] (a) Product obtained as orange-yellow crystals, mp 253–254° (authentic azine, orange-yellow crystals, mp 251.5–254° [lit.[4b] 250–253° dec)]; mmp with authentic azine, 252.5–254°; infrared spectra of both compounds as mineral oil mulls were identical. (b) D. Vorländer, *Ber.*, **39**, 808 (1906).

[5] G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

[6] In one experiment, $\mathrm{VCl_3}$ was observed to promote hydrazine formation under the conditions defined.

[7] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

[8] Observation made by Dr. D. Seeley, Stanford University.

**E. E. van Tamelen, R. B. Fechter, S. W. Schneller**

*Department of Chemistry, Stanford University*
*Stanford, California 94305*

*Received September 26, 1969*

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## σ-Alkyl or σ-Acyl Isocyanide Complexes of Nickel(II) and Palladium(II). Preparation and Successive Insertion Reactions

*Sir:*

σ-Alkyl metal carbonyl compounds are well known, and their insertion reactions of carbon monoxide into the metal–alkyl bond have been studied extensively.[1] However, little work has been done with σ-organo isocyanide complexes.[2]

We wish, therefore, to report preparations of alkyl or acyl isocyanide complexes of palladium and nickel, and also isocyanide insertion reactions. Of particular interest are the successive insertions of more than two isocyanide molecules, a type of reaction not observed for carbonyl derivatives.

Addition of $\mathrm{CH_3I}$ to $\mathrm{Pd(\mathit{t}\text{-}BuNC)_2}$ in *n*-hexane at 0° produced *trans*-$\mathrm{PdI(CH_3)(\mathit{t}\text{-}BuNC)_2}$[3] (**1**), in 42% yield, as diamagnetic, colorless crystals, mp 77–78°. Both the ir and nmr spectra (Table I) dictate the *trans* configuration for **1**. Under an inert atmosphere, **1** is fairly stable in the solid but unstable in solution. Even at 11° in toluene an insertion reaction takes place leading to an iminoacylpalladium (**2**), which was detected *in situ* by means of nmr spectra which show three singlets at $\tau$ 7.88 ($\mathrm{CH_3}$), 8.63 ($\mathrm{\mathit{t}\text{-}C_4H_9N{=}C}$), and 9.50 ($\mathrm{\mathit{t}\text{-}C_4H_9NC}$). The instability of the compound prevented its isolation.

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[1] F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, pp 526–617.

[2] A recent report discussed $\mathrm{Ni(R)(\pi\text{-}C_5H_5)(R'NC)}$ as a possible intermediate for formation of iminoacyl-metal compounds; see Y. Yamamoto, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 532 (1968); *J. Organometal. Chem.*, **18**, 189 (1969).

[3] Elemental analysis and molecular weight data conformed reasonably to the respective theoretical values.