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

$$N_2 + 4e^- + 4H^+ \longrightarrow N_2H_4$$

nitrogen to any compound other than ammonia.[2]

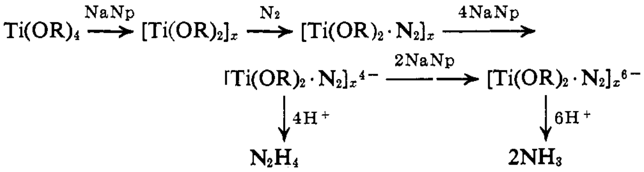
After addition during 15–90 min of titanium(IV) isopropoxide to a stirred THF solution of sodium naphthalide under nitrogen, all at room temperature and atmospheric pressure, immediately followed by hydrolysis,[1] there were liberated hydrazine and ammonia in proportions which were dependent upon the 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 $2NH_3$: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 $CoCl_2$, $MoCl_5$, WCl_6, $CrCl_3$, $NiBr_2$, or $FeCl_3$ 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] $(C_5H_5)_2Ti \cdot N_2$ dimer was exposed to water, alcohol, aqueous acid, aqueous base, or 2–4 molar equiv of NaNP in THF. Similarly, the $Ru^{II}(NH_3)_5N_2$[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 $2NH_3$: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



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

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

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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, VCl_3 was observed to promote hydrazine formation under the conditions defined.

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

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 CH_3I to $Pd(t\text{-}BuNC)_2$ in *n*-hexane at 0° produced *trans*-$PdI(CH_3)(t\text{-}BuNC)_2$[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 τ 7.88 (CH_3), 8.63 ($t\text{-}C_4H_9N{=}C$), and 9.50 ($t\text{-}C_4H_9NC$). 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 $Ni(R)(\pi\text{-}C_5H_5)(R'NC)$ 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.

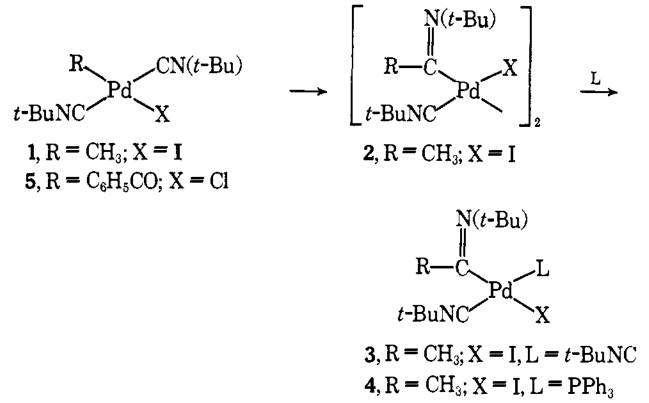
Table I. Infrared and Nmr Spectra

	Ir, cm^{-1} [a]			Nmr, τ [b]		
	C≡N	C═N	C═O	*t*-BuNC	*t*-BuN═C	CH$_3$
$\mathrm{CH_3Pd}(t\text{-BuNC})_2\mathrm{I}$ (**1**)	2180			9.42 (6)		8.99 (1)
$\mathrm{CH_3}(t\text{-BuN{=}C})\mathrm{Pd}$ (**3**) $(t\text{-BuNC})_2\mathrm{I}$	2180	1652		9.17 (6)	8.35 (3)	7.54 (1)
$\mathrm{CH_3}(t\text{-BuN{=}C})\mathrm{Pd}$ (**4**) $(t\text{-BuNC})(\mathrm{PPh_3})\mathrm{I}$	2183	1660		9.41 (3)	8.65 (3)	7.88 (1)
$\mathrm{PhCOPd}(t\text{-BuNC})_2\mathrm{Cl}$ (**5**)	2195		1657	9.40		
$\mathrm{PhCONi}(t\text{-BuNC})_3\mathrm{Cl}$ (**6**)	2178		1644			
$\mathrm{CH_3}(t\text{-BuN{=}C})_3\mathrm{Ni}$ (**7**)	2172	1667		9.07 (3)	8.42 (3)	8.08 (1)
$(t\text{-BuNC})\mathrm{I}$		1634			8.44 (3)	
		1610			8.55 (3)	
$\mathrm{PhCO}(t\text{-BuN{=}C})_5\mathrm{Ni}$ (**8**)	2174	1645 [c]	1675 [c]	9.15 (1)	8.24 (1)	
$(t\text{-BuNC})\mathrm{Cl}$		1638			8.29 (1)	
		1612			8.39 (1)	
		1598			8.55 (1)	
		1582			8.84 (1)	

[a] Ir spectra are taken in Nujol mull. [b] Nmr spectra are obtained in C_6D_6 or $C_6D_5CD_3$ with TMS as internal reference. Intensity ratios are indicated in parentheses. All the signals are observed as sharp singlets. [c] Tentative assignment.

It is likely that **2** is a dimer. Addition of a donor ($t\text{-}C_4H_9NC$ or PPh_3), either to the above solution of **2**, or directly to a *n*-hexane solution of **1** at room temperature, results in a stable tetracoordinated Pd(II) complex (**3** or **4**), and thus suggests that **2** is an intermediate (Scheme I).

Scheme I



1, R = CH$_3$; X = I

5, R = C$_6$H$_5$CO; X = Cl

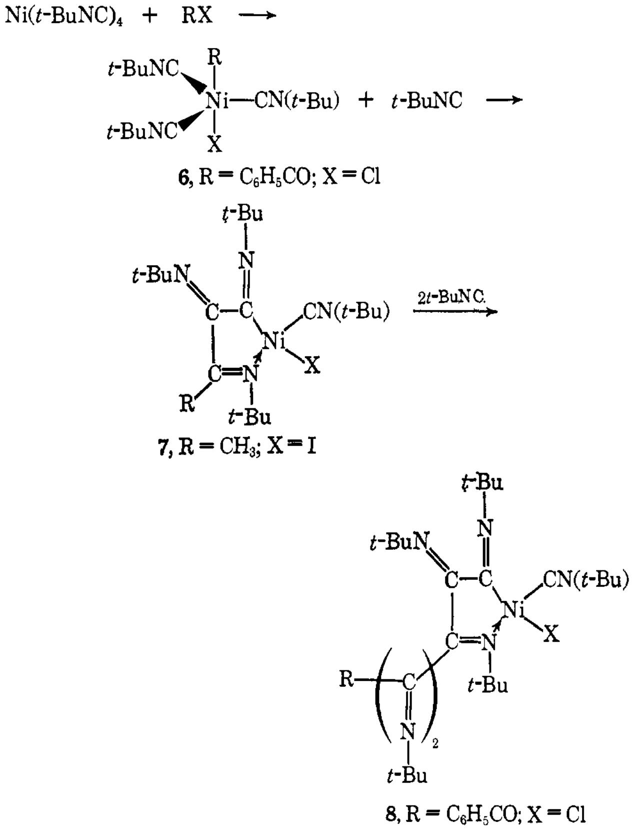
2, R = CH$_3$; X = I

3, R = CH$_3$; X = I, L = *t*-BuNC

4, R = CH$_3$; X = I, L = PPh$_3$

The complex **3**[3] is in the form of diamagnetic, pale yellow crystals, mp 135–138° dec. The ir and nmr spectra (Table I) indicate *trans* configuration. The complex **4**[3] (diamagnetic, colorless crystals, mp 95–97°) is kinetically and thermally less stable than **3**. The spectral data (Table I) do not allow one to unambiguously establish the positions of the four different ligands in **4**. By analogy with **3**, *trans* alignment of the iodo and the σ-iminoacyl groups has been tentatively postulated.

Scheme II



6, R = C$_6$H$_5$CO; X = Cl

7, R = CH$_3$; X = I

8, R = C$_6$H$_5$CO; X = Cl

Attempted preparation of a nickel analog of **3** from $\mathrm{Ni}(t\text{-BuNC})_2$[4] was unsuccessful. When $\mathrm{Ni}(t\text{-BuNC})_4$[4] was treated with CH_3I in *n*-hexane at ambient temperatures, successive insertion of three isocyanide molecules took place, affording a new σ-iminoacyl complex **7**,[3] in 91% yield, as diamagnetic, orange-yellow crystals (see Scheme II). Structural assignment of **7** was primarily based on its ir and nmr spectra (Table I). Chelate coordination through the lone pair electrons of the terminal imino nitrogen atom was deduced from the monomeric nature and enhanced stability of **7**. Again the iodo and the iminoacyl groups were postulated to be *trans*. An incipient species would be the pentacoordinated complex of type **6**. When C_6H_5COCl was employed in place of CH_3I, **6** was isolated (in 74% yield) as diamagnetic, pale yellow microcrystals,[3] mp 83–85°. The ir spectrum indicates a trigonal-bipyramidal structure (C_{3v}) for **6**. It is stable in solid state but unstable in solution at room temperature, and undergoes multiple successive insertion reactions. In the same reaction of C_6H_5COCl with $\mathrm{Ni}(t\text{-BuNC})_4$, a red crystalline complex was also found, in 8.2% yield. The red complex was formulated as **8**,[3] based on the ir and nmr spectra[5] (Table I). An intervening species

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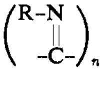
(4) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Am. Chem. Soc.*, **91**, 6994 (1969).

(5) The five different *t*-butyl proton signals are also consistent with a six-membered polyimino chelate structure instead of the five-membered chelate depicted.

between **6** and **7** is likely to be a nickel analog of **3**. However, the tendency of nickel(II) to achieve pentacoordination facilitates the insertions resulting in **7**.

When an excess of *t*-butyl or other isocyanide was heated above room temperature (30–60°) in the presence of **7**, the isocyanide was converted into polyisocyanide with a repeating unit[6]


$$\left(\begin{array}{c} R\text{-}N \\ \| \\ \text{-}C\text{-} \end{array}\right)_n$$

The above successive insertion reactions suggest a mechanism for the catalytic polymerization of isocyanides.

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[6] Y. Yamamoto and N. Hagihara, *Bull. Chem. Soc. Jap.*, 39, 1084 (1966).

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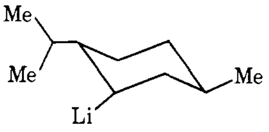
Cyclohexylmetal Compounds. IV. The Effect of Aggregate Size on the Reactivity of Alkyllithium Compounds[1]

Sir:

Subsequent to our original investigation of menthyllithium (I)[1,2] and 4-*t*-butylcyclohexyllithium,[1-3] we have discovered that the former is an extremely reactive alkyllithium compound by all available standards. For example, I reacts with bromobenzene in *n*-pentane (halogen–lithium interchange) and with 1,1-diphenylethylene (DPE) in benzene (addition) at rates too fast to measure by conventional techniques. By comparison, bromobenzene reacts with *n*-butyllithium and *sec*-butyllithium under similar conditions with half-lives of *ca.* 19 hr and 19 min, respectively.[4] Initial rates for the addition of RLi to DPE in benzene at 30° are 0.12×10^{-6} and 9.17×10^{-6} M/sec for *n*-butyllithium[5] and *sec*-butyllithium, respectively.[6] Under similar conditions, the addition of menthyllithium to DPE must have an initial rate greater than 625×10^{-6} M/sec.



I

Further evidence of the unusual reactivity of I is its ability to metalate toluene in the absence of basic catalysts. We have compared I to *n*-BuLi·TMEDA, *sec*-butyllithium, and cyclohexyllithium in this respect. Thus, 8.25 mmol of RLi and 47 mmol of toluene were allowed to react at 50° for 6 hr, followed by derivatization with chlorotrimethylsilane–diethyl ether. The trimethylsilylated derivatives were identified by glpc and nmr and quantitated by an internal standard. Yields of metalated products were R = cyclohexyl, 6.2%; *sec*-butyl 2.3%; *n*-butyl–TMEDA, 15.9%; and I, 35%. Under these conditions I produces approximately a 9:1 mole ratio of benzyllithium:dimetalated toluenes, the latter of as yet unspecified structures. With higher RLi:toluene ratios the yields of dimetalated and trimetalated toluenes increase significantly. Further work to determine the precise distribution of the polymetalated isomers is under way, and will be reported later.

Finally, we report that I will apparently react with tetraphenylethylene in hydrocarbon media, the first example of such a reaction involving an alkyllithium compound. Reaction of I with TPE in benzene yields a reddish brown, insoluble product. The observation of an esr signal during this reaction indicates that I transfers an electron to TPE forming the tetraphenylethylene radical anion. The fate of the latter under these conditions is probably the same as in more polar solvents, namely disproportionation to yield the dianion,[7] although proof of this is lacking at the moment.

The unusual reactivity of menthyllithium may be rationalized by an extension of ideas originally applied to a study of the rates of thermal decomposition of alkyllithium compounds.[8,9] Construction of models of the tetramer of *sec*-butyllithium suggested to us at that time that rather severe steric repulsions occur which are absent in *n*-butyllithium and *t*-butyllithium. We concluded that the tetramer structure of an alkyllithium compound would be unstable relative to the dimer if (a) the compound were a secondary or tertiary lithium compound, and (b) it were substituted at the position β to the carbon–lithium bond. If we furthermore assumed that the dimer species would be more reactive than the tetramer,[10] these considerations would predict that *sec*-butyllithium would be more reactive than *n*-butyllithium or *t*-butyllithium, as observed, but also that alkyllithium compounds with more bulky substituents in the β position would be even more reactive. That menthyllithium is branched in the β position with an isopropyl group and is, in fact, significantly more reactive than *sec*-butyllithium would seem to us to be confirmation of these ideas. In fact, we were amazed to

Table I. Molecular Association of Menthyllithium[a]

Solvent	Concn, *M*	Degree of association
Cyclohexane	0.23, 0.29	2.17, 1.95
Benzene	0.10, 0.38	1.93, 2.04

[a] Determined by depression of freezing point of solvent; solutions contained 90–96% carbon-bound lithium.

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[1] Part III: W. H. Glaze, C. M. Selman, A. L. Ball, Jr., and L. E. Bray, *J. Org. Chem.*, 34, 641 (1969).

[2] W. H. Glaze and C. M. Selman, *ibid.*, 33, 1987 (1968).

[3] W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, 11, P3 (1968).

[4] Kinetic data for bromobenzene–RLi reactions were obtained by monitoring bromobenzene and alkyl bromide by glpc. Aliquots were removed with a microliter syringe from reaction vessels fitted with syringe caps. An internal standard was employed. The identity of the alkyl bromide was established by spiking with known material and observing the glpc pattern.

[5] A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961).

[6] Initial rates for RLi–DPE reactions were measured spectrophotometrically at or near the absorption maximum of the adduct $CH_2RC(Li)Ph_2$ (440 mμ for *sec*-butyllithium and menthyllithium). The initial rates referred to above were measured at initial concentrations of RLi and DPE of 2.46×10^{-2} and 8.88×10^{-3} M, respectively. The initial rate for *n*-butyllithium was calculated from the data of Evans and George[5] under identical conditions.

[7] A. G. Evans, J. C. Evans, E. D. Owens, B. J. Tabner, and J. E. Bennett, *Proc. Chem. Soc.*, 226 (1962).

[8] W. H. Glaze, J. Lin, and E. G. Felton, *J. Org. Chem.*, 31, 2643 (1966).

[9] W. H. Glaze and G. M. Adams, *J. Amer. Chem. Soc.*, 88, 4653 (1966).

[10] T. L. Brown, *J. Organometal. Chem.*, 5, 191 (1966).