Amine Formation in Molecular Nitrogen Fixation: Nitrogen Insertion into Transition Metal–Carbon Bonds

By M. E. VOLPIN,* V. B. SHUR, R. V. KUDRYAVTSEV, and L. A. PRODAYKO

(*Institute of Organo-Element Compounds, Academy of Science of the U.S.S.R., Vavilova Street,* 28, *Moscow, U.S.S.R.*)

WE have found that a number of systems based on transition-metal compounds and reducing agents are capable of reacting with molecular nitrogen, under mild conditions.[1] Upon hydrolysis of the reaction products ammonia is formed. The nitrogen fixation by these systems seems to proceed *via* intermediate nitrogen complexes of transition-metal compounds.

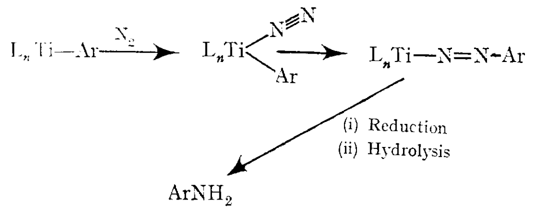
Carbon monoxide, olefins, and acetylenes are well known to be capable of insertion into transition metal–carbon bonds. The corresponding complexes of unsaturated compounds with a transition-metal atom are intermediate in these reactions.

It appeared that molecular nitrogen could also undergo similar insertions to give organic nitrogen compounds. We have found that detectable amounts of amines are formed by reaction of nitrogen with some systems involving transition-metal derivatives and organometallic compounds, *i.e.* under the conditions for transition metal–carbon bond formation.

Thus, on bubbling nitrogen through a mixture of $(C_5H_5)_2TiCl_2$ or $(C_5H_5)_2TiPh_2$ and a 5-fold excess of PhLi, in ether (room temperature and atmospheric pressure), aniline (0·03 mol.[†]) and ammonia (0·17 mol.) are formed after hydrolysis. With increased nitrogen pressure (up to 100 atmos.), the yields of aniline and ammonia increase to 0·15 and 0·65 mol. respectively (reaction time 11 hr.).[3] Together with the aniline a small amount of *o*-aminodiphenyl is formed. Similar aniline yields have been obtained from other titanium compounds [$C_5H_5TiCl_3$, $TiCl_4$, $Ti(OBu)_4$, *etc.*] with PhLi, in ether.[‡]

The nitrogen reaction with $(C_5H_5)_2TiCl_2$ and *p*-tolyl-lithium (11 hr., nitrogen pressure 100 atmos.) yields *p*-toluidine (0·07 mol.[§]) contaminated with 4% of *m*-isomer. Under the same conditions *m*-tolyl-lithium gives toluidines (0·04 mol.[§]), containing 97% of *m*-toluidine and nearly 3% of *p*-isomer. Thus nitrogen enters mainly to replace the metal atom in the original organometallic compound.

Amine formation in this reaction appears likely to involve insertion of molecular nitrogen into the Ti–Ar bond of some low-valent titanium derivative arising as a result of the reduction of the initial titanium compound with excess of ArLi.[2]

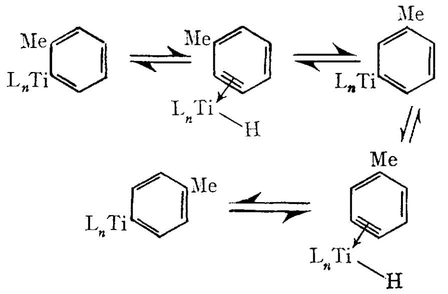


L = ligand

The intermediate arylazo-derivative of titanium is subjected to further reductive cleavage with production of an *N*-metal-substituted amine, yielding free amine on hydrolysis.

Arylazo-derivatives of this kind have been recently obtained in an indirect way for platinum[4] [$ArN{=}N{-}PtCl(PEt_3)_2$], molybdenum[5] [$ArN{=}N{-}Mo(CO)_2C_5H_5$], and tungsten[6] [$ArN{=}N{-}W(CO)_2{-}C_5H_5$]. Under the action of reducing agents the arylazo-group in these compounds is indeed capable of reductive cleavage to form aromatic amines.

Unexpected results have been obtained in the reaction of molecular nitrogen with *o*-tolyl-lithium and $(C_5H_5)_2TiCl_2$, when a mixture of all three isomeric toluidines (*o*-,*m*-, and a little of the *p*-isomer) was formed, in a total yield as high as 0·06 mol.[§] The isomer content in the mixture varied in different runs, generally being 40–77% for *o*-toluidine, 52—21% for the *m*-, and 8—2% for the *p*-isomer. The data obtained may be due to mutual isomerization of *o*-, *m*-, and *p*-tolyl–titanium bonds, probably brought about *via* benzyne-like compounds. The sterically less stable *o*-tolyl–titanium bond is isomerized to the more stable *m*-tolyl–titanium bond.



The formation of benzyne compounds in these reactions finds support in the detection of triphenylene (product of the cyclo-trimerization of benzyne) in the products of the reaction of $(C_5H_5)_2TiCl_2$ or $(C_5H_5)_2TiPh_2$ with PhLi.[2]

Benzyne formation also explains the presence of small amount of *o*-aminodiphenyl in the products of the reaction of nitrogen with $(C_5H_5)_2TiCl_2$ and PhLi. The origin of this amine seems to be *o*-diphenyl-lithium which can be formed in the benzyne reaction with an excess of PhLi.

The possibility of aliphatic amine formation in the reaction of molecular nitrogen with $(C_5H_5)_2TiCl_2$ and aliphatic organo-lithium and -magnesium compounds, such as C_2H_5MgBr, Bu^nLi *etc.*, has also been investigated: in such cases aliphatic amines either are not formed at all, or are formed in very low yields (*ca.* 0·002 mol.).

[†] Yields throughout are based on in moles per mole of the titanium compound.

[‡] Phenyl-lithium itself, without any added titanium compound, does not react with nitrogen under these conditions, neither do $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2TiPh_2$, and other titanium compounds investigated react with nitrogen without the excess of PhLi.

[§] Together with ammonia (0·2—0·3 mol.).

Thus, in passing from PhLi to MeC_6H_4Li and then to lithium alkyls, the yields of amines are sharply decreased. The stability of Ti–R bonds decreases in the same sequence, in agreement with the mechanism of amine formation, which involves the nitrogen insertion step into the titanium–carbon bond: the less the lifetime of the Ti–R bond in solution, the less the probability of nitrogen insertion into this bond.

(*Received, April* 30*th*, 1968; *Com.* 526.)

---

[1] M. E. Volpin and V. B. Shur, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 1102; M. E. Volpin and V. B. Shur, *Vestnik Akad. Nauk S.S.S.R.*, 1965, No. 1, 51; M. E. Volpin and V. B. Shur, *Zhur. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva*, 1967, **12**, 31; M. E. Volpin and V. B. Shur, *Nature*, 1966, **209**, 1236.

[2] V. N. Latyaeva, L. I. Vyshinskaya, V. B. Shur, L. A. Fiodorov, and M. E. Volpin, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 875.

[3] M. E. Volpin and V. B. Shur, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1966, 1873.

[4] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133; 1967, **89**, 1822.

[5] R. B. King, M. B. Bisnette, *J. Amer. Chem. Soc.*, 1964, **86**, 5694; *Inorg. Chem.*, 1966, **5**, 300.

[6] A. N. Nesmeyanov, Yu. A. Chapovsky, N. A. Ustynyuk, and L. G. Makarova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 449.