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Toward direct synthesis of organo-nitrogen compounds from molecular nitrogen

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Abstract

Direct synthesis of organo-nitrogen compounds from molecular nitrogen is a challenging subject in the chemistry of nitrogen fixation. Toward this direction, we have long been investigating novel chemical transformations of coordinated dinitrogen. Described herein are our recent results on (1) synthesis of nitrogen-heterocycles from molecular nitrogen via condensation reactions of hydrazido complexes with dialdehydes or their equivalents, (2) bimetallic arylation of molecular nitrogen by using reactions of anionic dinitrogen complexes with η^6-fluoroarene complexes, and (3) catalytic silylation of molecular nitrogen.

Keywords: Nitrogen; Tungsten; Molybdenum; Heterocycles; Arylation; Silylation; Silylamines

1. Introduction

Molecular nitrogen is the most abundant but the least reactive nitrogen compound, and direct synthesis of organo-nitrogen compounds using molecular nitrogen as a nitrogen source is a challenging goal in organic synthesis. Dinitrogen complexes of transition metals have been attracting broad interest because coordinated dinitrogen shows a variety of reactivities forming nitrogen–carbon and nitrogen–hydrogen bonds under mild conditions [1,2]. Despite extensive studies on reactivities of dinitrogen complexes, nitrogen-containing compounds derived from dinitrogen complexes have still been limited to ammonia, hydrazine, simple alkylamines, and azines. Aiming at developing direct synthetic methods for more valuable organo-nitrogen compounds from molecular nitrogen, we have continuously been investigating reactivities of coordinated dinitrogen in complexes of the type $M(N_2)_2(L)_4$ (M = Mo, W; L = phosphine). Here we wish to summarize our recent results.

2. Synthesis of nitrogen heterocycles from molecular nitrogen

Synthesis of nitrogen-heterocyclic compounds from dinitrogen is quite an interesting subject because of their widespread occurrence in biological systems. We have found some novel reactions which enable effective construction of nitrogen-heterocycles from coordinated dinitrogen and selective liberation of the heterocycles from the resultant complexes.

We have previously reported that dinitrogen complexes of the type $M(N_2)_2(L)_4$ (M = Mo, W; L = phosphine) react with acids to give hydrazido complexes with a NNH_2 ligand, which can readily

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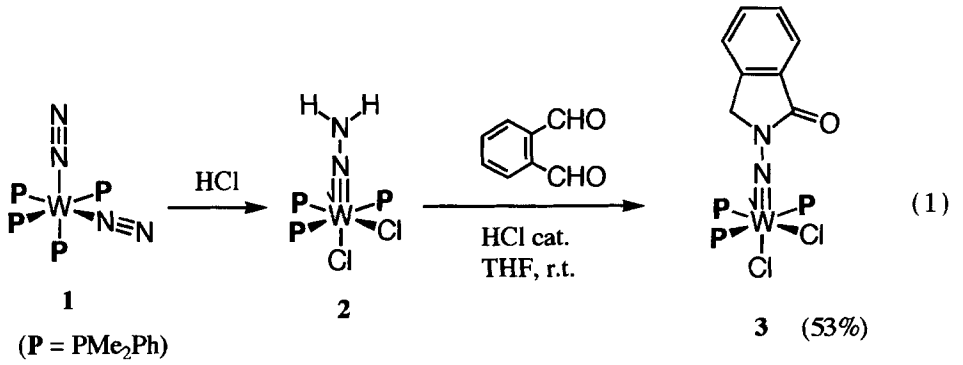


Scheme 1.

be converted into diazoalkane complexes with a N_2CRR' ligand by treatment with carbonyl compounds ($RR'C{=}O$) [3]. This reaction provides one of the most potential and convenient methods for nitrogen–carbon bond formation at the coordinated dinitrogen. This condensation method has now been applied to dialdehydes or their equivalents to obtain nitrogen-heterocycles from molecular nitrogen.

The reaction between phthalaldehyde and the tungsten hydrazido complex $[WCl_2(NNH_2)(PMe_2Ph)_3]$ (**2**), which is readily obtained from the dinitrogen complex $[W(N_2)_2(PMe_2Ph)_4]$ (**1**), proceeded smoothly at room temperature in the presence of catalytic amounts of HCl to afford the *N*-phthalimidylimido complex

$[WCl_2(NNCOC_6H_4CH_2)(PMe_2Ph)_3]$

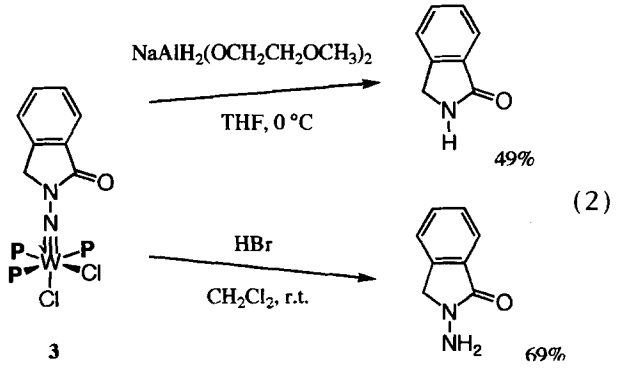
(**3**) (Eq. 1, depicted in Scheme 1) [4]. The structure of complex **3** has been unequivocally determined by X-ray analysis.

Liberation of the heterocyclic moiety from complex **3** has been achieved by reduction with $NaAlH_2(OCH_2CH_2OMe)_2$ and acidolysis with HBr to form phthalimidine and *N*-aminophthalimidine in 49 and 69% yields, respectively (Eq. 2, depicted in Scheme 2).

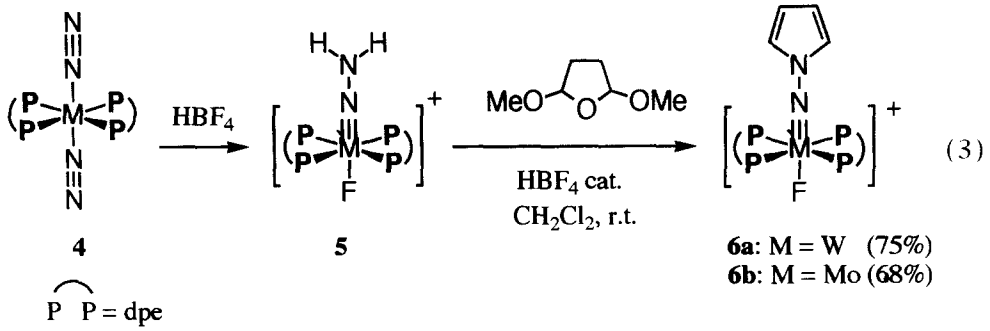
On the other hand, the condensation reaction of 2,5-dimethoxytetrahydrofuran and hydrazido complexes $[MF(NNH_2)(dpe)_2][BF_4]$ (**5a**, M = W; **5b**, M = Mo), derived from dinitrogen complexes $[M(N_2)_2(dpe)_2]$ (**4a**, M = W; **4b**, M = Mo) and HBF_4, gave 1-pyrrolylimido complexes

$[MF(NNCH{=}CHCH{=}CH)(dpe)_2][BF_4]$

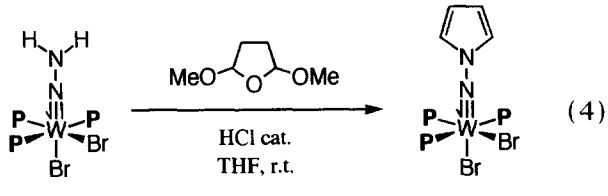
(**6a**, M = W **6b**, M = Mo) in good yields (Eq. 3, depicted in Scheme 3) [5]. The structures have been characterized by ^1H and ^{13}C NMR spectra. Thus, the ^{13}C NMR spectrum of the tungsten complex **6a** showed signals at 106.6 and 119.4 ppm due to the α- and β-carbons of the pyrrole ring,



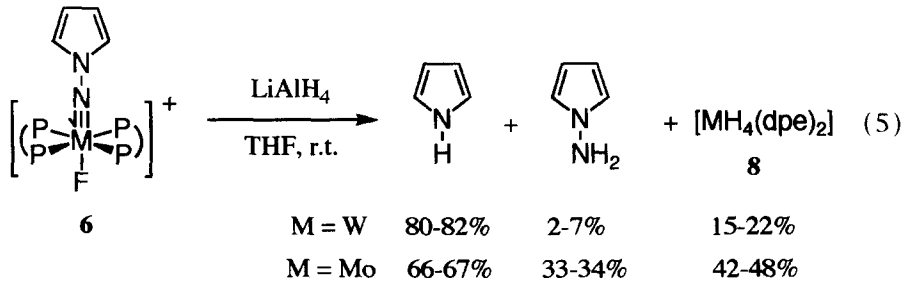
Scheme 2.



Scheme 3.



Scheme 4.

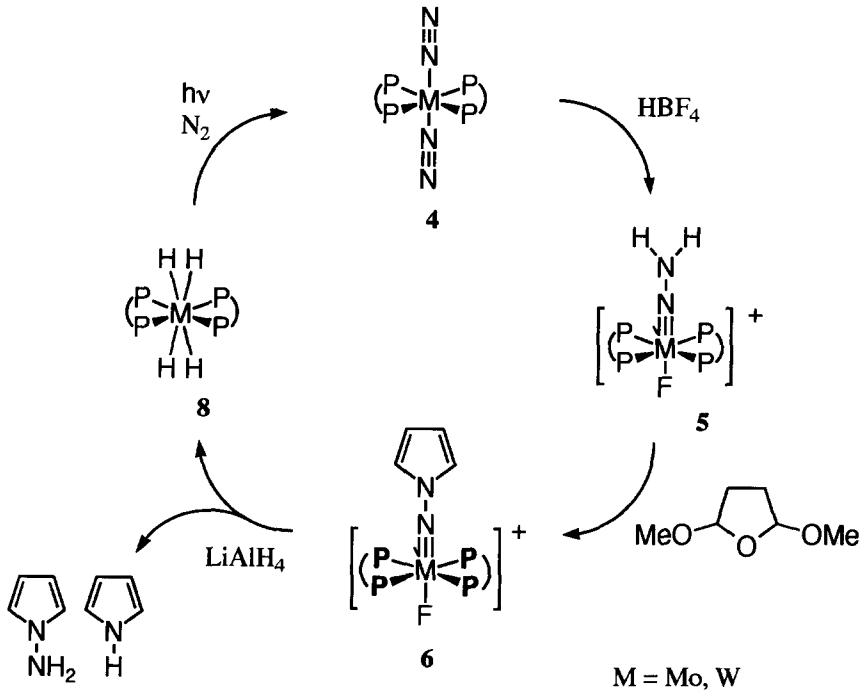


Scheme 5.

respectively. In the ^{1}H NMR spectrum, two triplets were observed at δ 4.88 and 5.41 ppm, which were assigned to the α- and β-protons of the pyrrole ring, respectively. The higher field shift of the resonance assigned to the α-protons is remarkable, since the resonance due to the α-protons of free pyrrole appears at 6.6 ppm. This may be caused by the shielding effect of the phenyl groups of the dpe ligands. By a similar reaction, the pyrrolylimido tungsten complex with PMe_2Ph ligands (**7**) was prepared in a high yield (Eq. 4, depicted in Scheme 4).

The molecular structure of the tungsten pyrrolylimido complex **6a** has further been confirmed by the X-ray diffraction method. The terminal nitrogen atom of the hydrazido ligand is incorporated in the pyrrole ring to form the pyrrolylimido ligand. The W–N–N bond is nearly linear, and the tungsten and nitrogen atoms lie almost on the plane of the pyrrole ring. The N–N bond distance of 1.41(1) Å is longer than those of usual hydrazido complexes (1.25–1.38 Å). This may be accounted for by the participation of the lone pair electrons on the pyrrole–nitrogen atom in forming the 6π aromatic system instead of their delocalizing over the W–N–N moiety.

Liberation of pyrrole and *N*-aminopyrrole from complexes **6** and **7** was also investigated. Reduction with $LiAlH_4$ was found to be effective for liberating pyrrole from the cationic pyrrolylimido complex **6a** (Eq. 5, depicted in Scheme 5). The reaction occurred at room temperature in THF and pyrrole was obtained in over 80% yield after 20 h, concurrent with formation of ammonia (70–74%), *N*-aminopyrrole (2–7%) and tungsten tetrahydride $[WH_4(dpe)_2]$ (**8a**, 15–22%). Inter-



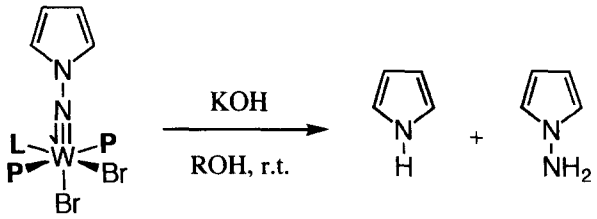
Scheme 6.

estingly this reaction proceeded smoothly under much milder conditions than the known hydride reductions of dialkylhydrazido or alkyldiazenido complexes with dpe ligands, where temperatures higher than 75°C and much longer reaction time were required [6,7]. The facile cleavage of the N–N bond observed here is considered to reflect the relatively long N–N bond distance described above. A similar reaction of the molybdenum analogue **6b** also gave pyrrole (66–67%), *N*-aminopyrrole (33–34%), and $[MoH_4(dpe)_2]$ (**8b**) (42–48%). It is of particular interest to point out that the tetrahydrides **8a** and **8b** can be converted to dinitrogen complexes **4a** and **4b**, respectively, by irradiation under a nitrogen atmosphere [8–10]. Therefore, a reaction cycle can be accomplished to prepare pyrrole and *N*-aminopyrrole from molecular nitrogen by using dinitrogen complexes **4** (Scheme 6).

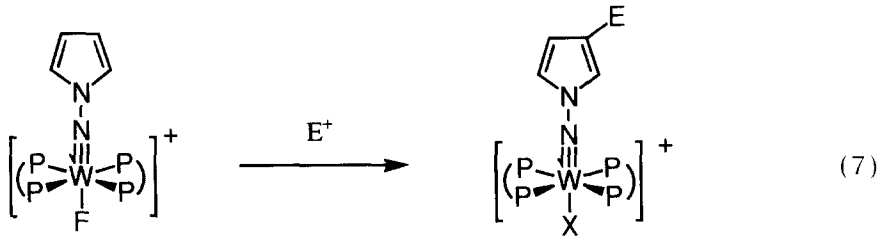
In contrast, treatment of the pyrrolylimido complex **7** with potassium hydroxide in ethanol at room temperature gave *N*-aminopyrrole as the major product (Eq. 6, depicted in Scheme 7). When one PMe_2Ph ligand in **7** was replaced by a CO ligand and 2-propanol was used instead of ethanol, the selectivity of *N*-aminopyrrole was improved up to nearly 100%.

The reactivity of the pyrrole ring newly formed on the tungsten complex **6a** is also worth mentioning. We have found that it undergoes highly β-selective electrophilic substitution reactions (Eq. 7, depicted in Scheme 8). For example, when this complex was treated with NBS in THF at −10°C, the β-bromo derivative **9a** was obtained in 74% yield and no α-brominated complex was detected. Further, exclusive β-cyanation was achieved by a reaction with chlorosulfonyl isocyanate and DMF, whereas β-benzoylation was performed by a reaction with benzoyl chloride in the presence of $AlCl_3$.

Because electrophilic substitutions of free pyrrole are known to occur predominantly at the α-position, it is of interest that the regioselectivity was completely changed in the reaction of the pyrrolylimido complex **6a**. This fact may be explained by the steric effect of dpe ligands surrounding the pyrrole ring, which causes the protection of the α-position of the pyrrole ring and leads to the exclusive attack of electrophiles at the β-position. The β-selective substitution reactions



Scheme 7.



Scheme 8.

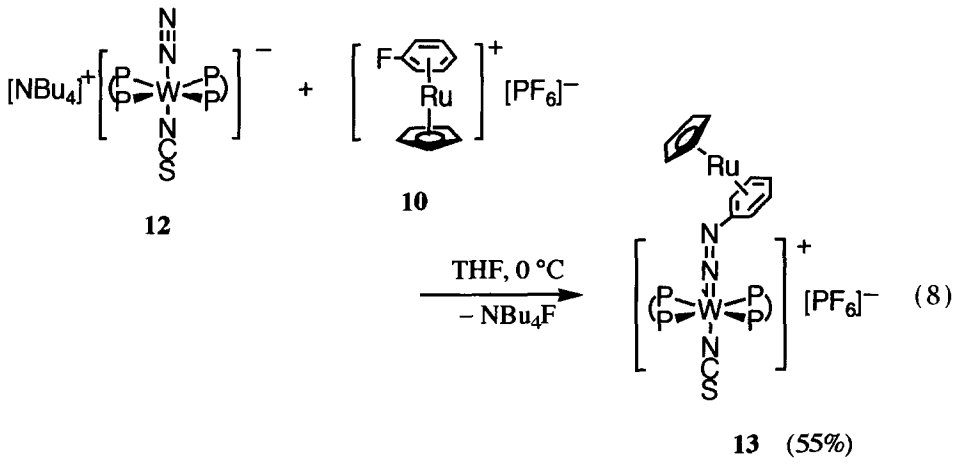
coupled with the $LiAlH_4$ reduction shown above can be applied to the synthesis of β-substituted pyrroles, which can hardly be obtained from pyrrole by conventional methods.

3. Bimetallic arylation of molecular nitrogen

Arylation of molecular nitrogen may be of particular interest from an industrial point of view. However, arylation of coordinated dinitrogen has rarely been achieved. Prior to our study, the only example of the direct arylation of coordinated dinitrogen was found in the reaction of a molybdenum dinitrogen complex with a tetrathia-macrocycle ligand $[Mo(N_2)_2(Me_8[16]aneS_4)]$ with iodo- or bromoarenes to give aryldiazenido complexes [11]. In contrast, it has been claimed that dinitrogen complexes of the type $M(N_2)_2(L)_4$ (M = Mo, W; L = phosphine) do not undergo direct arylation of coordinated dinitrogen [12]. We have now adopted bimetallic approach for arylation of molecular nitrogen: a reaction between dinitrogen complexes and haloarene complexes [13].

At first, we examined reactions of dinitrogen complexes **1** and **4a** with several haloarene complexes such as $[RuCp(\eta^6\text{-}C_6H_5F)][PF_6]$ (**10**) and $[Cr(\eta^6\text{-}p\text{-}FC_6H_4COOMe)(CO)_3]$ (**11**), but in all cases no distinct reaction was observed at room temperature. In contrast, an anionic dinitrogen complex $[NBu_4][W(NCS)(N_2)(dpe)_2]$ (**12**), which is readily prepared by irradiation of **4a** in the presence of NBu_4SCN with a tungsten-filament lamp [14], reacted with **10** in THF at room temperature to give a dark red new complex $[W(NCS)\{N{=}N[(\eta^6\text{-}C_6H_5)RuCp]\}(dpe)_2][PF_6]$ (**13**) in 55% yield (Eq. 8, depicted in Scheme 9). Obviously the activation of the fluoroarene is essential for the reaction, since free fluoroarenes did not react with **12**.

Introduction of various aryl groups (Ph, Tol, C_6H_4OMe, C_6H_4COOMe) onto the coordinated dinitrogen was achieved by the use of $RuCp^+$ as the activating group for the fluoroarenes. Chromium complex **11** also underwent similar *N*-aryl



(8)

Scheme 9.

bond formation to give [W(NCS){N=N[(η^6-*p*-C_6H_4COOMe)$Cr(CO)_3$]}$(dpe)_2$] (**14**), but other fluoroarene–chromium complexes could not be used for the introduction of other aryl groups. In this respect, $RuCp^+$ is the more efficient activating group for fluoroarenes than $Cr(CO)_3$.

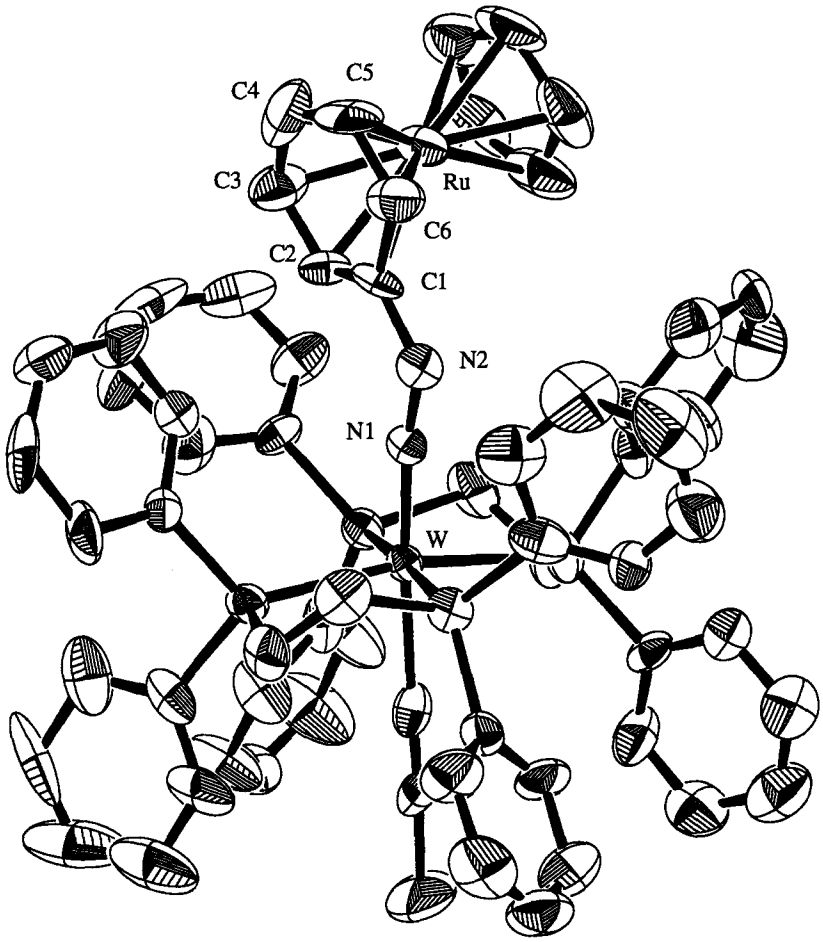
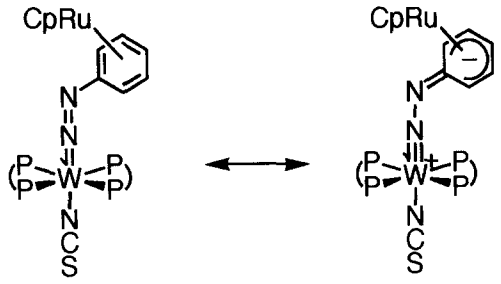


Fig. 1. ORTEP drawing for the cationic part of complex **13**.



(9)

15

Scheme 10.

However, $[RuCp(\eta^6\text{-}C_6H_5Cl)][PF_6]$ failed to undergo the arylation reaction with **12**.

The detailed molecular structure of the bimetallic complex **13** has been unambiguously determined by X-ray diffraction study. The ORTEP view is shown in Fig. 1. The bond angles for the W–N–N (166(1)°) and N–N–C (122(1)°) linkages indicate that complex **13** belongs to a singly bent diazenido complex. However, the N=N bond distance (1.28 (1) Å) is longer than those reported for similar singly bent diazenido complexes (1.16–1.29 Å) and lie in the range of the N–N bond distances observed in hydrazido and diazoalkane complexes. This indicates that the N=N bond multiplicity in complex **13** is considerably reduced. In addition, notable change in the η^6-coordination mode of the aryl group was observed. Thus, the Ru–C(1) bond (2.39(2) Å) is much longer than the other Ru–arene (av. 2.17 Å) carbon bonds, indicating that the Ru atom is displaced away from the N(2) atom. All the structural characteristics described above strongly suggest that the μ-aryldiazenido complex **13** receives a large contribution of the unique zwitterionic resonance structure **15** (Eq. 9, depicted in Scheme 10). Similar structural features were also found in complex **14**. Obviously the existence of both the electron rich W(II) center and the electron withdrawing $RuCp^+$ or $Cr(CO)_3$ group leads to the significant contribution of the charge separated resonance structure.

The mechanism for alkylation of coordinated dinitrogen in **4** with alkyl halides (RX) has been postulated to include an electron transfer process from **4** to the alkyl halides and attack of the resultant alkyl radical R on coordinated dinitrogen [11,12,14]. In sharp contrast, the reaction of the anionic dinitrogen complex **12** with fluoroarene complexes **10** and **11** does not include electron transfer process. This is strongly supported by electrochemical measurements of **10**, **11** and **12**. Further, when $[FeCp(\eta^6\text{-}C_6H_5F)][PF_6]$, which undergoes electrochemical reduction at -1.22 V vs. SCE to give a 19-electron species, was used instead of **10**, only the one electron oxidation of **12** occurred and no *N*-arylation product was obtained. Therefore, the bimetallic arylation of Eq. 8 (depicted in Scheme 9) is considered to proceed via the direct nucleophilic substitution on the η^6-fluoroarene by the terminal nitrogen atom in **12**, rather than the radical mechanism proposed for the alkylation. The higher reactivity of the η^6-C_6H_5F complex than the η^6-C_6H_5Cl analogue agrees with the general reactivity order of haloarene complexes in nucleophilic substitutions. It should also be pointed out that the ligating dinitrogen in **12** is endowed the higher nucleophilicity than that in **1** and **4a** since the stronger back-donation to the ligating dinitrogen is expected from the anionic tungsten center.

3.1. Catalytic silylation of molecular nitrogen

We have recently found that silylation of coordinated dinitrogen occurs when dinitrogen complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo, W; L = phosphine) are treated with Me_3SiI [15], R_3SiCl/NaI, [16] or $ClMe_2SiCH_2CH_2SiMe_2Cl/NaI$ [17]. A series of silylhydrazido and silyldiazenido complexes were obtained by this method.

Detailed investigation of the reactivity of trimethylsilyldiazenido complexes has eventually led to discovery of the catalytic system in which molecular nitrogen is converted into silylamines in the presence of the molybdenum dinitrogen complex $[Mo(N_2)_2(PMe_2Ph)_4]$ (Eq. 10) [18]. The silylamines were obtained with the turnover number up to 25 mol/Mo atom concurrent with formation of $Me_3SiSiMe_3$. This provides quite a rare example of the catalytic nitrogen fixation promoted by transition metal complexes.

$$Me_3SiCl + Na + N_2 \xrightarrow{\text{cis-}[Mo(N_2)_2(PMe_2Ph)_4]} N(SiMe_3)_3 + HN(SiMe_3)_2 + Me_3SiSiMe_3 \quad (10)$$

References

[1] M. Hidai and Y. Mizobe, in P.S. Braterman (Ed.), Reactions of Coordinated Ligands, Vol. 2, Plenum Press, London, 1988, p. 53.

[2] M. Hidai and Y. Mizobe, in E.I. Stiefel, D. Coucouvanis, W.E. Newton (Eds.), Molybdenum Enzymes, Cofactors and Model Systems, ACS Symposium Series 535, American Chemical Society, Washington, DC, 1993, Chapter 22.

[3] M. Hidai, Y. Mizobe, M. Sato, T. Kodama and Y. Uchida, J. Am. Chem. Soc., 100 (1978) 5740.

[4] H. Seino, Y. Ishii and M. Hidai, unpublished results.

[5] H. Seino, Y. Ishii and M. Hidai, J. Am. Chem. Soc., 116 (1994) 7433.

[6] G.E. Bossard, D.C. Busby, M. Chang, T.A. George and S.D. A. Iske, J. Am. Chem. Soc., 102 (1980) 1001.

[7] P.C. Bevan, J. Chatt, G.J. Leigh and E.G. Leelamani, J. Organomet. Chem., 139 (1977) C59.

[8] M. Hidai, K. Tominari and Y. Uchida, J. Am. Chem. Soc., 94 (1972) 110.

[9] R. Pierantozzi and G.L. Geoffroy, Inorg. Chem., 19 (1980) 1821.

[10] A.P. Pivovarov, Y.V. Gak, T.N. Doronina, V.D. Makhaev, A.P. Borisov, Y.G. Borod'ko, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1207.

[11] T. Yoshida, T. Adachi, T. Ueda, M. Kaminaka, N. Sasaki, T. Higuchi, T. Aoshima, I. Mega, Y. Mizobe and M. Hidai, Angew. Chem., Int. Ed. Engl., 28 (1989) 1040.

[12] J. Chatt, R.A. Head, G.J. Leigh and C.J. Pickett, J. Chem. Soc., Dalton Trans., (1978) 1638.

[13] Y. Ishii, M. Kawaguchi, Y. Ishino, T. Aoki and M. Hidai, Organometallics, 114 (1994) 5429.

[14] J. Chatt, G.J. Leigh, H. Neukomm, C.J. Pickett and C.D. R. Stanley, J. Chem. Soc., Dalton Trans., (1980) 121.

[15] K. Komori, S. Sugiura, Y. Mizobe, M. Yamada and M. Hidai, Bull. Chem. Soc. Jpn., 62 (1989) 2953.

[16] H. Oshita, Y. Mizobe and M. Hidai, M., J. Organomet. Chem., 456 (1993) 213.

[17] H. Oshita, Y. Mizobe and M. Hidai, Organometallics, 11 (1992) 4116.

[18] K. Komori, H. Oshita, Y. Mizobe and M. Hidai, J. Am. Chem. Soc., 111 (1989) 1939.