3764 Organometallics **1994**, *13*, 3764−3766

Preparation of Heterobimetallic Complexes with a Bridging Dinitrogen Ligand, $[WX(PMe_2Ph)_4(\mu\text{-}N_2)MCp_2Cl]$ (M = Ti, X = Cl; M = Zr, Hf, X = I), and X-ray Structure of $[WI(PMe_2Ph)_3(py)(\mu\text{-}N_2)ZrCp_2Cl]$ (py = Pyridine)[1]

Yasushi Mizobe, Youhei Yokobayashi, Hiroyuki Oshita,
Tamotsu Takahashi,[†] and Masanobu Hidai[*]

*Department of Chemistry and Biotechnology, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan*

Received June 3, 1994[⊗]

Summary: Reactions of cis-$[W(N_2)_2(PMe_2Ph)_4]$ *with either* $[Cp_2TiCl_2]$ *(Cp =* η^5-C_5H_5*) alone or a mixture of* $[Cp_2MCl_2]$ *(M = Zr, Hf) and excess NaI afforded heterobimetallic complexes with a bridging dinitrogen ligand,* $[WX(PMe_2Ph)_4(\mu\text{-}N_2)MCp_2Cl]$ *(M = Ti, X = Cl; M = Zr, Hf, X = I). The W−Zr complex was further converted into the related dinitrogen complex* $[WI(PMe_2Ph)_3(py)(\mu\text{-}N_2)ZrCp_2Cl]$ *(py = pyridine) by treatment with excess py, whose structure has been determined by an X-ray analysis.*

Activation of molecular nitrogen by transition-metal compounds is currently attracting much attention, and a number of dinitrogen complexes have been isolated for various transition metals.[2−5] Intensive studies on these complexes have shown that coordinated dinitrogen in certain complexes can display versatile reactivities, forming nitrogenous ligands or compounds under mild conditions. However, well-defined reactions reported to data are limited mostly to the terminally bound dinitrogen in monomeric Mo and W complexes.[6−10] Despite the increasing interest in the reactivities of dinitrogen coordinated to more than two metals in relation to the active site model deduced from the single-crystal X-ray diffraction data[11,12] as well as from EXAFS studies of the FeMo protein of nitrogenase,[13,14] the chemistry of multimetallic dinitrogen complexes is still underdeveloped.[15] We wish to report here the syntheses and characterization of new heterobimetallic complexes containing an η^1:η^1-dinitrogen bridge between W and group 4 transition metals. Apart from $[ReCl(PMe_2Ph)_4(\mu\text{-}N_2)MoCl_4(OMe)]$,[16] $[\{ReCl(PMe_2Ph)_4(\mu\text{-}N_2)\}_2MoCl_4]$,[17] and $[(C_5Me_5)MoMe_3(\mu\text{-}N_2)W(C_5Me_4Et)Me_3]$,[18] crystallographically characterized complexes containing the dinitrogen ligand bound to two different transition metals are still rare,[19] although the related homobimetallic complexes have more precedent.[15]

When *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) in benzene was reacted with equimolar $[Cp_2TiCl_2]$ (Cp = η^5-C_5H_5) at 50 °C under rigorously dry conditions, the dark brown complex $[WCl(PMe_2Ph)_4(\mu\text{-}N_2)TiCp_2Cl]$ (**2**) was isolated in 73% yield upon addition of hexane to the concentrated reaction solution. Although reactions of **1** with $[Cp_2MCl_2]$ (M = Zr, Hf) did not proceed under similar conditions, the related dinitrogen complexes $[WI(PMe_2Ph)_4(\mu\text{-}N_2)MCp_2Cl]$ (**3**, M = Zr; **4**, M = Hf) were readily obtained in 66 and 60% yields as dark red and yellow-brown solids, respectively, when reactions were performed in the presence of excess NaI (ca. 13 equiv of **1**) followed by the analogous workup of the filtered reaction mixtures (Scheme 1). IR spectra of **2**−**4** exhibit characteristic ν(NN) bands with medium intensities in the region of 1468−1545 cm^{-1}, while the ^{1}H NMR spectra show a sharp singlet as well as a slightly broadened singlet assignable to the Cp and PMe protons, respectively.[24] The latter feature is indicative of the trans

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[†] Present address: Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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(19) Other μ-N_2 heterobimetallic complexes spectroscopically characterized include $[ReCl(PMe_2Ph)_4(\mu\text{-}N_2)MCl_5]$ (M = Nb, Ta),[20] $[ReCl(PMe_2Ph)_4(\mu\text{-}N_2)TiCl_4(THF)]$,[21] $[ReCl(PMe_2Ph)_4(\mu\text{-}N_2)CrCl_3(THF)_2]$,[22] and $[(C_5Me_5)WMe_3(\mu\text{-}N_2)Ta(C_5Me_5)Me_2]$.[23]

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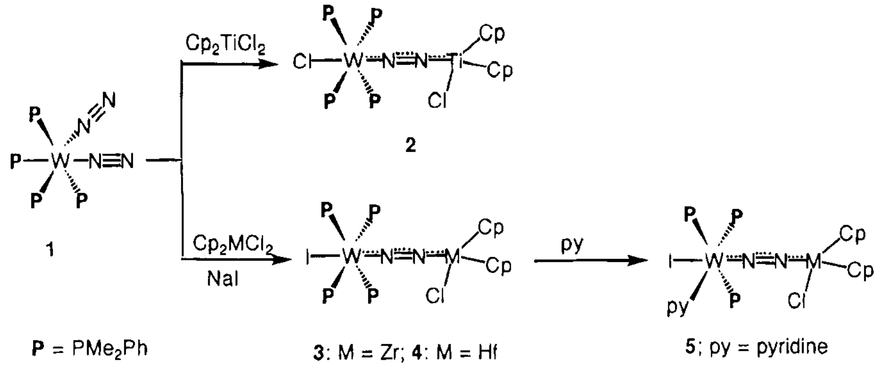
Scheme 1



configuration around the W atom in all these complexes, as previously demonstrated for *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$][25] and *trans*-[WI(NNGePh$_3$)(PMe$_2$Ph)$_4$].[26] In spite of much effort to prepare single crystals of **2**−**4**, those suitable for an X-ray analysis were not available.

On the other hand, treatment of **3** with excess pyridine (py) and a subsequent crystallization of the product from toluene−py−hexane gave [WI(PMe$_2$Ph)$_3$(py)(μ-N$_2$)ZrCp$_2$Cl] (**5**) as dark red crystals in 44% yield (Scheme 1), and the structure of **5** has been unequivocally determined by an X-ray diffraction study.[27] An ORTEP drawing of **5** is shown in Figure 1 together with some important bonding parameters. As expected, **5** contains an η^1:η^1-dinitrogen bridge between the W and Zr atoms. The W atom has an octahedral configuration with three mutually meridional PMe$_2$Ph and one py ligand comprising the basal plane, while the remaining sites are occupied by mutually trans μ-N$_2$ and iodide ligands. The W−N−N−Zr array is almost linear, and the N−N distance at 1.24(2) Å corresponds to the bond order of ca. 2. Both the W−N and Zr−N bond lengths of 1.80(1) and 1.98(1) Å, respectively, suggest considerable multiple-bonding nature. The IR spectrum showing the ν(NN) band at 1541 cm^{-1} (KBr disk) and the ^{1}H NMR data[28] for **5** are diagnostic of the structure demonstrated by the X-ray analysis, although **5** redissolved in benzene or THF proved to decompose gradually, yielding an unidentified species.

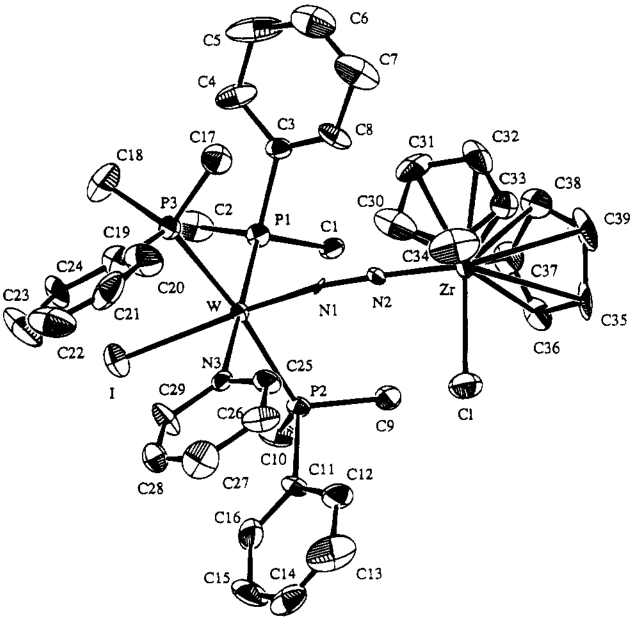


Figure 1. Molecular structure of **5**. Solvated py is omitted. Important bond distances (Å) and angles (deg): W−I, 2.869(2); W−P(1), 2.459(4); W−P(2), 2.478(5); W−P(3), 2.483(5); W−N(1), 1.80(1); W−N(3), 2.26(1); Zr−Cl, 2.518(6); Zr−N(2), 1.98(1); N(1)−N(2), 1.24(2); I−W−N(1), 175.4(3); Cl−Zr−N(2); 93.4(4); W−N(1)−N(2), 172(1); Zr−N(2)−N(1), 175(1).

The series of nitrogen complexes reported here represents the first well-defined complex having a dinitrogen bridge between group 6 and group 4 metals. It is interesting to note that the coordinated dinitrogen in **2**−**5** can be considered as a formal (N$_2$)$^{2-}$ (diazenido(2−)) ligand, since the oxidation state of the diamagnetic metal centers in these complexes may be assigned to be +2 for W and +4 for Ti, Zr, and Hf. The η^1:η^1-N$_2$ complexes reported to data may be classified into two types, e.g., formal (N$_2$)^0 (M−N≡N−M′) and (N$_2$)$^{4-}$ (M═N−N═M′) complexes; the formal (N$_2$)$^{2-}$ (M−N═N−M′) complexes are rare, although the bonding parameters determined by the X-ray analyses are often inconsistent with these extreme formalisms, especially for (N$_2$)$^{4-}$ complexes, and the choice of the formulation becomes arbitrary.[8,15]

Reactivities of the dinitrogen ligand in heterobimetallic complexes **2**−**5** are of significant interest, and the reactions of **2** and **3** with acid have been undertaken. Thus, treatment of **2** with 10 molar equiv of H$_2$SO$_4$ in MeOH at room temperature gave 0.86 mol of NH$_3$ and 0.08 mol of N$_2$H$_4$ per mole of **2**, while **3** afforded 0.33 mol of NH$_3$ and 0.16 mol of N$_2$H$_4$ per mole of **3** under similar conditions.[29] Essentially no N$_2$ gas was evolved during these reactions (<0.02 mol/mol of complex). Further study is in progress to elucidate the reactivities

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(24) Satisfactory C, H, and N analysis data were obtained for all new complexes reported here. IR (KBr disk, cm^{-1}; ν(NN)): **2**, 1468; **3**, 1518; **4**, 1545. ^{1}H NMR (C$_6$D$_6$, ppm): **2**, 6.30 (s, 10H, Cp), 1.57 (s, 24H, PMe); **3**, 6.33 (s, 10H, Cp), 1.71 (s, 24H, PMe); **4**, 6.29 (s, 10H, Cp), 1.77 (s, 24H, PMe). Phenyl protons are omitted.

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(27) Crystal data: C$_{39}$H$_{48}$N$_3$ClP$_3$WZr·0.5C$_5$H$_5$N; M_r = 1128.8; monoclinic; space group $C2/c$; a = 39.194(10) Å, b = 12.678(7) Å, c = 18.726(7) Å; β = 107.14(2)°; V = 8891(5) Å^3; Z = 8; $D_{\rm calc}$ = 1.686 g cm^{-3}; F(000) = 4424; μ(Mo Kα) = 37.18 cm^{-1}; final R = 0.052 and R_w = 0.062 for 4041 reflections ($I > 3\sigma(I)$) out of 10 701 unique data recorded on a Rigaku AFC7R diffractometer; absorption correction by ψ-scan methods; structure analysis by SIR88 direct methods, full-matrix least-squares refinement by TEXSAN programs with non-H atoms anisotropic and H atoms fixed at calculated positions (469 variables).

(28) ^{1}H NMR (THF-d_8, ppm): 6.24 (s, 10H, Cp), 1.90 (d, 6H, PMe), 1.59 (t, 6H, PMe), 1.50 (t, 6H, PMe), together with the resonances of Ph groups and py.

of the coordinated N_2 in these complexes, which will be reported in a subsequent paper.

Acknowledgment. Financial support by the Ministry of Education, Science, and Culture of Japan is appreciated.

Supplementary Material Available: Tables giving details of the X-ray analysis, atomic coordinates, thermal parameters, and bond lengths and angles for **5** and elemental analysis data for **2**–**5** and a figure showing a whole view of **5**·0.5py (14 pages). Ordering information is given on any current masthead page.

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(29) Into a brown or red suspension of **2** or **3** (120–150 mg) in MeOH (5 mL) was added concentrated H_2SO_4 (10 equiv) under Ar, and the mixture was stirred at room temperature for several hours. After the quantity of N_2 in the gaseous phase was analyzed by GLC, the resultant orange or greenish brown solution obtained from the reaction of **2** or **3**, respectively, was dried up and the amounts of ammonia and hydrazine included in the evaporated residue were determined as described previously.[30]

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