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# Preparation of Molybdenum and Tungsten Diazoalkane–Aminocarbene Complexes *cis,trans*–$[MX_2(NN{=}CMePh)\{{=}C(Me)NHBu^t\}(PMe_2Ph)_2]$ (M = Mo, W; X = Cl, Br) from Dinitrogen Complexes *cis*–$[M(N_2)_2(PMe_2Ph)_4]$[1)]

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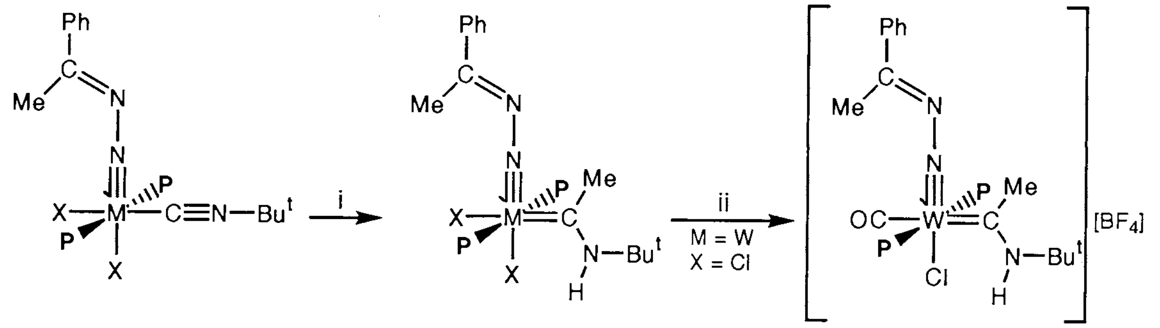
Molybdenum and tungsten diazoalkane-isocyanide complexes *cis, trans*–$[MX_2(NN{=}CMePh)(CNBu^t)(PMe_2Ph)_2]$ (M = Mo: X = Cl; M = W: X = Cl, Br), derived from *cis*–$[M(N_2)_2(PMe_2Ph)_4]$, reacted with $AlMe_3$ to give diazoalkane–aminocarbene complexes *cis,trans*–$[MX_2(NN{=}CMePh)\{{=}C(Me)NHBu^t\}(PMe_2Ph)_2]$ (**3**) after hydrolysis, whose structure has been determined by an X–ray analysis for **3a** (M = W, X = Cl).

Transformation of molecular nitrogen into nitrogen–containing organic compounds under mild conditions is of substantial importance and the reactions of the coordinated dinitrogen in metal complexes to form organo–nitrogen ligands are therefore attracting much attention.[2)] We have previously reported the synthesis of diazoalkane complexes *trans*–$[MF(NN{=}CRR')(Ph_2PCH_2CH_2PPh_2)_2]^+$ [3)] and *cis,mer*–$[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ (**1**)[4)] (M = Mo, W; X = Cl, Br, I) from bis(dinitrogen) complexes *trans*–$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and *cis*–$[M(N_2)_2(PMe_2Ph)_4]$, which demonstrates one of the most general methods to form a N–C bond at the dinitrogen ligand. It is also noteworthy that these diazoalkane complexes can serve as the potential precursors to prepare various organo–nitrogen complexes and compounds under certain conditions.[4a,5)]

Recently we have shown that the diazoalkane complexes **1** undergo the substitution of a series of π–acceptor ligands (L) for one $PMe_2Ph$ ligand, giving new diazoalkane complexes *cis,trans*–$[MX_2(NN{=}CRR')(L)(PMe_2Ph)_2]$ (L = alkenes, aldehydes, $Bu^tNC$, CO).[5b)] Now we have found that the diazoalkane–$Bu^tNC$ complexes *cis,trans*–$[MX_2(NN{=}CMePh)(CNBu^t)(PMe_2Ph)_2]$ (**2**) are readily converted into the novel diazoalkane–aminocarbene complexes *cis,trans*–$[MX_2(NN{=}CMePh)\{{=}C(Me)NHBu^t\}(PMe_2Ph)_2]$ (**3**) (Scheme 1). Besides $[Cp(CO)_3MoMo(CAr_2)(NNCAr_2)Cp]$ (Cp = $\eta^5$–$C_5H_5$; Ar = 4–$MeC_6H_4$) prepared from $[Cp_2Mo_2(CO)_4(\mu\text{–}CAr_2)]$ and $Ar_2CN_2$,[6)] few carbene–diazoalkane complexes are known.

Treatment of **2a** (M = W, X = Cl) with one equiv of $AlMe_3$ in toluene at room temperature for 1 h, followed by addition of one equiv of $H_2O$, resulted in the formation of a brown solution. Addition of hexane to the concentrated reaction mixture afforded brown crystals of **3a** (M = W, X = Cl) in 39% yield. Complexes **3b** (M = W, X = Br) and **3c** (M = Mo, X = Cl) were obtained similarly as brown crystals from the corresponding diazoalkane–$Bu^tNC$ complexes in 19 and 30% yields, respectively.[7)] The single crystal X–ray analysis has been undertaken for **3a**,[8)] which has demonstrated unambiguously the presence of the aminocarbene ligand cis to the diazoalkane ligand in a slightly distorted octahedron (Fig. 1). The C(1),



**2a**: M = W, X = Cl;
**2b**: M = W, X = Br;
**2c**: M = Mo, X = Cl

**3a**: M = W, X = Cl;
**3b**: M = W, X = Br;
**3c**: M = Mo, X = Cl

**4**

P = PMe$_2$Ph

Scheme 1. Reaction conditions: (i) 1) AlMe$_3$ / toluene, 2) H$_2$O / toluene; (ii) [Me$_3$O][BF$_4$] / CO / ether.

C(2), N(1) and C(3) atoms in the carbene ligand as well as the W atom are coplanar and this plane is perpendicular to the basal plane defined by the P(1), P(2), Cl(1) and C(1) atoms. The latter feature can be interpreted in terms of the effective overlap of the empty p orbital on the sp$^2$ hybridised carbene carbon atom with the filled d$_{xy}$ orbital (HOMO) on the W atom, where the $x$–$y$ plane is defined as coincident with the basal plane of **3a**. Relating strong π–back donating ability towards the direction cis to the metal–ligand multiple bonds has been demonstrated for the d$^2$ metal centers in [WCl$_2$(E)(L)(PR$_3$)$_2$] (E = S, O, NR'; L = olefins, Bu$^t$NC, etc.)[9] and *cis,trans*–[WX$_2$(NN=CRR')(L)(PMe$_2$Ph)$_2$] shown above.[5b] The W–C(1) bond length [2.05(2) Å] is in the range of the common W–C(carbene) distances reported previously (1.83 – 2.14 Å),[9a] while the C(1)–N(1) bond length at 1.35(3) Å is indicative of partial double–bond character as observed generally in the other aminocarbene ligands (e.g., [Cr{=C(Me)NHMe}(CO)$_5$]: 1.33(3) Å[10]). The bond distances and angles pertinent to the diazoalkane ligand are comparable to those of the analogous four–electron donor diazoalkane ligands in *cis,trans*–[WCl$_2$(NN=CMeR)(L)(PMe$_2$Ph)$_2$] (R = Me, L = $\eta^2$–CH$_2$CH$_2$; R = Ph, L = $\eta^2$–MeC$_6$H$_4$CHO).[5b] Spectroscopic data for **3**[7] are consistent with this structure. The IR spectra exhibit one weak and one strong bands characteristic of $\nu_{NH}$ and $\nu_{CN}$ (vide infra), respectively. Appearance of only one set of the C(Me)NHBu$^t$ resonances in the $^1$H NMR spectra indicates that the solid state structure of the aminocarbene ligand disclosed by the X–ray analysis is preserved exclusively in solution, where the Me and Bu$^t$ groups are in mutually syn disposition with respect to the CN bond having some multiple–bonding nature.

Despite a numerous body of carbene complexes reported to date, the aminocarbene complexes of the type M=C(R)NHR' are relatively limited.[11] Treatment of coordinated isocyanide with AlMe$_3$ followed by hydrolysis reported here presents a new synthetic pathway towards the aminocarbene complexes of this class, although the related method including protonation of the imido type M–C(R)=NR' ligands obtained from insertion of RNC into a M–R' bond has appeared for preparing Fe and Ni aminocarbene complexes.[11c]

Complex **3a** suspended in ether was reacted with 1.1 equiv of [Me$_3$O][BF$_4$] at room temperature under CO to give a cationic carbonyl–diazoalkane–aminocarbene complex *trans*–[WCl(NN=CMePh)–{=C(Me)NHBu$^t$}(CO)(PMe$_2$Ph)$_2$][BF$_4$] (**4**), which was isolated as red–purple crystals in 73% yield by crystallization of the produced solid from CH$_2$Cl$_2$/hexane (Scheme 1).[12] The IR spectrum of **4** exhibits an intense band at 1977 cm$^{-1}$ assignable to $\nu_{CO}$, which is comparable to the $\nu_{CO}$ value of the cationic diazoalkane complex *mer*–[WCl(NN=CMe$_2$)(CO)(PMe$_2$Ph)$_3$]$^+$ (1990 cm$^{-1}$).[5d] The spectrum also shows

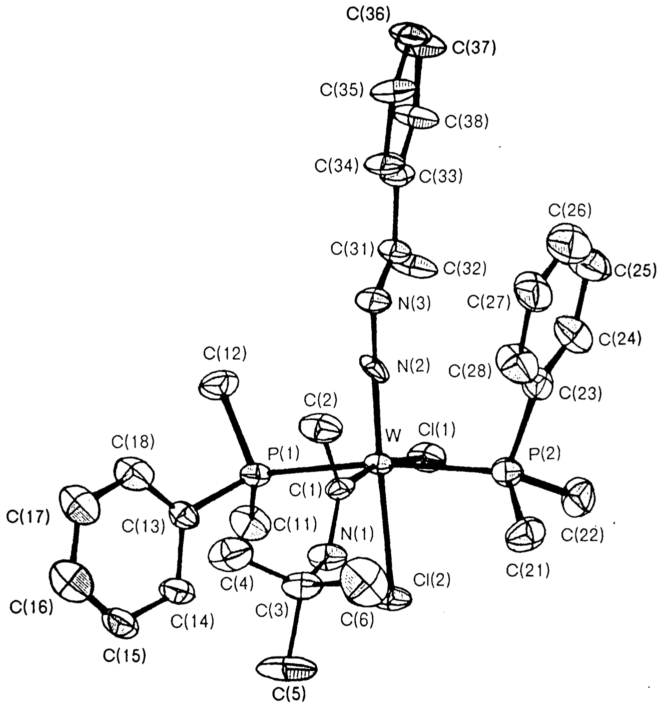


Fig. 1. Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): W–N(2) 1.770(17), W–C(1) 2.052(16), C(1)–N(1) 1.35(3), N(2)–N(3) 1.31(2), N(3)–C(31) 1.32(3), W–C(1)–N(1) 125.1(11), W–C(1)–C(2) 121.6(14)), N(1)–C(1)–C(2) 113.3(14), W–N(2)–N(3) 170.6(13), N(2)–N(3)–C(31) 118.1(13).

two bands with medium intensities at 1543 and 1524 cm$^{-1}$. Since the $\nu_{CN}$ values in the NNCMePh ligand fall in the range of 1510–1530 cm$^{-1}$ for a variety of related W(IV) and even W(V) diazoalkane complexes isolated to date, the latter band might be assignable to $\nu_{CN}$ associated with the diazoalkane ligand. The former accordingly seems to be ascribable to the aminocarbene ligand and the observed frequency is comparable to those reported for the Ni, Rh, and Ir aminocarbene complexes (1530–1620 cm$^{-1}$).[11c–e] In **3**, these two CN stretching bands are presumably overlapping and therefore recorded with unusually large intensities at 1518–1530 cm$^{-1}$.

Further studies on reactivities of **3** are in progress, in which the carbene and diazoalkane ligands are bound to the metal in mutually cis positions. This might lead to the development of new potential routes for the transformation of coordinated dinitrogen into organo-nitrogenous compounds. Financial support by the Ministry of Education, Science, and Culture of Japan is appreciated.

## References

1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 44. Part 43: H. Seino, Y. Ishii, and M. Hidai, *Organometallics*, **13**, 364 (1994).

2) M. Hidai and Y. Mizobe, "Molybdenum Enzymes, Cofactors, and Model Systems," ed by E. I. Stiefel, D. Coucouvanis, and W. E. Newton, American Chemical Society, Washington, DC (1993), pp. 346–362; M. Hidai and Y. Mizobe, "Reactions of Coordinated Ligands," ed by P. S. Braterman, Plenum, New York (1989), Vol. 2, pp. 53–114; M. Hidai, "Molybdenum Enzymes," ed by T. G. Spiro, Wiley-

Interscience, New York (1985), pp. 285–341; and references cited therein.

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

4) a) P. C. Bevan, J. Chatt, M. Hidai, and G. J. Leigh, *J. Organomet. Chem.*, **160**, 165 (1978); b) Y. Mizobe, Y. Uchida, and M. Hidai, *Bull. Chem. Soc. Jpn.*, **53**, 1781 (1980).

5) a) M. Hidai, S. Aramaki, K. Yoshida, T. Kodama, T. Takahashi, Y. Uchida, and Y. Mizobe, *J. Am. Chem. Soc.*, **108**, 1562 (1986); b) T. Aoshima, T. Tamura, Y. Mizobe, and M. Hidai, *J. Organomet. Chem.*, **435**, 85 (1992); c) Y. Ishii, H. Miyagi, S. Jitsukuni, H. Seino, B. S. Harkness, and M. Hidai, *J. Am. Chem. Soc.*, **114**, 9890 (1992); d) T. Aoshima, T. Tanase, Y. Mizobe, Y. Yamamoto, and M. Hidai, *J. Chem. Soc., Chem. Commun.*, **1992**, 586; e) H. Oshita, Y. Mizobe, and M. Hidai, *J. Organomet. Chem.*, **461**, 43 (1993).

6) M. D. Curtis and L. Messerle, *Organometallics*, **6**, 1713 (1987).

7) Anal. **3a**. Found: C, 47.29; H, 5.68; N, 5.66%. Calcd for $C_{30}H_{43}N_3Cl_2P_2W$: C, 47.26; H, 5.70; N, 5.51%. **3b**. Found: C, 42.33; H, 5.09; N, 4.94%. Calcd for $C_{30}H_{43}N_3Br_2P_2W$: C, 41.70; H, 4.80; N, 5.17%. **3c**·$CH_2Cl_2$. Found: C, 48.43; H, 5.88; N, 5.25%. Calcd for $C_{31}H_{45}N_3Cl_4P_2Mo$: C, 49.03; H, 5.97; N, 5.53%. $^1H$ NMR (270 MHz, $C_6D_6$). **3a**: δ 8.69 (s, 1H, NH), 3.43 (t, $J_{PH}$ = 1.6 Hz, 3H, WCMe), 1.98 (t, $J_{PH}$ = 0.7 Hz, 3H, NNCMe), 1.96 and 1.89 (t, $J_{PH}$ = 3.9 Hz, 6H each, PMe), 1.03 (s, 9H, $Bu^t$). **3b**: δ 8.81 (s, 1H, NH), 3.35 (s, 3H, WCMe), 1.91 (s, 3H, NNCMe), 2.06 and 1.98 (t, $J_{PH}$ = 4.4 Hz, 6H each, PMe), 1.02 (s, 9H, $Bu^t$). **3c**: δ 9.86 (s, 1H, NH), 2.89 (s, 3H, MoCMe), 2.20 (s, 3H, NNCMe), 1.93 and 1.84 (t, $J_{PH}$ = 3.7 Hz, 6H each, PMe), 0.98 (s, 9H, $Bu^t$), 5.2 (s, 2H, $CH_2Cl_2$). Phenyl protons appeared as multiplets. IR (KBr, $cm^{-1}$). **3a**: 3298 ($\nu_{NH}$), 1524 ($\nu_{CN}$). **3b**: 3285 ($\nu_{NH}$), 1530 ($\nu_{CN}$). **3c**: 3279 ($\nu_{NH}$), 1518 ($\nu_{CN}$).

8) Crystal data for **3a**: $C_{30}H_{43}N_3P_2Cl_2W$, $M$ = 762.4, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 12.619(20), $b$ = 13.700(16), $c$ = 10.739(12) Å, α = 94.52(10), β = 104.56(12), γ = 68.51(10)°, $V$ = 1672(4) Å$^3$, $Z$ = 2, $D_c$ = 1.514 g cm$^{-3}$, μ(Mo Kα) = 38.07 cm$^{-1}$. The final $R$ and $R_w$ values are 0.080 and 0.093 for 344 variables and 5037 unique reflections corrected for absorption $[|F_o| > 5\sigma(|F_o|)]$.

9) a) W. A. Nugent and J. M. Mayer, "Metal–Ligand Multiple Bonds," Wiley–Interscience, New York (1988); b) F.–M. Su, J. C. Bryan, S. Jang, and J. M. Mayer, *Polyhedron*, **8**, 1251 (1989); c) F.–M. Su, C. Cooper, S. J. Geib, A. L. Rheingold, and J. M. Mayer, *J. Am. Chem. Soc.*, **108**, 3545 (1986).

10) P. E. Baike, E. O. Fischer, and O. S. Mills, *Chem. Commun.* **1967**, 1199.

11) a) E. Moser and E. O. Fischer, *J. Organomet. Chem.*, **16**, 275 (1969); b) E. O. Fischer, P. Stückler, H.–J. Beck, and F. R. Kreißl, *Chem. Ber.*, **109**, 3089 (1976); c) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **48**, 3681 (1975); d) M. F. Lappert and A. J. Oliver, *J. Chem. Soc., Dalton Trans.*, **1974**, 65; e) B. L. Booth and A. C. Wickens, *J. Organomet. Chem.*, **445**, 283 (1993).

12) **4**·1/2$CH_2Cl_2$. Anal. Found: C, 42.55; H, 5.10; N, 4.93%. Calcd for $C_{31.5}H_{44}N_3OBF_4Cl_2P_2W$: C, 42.79; H, 5.02; N, 4.75%. $^1H$ NMR ($CD_2Cl_2$): δ 9.6 (br, 1H, NH), 2.9 (s, 3H, WCMe), 1.55 (s, 3H, NNCMe), 1.97 and 1.91 (t, $J_{PH}$ = 4.0 Hz, 6H each, PMe), 1.26 (s, 9H, $Bu^t$). Amount of solvating $CH_2Cl_2$ was determined by the spectrum recorded in $CDCl_3$. IR (KBr, $cm^{-1}$): 3250 ($\nu_{NH}$), 1543 and 1524 ($\nu_{CN}$).

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