Unprecedented Conversion of Benzylideneanilines into Aryl Isocyanides Promoted by a Low-Valent Molybdenum Complex. X-ray Structure of *trans*-[Mo(CNPh)(N_2)($Ph_2PCH_2CH_2PPh_2$)$_2$][1]

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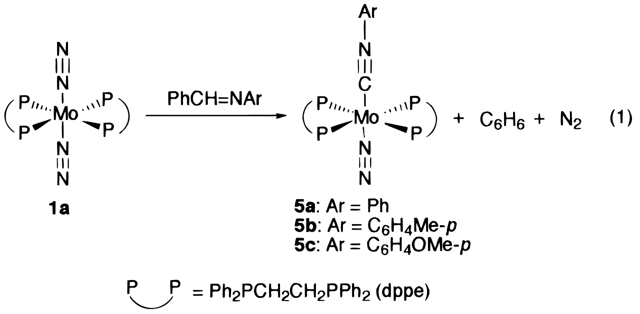
*Summary: The molybdenum dinitrogen complex trans-[Mo(N_2)$_2$(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with an excess of PhCH═NAr (Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$) in benzene at reflux under N_2 to give novel isocyanide−dinitrogen complexes, trans-[Mo(CNAr)(N_2)(dppe)$_2$] (**5**), in moderate yield. An X-ray diffraction study of **5a** (Ar = Ph) is reported.*

Our previous studies on the Mo and W dinitrogen complexes of the type [M(N_2)$_2$(**P**)$_4$] (**P** = tertiary phosphine) have clarified that the N_2 ligand in these complexes is highly reactive and readily transformed into a range of nitrogenous compounds.[3] Another important feature of these complexes, especially *trans*-[M(N_2)$_2$(dppe)$_2$] (**1**; M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$), is that they can serve as versatile precursors for the preparation of Mo and W complexes exhibiting unique reactivity. Thus, the monocarbonyl complexes *trans*-[M(CO)(DMF)(dppe)$_2$] (**2**; M = Mo,[4] W;[5] DMF = $HCONMe_2$) are readily available through the reactions of **1** with DMF, which can be converted further to *trans*-[M(CO)(N_2)(dppe)$_2$] (**3**) and then to numerous novel complexes with the {M(CO)(dppe)$_2$} moiety[6] including a H_2 complex.[6c,d]

The above decarbonylation reaction of DMF promoted by **1** appears to proceed via initial cleavage of the aldehydic C−H bond by the zerovalent Mo or W center. This has been substantiated by the isolation of the hydrido−carbamoyl complex [WH(η^2-$CONMe_2$)(dppe)$_2$] (**4**) in the reaction of **1b** (M = W) with DMF under controlled conditions.[5] In the presence of DMF, **4** is readily converted to **2b** (M = W) with concurrent formation of $HNMe_2$. It has also been found that **1a** (M = Mo) promotes analogous decarbonylation reactions of aldehydes and formate esters.[7]

Now we have extended these decarbonylation reactions observed for aldehydic compounds to the reactions of benzylideneanilines PhCH═NAr (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$). Treatment of **1a** with 1−2 equiv of PhCH═NAr in benzene at reflux for 2 h gives novel isocyanide−dinitrogen complexes, *trans*-[Mo(CNAr)(N_2)(dppe)$_2$] (**5**), in moderate yield (eq 1).[8] Concurrent formation of benzene was confirmed by GLC analysis of the reaction mixture of **1a** and PhCH═NPh in toluene at reflux (0.83 mol of C_6H_6/mol of **1a**).[9] Complexes **5** have been characterized on the basis of spectroscopic and analytical data,[10] and the structure of **5a** has been determined by single-crystal X-ray analysis.[11]



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[8] In a typical run, **1a** (166 mg, 0.175 mmol) and PhCH═NPh (33 mg, 0.18 mmol) were dissolved in benzene (2 mL) under N_2 and the solution was heated at reflux for 2 h. Addition of ether to the resulting dark red solution afforded **5a**·$2C_6H_6$ as dark red crystals (129 mg, 62%). Complexes **5b**·C_6H_6 and **5c**·$^3/_2C_6H_6$ were obtained by essentially the same procedure in 52% and 46% yields, respectively.

[9] GLC analysis of the reaction mixture of **1a** and PhCH═NC_6H_4-Me-*p* in *p*-xylene at 80 °C showed the presence of only C_6H_6 (0.73 mol/mol of **1a**), indicating that both C−C and C−H bond cleavage occurs on the benzylidene carbon.

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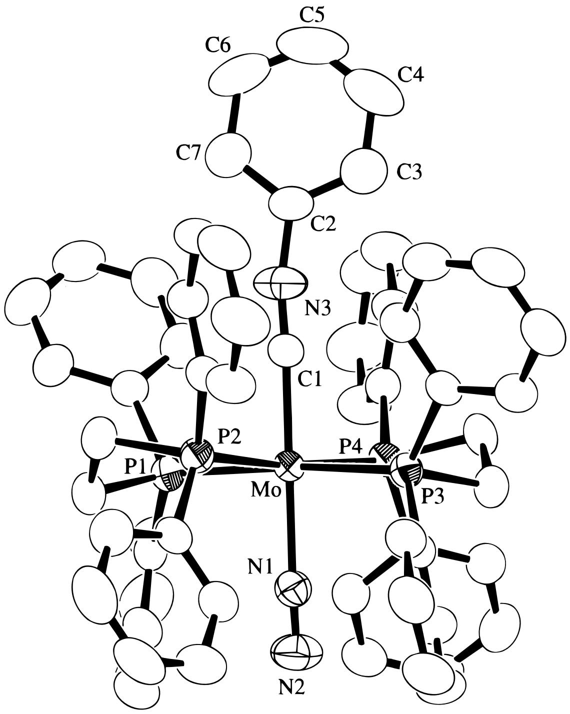

Figure 1. ORTEP drawing of **5a**. Hydrogen atoms are omitted for clarity. Important bonding parameters are as follows: Mo−N(1), 2.114(3); N(1)−N(2), 1.095(3); Mo−C(1), 1.998(3); C(1)−N(3), 1.171(4); N(3)−C(2), 1.388(4) Å; Mo−N(1)−N(2), 177.0(3); Mo−C(1)−N(3), 176.4(3); C(1)−N(3)−C(2), 167.6(4)°.

As shown in Figure 1, **5a** has an octahedral configuration with PhNC and N_2 ligands in a mutually trans position. Both ligands bind to the Mo center in an end-on fashion, and the Mo−C−N bond in the former as well as the Mo−N−N linkage in the latter are both linear. In the PhNC ligand, the C(1)−N(3)−C(2) bond (167.6(4)°) is also essentially linear, which is a common feature observed when aryl isocyanide ligands are bound to an electron-rich metal center in the absence of other strong π-acidic ligands. This is in sharp contrast to the substantially bent C−N−C array found in the corresponding alkyl isocyanide complexes.[12,13] The C(1)−N(3) distance at 1.171(4) Å is compatible with the observation of the ν(NC) band at 1910 cm^{-1}. For the N_2 ligand, the N−N distance at 1.095(3) Å is not exceptional for a terminally bound N_2 ligand and is comparable to that of 1.09(2) Å in **3a** (M = Mo),[4] which is reflected in the ν(NN) value of 2049 cm^{-1} for **5a**. Complexes **5** are new examples of Mo(0) dinitrogen complexes of the type *trans*-[Mo(L)(N_2)$(dppe)_2$], among which those with σ-donor/π-acceptor ligands L = CO (**3a**),[4] N_2 (**1a**),[16] and RCN[17] are known. It is interesting to note that the ν(NN) frequencies displayed by these complexes decrease in the order of L = CO > PhNC > N_2 > PhCN, viz., 2128 cm^{-1} for L = CO, 2049 for L = PhNC, 2020 vw (symmetric) and 1970 s cm^{-1} (asymmetric) for L = N_2, and 1945 cm^{-1} for L = PhCN. Force constants k_{NN} calculated from these ν(NN) values are 18.7, 17.3, 16.4, and 15.6 mdyne/Å for CO, PhNC, N_2, and PhCN, respectively.[18] This presumably demonstrates that the *net* π-donating nature of the {Mo(L)-$(dppe)_2$} toward the N_2 ligand increases in this order for L from CO to PhCN, at least among this series of complexes.

To our knowledge, little is known about the direct transformation of imines into isocyanides. In contrast, insertion of isocyanides into M−R bonds leading to η^1- or η^2-iminoacyls is a known process,[19] although it has been studied less extensively than the corresponding reactions of CO to form metal acyls. For certain metal iminoacyls, formation of imines by successive alkyl migration onto the iminoacyl carbon is also known.[20] The novel conversion of benzylideneanilines into isocyanides reported here may proceed by following these processes in the reverse direction. Thus, the cleavage of the benzylidene C−H bond initially takes place at the coordinatively unsaturated Mo(0) center generated by thermolysis of **1a** to give a hydrido−iminoacyl intermediate [MoH{C(=NAr)Ph}$(dppe)_2$] (**7a**), whose structure is presumably analogous to that of **4**. Degradation of the iminoacyl ligand in **7a** to the phenyl and aryl isocyanide ligands and subsequent reductive elimination of benzene affords {Mo(CNAr)$(dppe)_2$}, which rapidly coordinates N_2 to produce **5**. At present, however, intermediate stages have not been isolated or detected in reactions using **1a**.[21]

In the systems reported here, only the stoichiometric conversion takes place and even in the presence of an excess of an imine formation of isocyanides did not proceed catalytically. Modifications of the reaction system are underway in order to develop more effective routes for the preparation of isocyanides from imines, as are further efforts to isolate and characterize the intermediate stages of this transformation. Preparation

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(10) Data for **5a**·$2C_6H_6$. Anal. Calcd for $C_{71}H_{65}N_3MoP_4$: C, 72.26; H, 5.55; N, 3.56. Found: C, 71.99; H, 5.70; N, 3.37. IR (KBr, cm^{-1}): ν(NN), 2049; ν(NC), 1910. $^{31}P\{^1H\}$ NMR(C_6D_6): 68.9 (s). **5b**·C_6H_6. Anal. Calcd for $C_{66}H_{61}N_3MoP_4$: C, 71.03; H, 5.51; N, 3.77. Found: C, 71.02; H, 5.73; N, 3.23. IR (KBr, cm^{-1}): ν(NN), 2053; ν(NC), 1914. ^1H NMR (C_6D_6): 2.11 (s, 3H, *p*-Me). $^{31}P\{^1H\}$ NMR(C_6D_6): 69.1 (s). **5c**·$^3/_2C_6H_6$. Anal. Calcd for $C_{69}H_{64}N_3OMoP_4$: C, 70.77; H, 5.51; N, 3.59. Found: C, 70.12; H, 5.74; N, 3.11. IR (KBr, cm^{-1}): ν(NN), 2054; ν(NC), 1908. ^1H NMR (C_6D_6): 3.31 (s, 3H, *p*-MeO). $^{31}P\{^1H\}$ NMR(C_6D_6): 69.0 (s). Amounts of the solvating C_6H_6 in these crystals have been confirmed by either the X-ray crystallography (for **5a**·$2C_6H_6$ and **5c**·$^3/_2C_6H_6$) or GLC analysis of a toluene solution of the compound (for **5b**·C_6H_6).

(11) Crystallographic data for **5a**·$2C_6H_6$: a = 15.713(2) Å, b = 17.645(2) Å, c = 11.345(1) Å, α = 93.183(6)°, β = 103.892(7)°, and γ = 97.286(9)° with $Z = 2$ in space group $P\bar{1}$ (No. 2). R (R_w) = 0.036 (0.024) for 7090 data with $I > 3.0\sigma(I)$ and anisotropic refinements of the model with idealized hydrogen atoms.

(12) See the discussion in: Hu, C.; Hodgeman, W. C.; Bennett, D. W. *Inorg. Chem.* **1996**, *35*, 1621.

(13) The C−N−C linkage in *trans*-[Mo(CNMe)$_2$(dppe)$_2$] is significantly bent at 156(1)°,[14] while that in *trans*-[Mo(CNPh)$_2$(dppe)$_2$] is essentially linear (172.9(8)°).[15]

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(21) Reaction of the W analogue **1b** with PhCH=NPh seems to produce only an iminoacyl complex **7b** (M = W) instead of a corresponding W isocyanide−dinitrogen complex, although assignment of **7b** is still tentative.

of a series of Mo(0) complexes *trans*-[Mo(CNAr)(L)(dppe)$_2$] also is in progress.

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Supporting Information Available: Tables listing details of X-ray crystallography, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **5a** and **5c** (23 pages). Ordering information is given on any current masthead page.

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