# Reaction Mechanism of the C≡N Triple Bond Cleavage of $\beta$-Ketonitriles on a Molybdenum(0) Center[1]

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**Abstract:** The molybdenum dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$ (**2**) reacted with 2−2.5 equiv of various $\beta$-ketonitriles at room temperature to afford the (nitrido)(nitrile-enolato) complexes *trans*-$[Mo(N)(NCCR^1COR^2)(dppe)_2]$ (**4**; $R^1 = H$, $R^2 = 4\text{-}MeOCOC_6H_4$, $4\text{-}ClC_6H_4$, 4-Tol, $4\text{-}MeOC_6H_4$, $2\text{-}C_4H_3O$, $2\text{-}C_4H_3S$, $Pr^i$; $R^1 = CN$, $R^2 = Me$, Ph; dppe = $Ph_2PCH_2CH_2PPh_2$) via the C≡N triple bond cleavage of the nitriles on the molybdenum center. On the other hand, the reaction of complex **2** with 2 equiv of pivaloylacetonitrile at room temperature led to the isolation of the (alkylideneamido)(nitrile-enolato) complex *trans*-$[Mo(NCHCH_2COBu^t)(NCCHCOBu^t)(dppe)_2]$ (**5k**), which further underwent the cleavage of the C═N double bond of the alkylideneamido ligand to give the corresponding (nitrido)(nitrile-enolato) complex *trans*-$[Mo(N)(NCCHCOBu^t)(dppe)_2]$ together with 4,4-dimethyl-1-penten-3-one. Furthermore, treatment of **2** with large excess amounts of 4-chlorobenzoylacetonitrile followed by anion metathesis with $[NHEt_3][OTf]$ (OTf = $OSO_2CF_3$) resulted in the isolation of the cationic (imido)(nitrile-enolato) complex *trans*-$[Mo\{NCH_2CH_2CO(C_6H_4Cl\text{-}4)\}\{NCCHCO(C_6H_4Cl\text{-}4)\}(dppe)_2][OTf]$ ($\mathbf{6c}^+[OTf]^-$). The solid-state structures of $\mathbf{4h}\cdot 1.5C_2H_4Cl_2$ ($R^1 = CN$, $R^2 = Me$), $\mathbf{5k}\cdot C_6H_6$, and $\mathbf{6c}^+[OTf]^-$ were determined by single-crystal X-ray analyses. The detailed NMR analysis of the reaction of **2** with aroylacetonitriles revealed that the (alkylideneamido)(nitrile-enolato) complexes *trans*-$[Mo(NCHCH_2COR)(NCCHCOR)(dppe)_2]$ (**5**) act as the key intermediates for the C≡N triple bond fission, and the rate constants for the conversion of the complexes **5** into the nitrido complexes **4** showed good correlation with the Hammett $\sigma_p$ or $\sigma_a$ constants for the aroyl substituents, where positive $\rho$ values were obtained ($\rho_p$, 1.42; $\rho_a$, 0.41). A reaction mechanism for the nitrido complex formation is proposed, which includes (1) the substitution of a dinitrogen ligand in **2** with a $\beta$-ketonitrile molecule, (2) the fast protonation of the nitrile ligand by a second $\beta$-ketonitrile molecule leading to the formation of complex **5**, (3) the relatively slow proton shift from the α-position of the carbonyl group to the amido carbon in the alkylideneamido ligand to form an enolated imido ligand, and (4) the fast elimination of a vinyl ketone from the imido ligand giving the nitrido complex **4** as the final product.

## Introduction

Recent studies on the transition-metal complexes of organonitriles have revealed that the coordinated nitriles are endowed with rich reactivities.[2−6] Most of the metal-promoted reactions of nitriles reported so far are concerned with the nitrile ligands coordinated to electron-deficient metal centers through their nitrogen atoms. In such complexes, the $\sigma$-donating character of the nitrile ligands enhances the reactivity of the cyano group toward nucleophiles or facilitates the deprotonation or oxidative addition of the α-CH group. In contrast, the nitriles coordinated to $\pi$-donating metal complexes are expected to be susceptible to attack by electrophiles owing to their $\pi$-accepting character. However, nitrile complexes with strongly $\pi$-donating low-valent metal centers have been considerably limited in number, and the reactivities of nitriles in such complexes remain to be developed.[7−11]

In the course of our continuing investigation into the reactivities of the coordinated dinitrogen in low-valent molybdenum and tungsten dinitrogen complexes of the type $[M(N_2)_2(\mathbf{P})_4]$ (M = Mo, W; **P** = tertiary phosphine),[12−17] we previously

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synthesized a series of Mo(0) dinitrogen-nitrile complexes *trans*-[Mo(N$_2$)(NCR)(dppe)$_2$] (**1**; R = alkyl, aryl; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) by the reaction of the bis(dinitrogen) complex *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (**2**) with RCN.[18] The analogous tungsten compound *trans*-[W(N$_2$)(NCR)(dppe)$_2$] (**3**) was later prepared similarly.[19] These Mo(0) and W(0) nitrile complexes **1** and **3** show a large low-frequency shift of the C≡N stretching in their IR spectra (42−125 cm$^{-1}$), reflecting the effective $\pi$-donation from the metal centers, and are therefore expected to react with electrophiles. Although complexes **1** and **3** were found to undergo the electrophilic attack by H$_2$SO$_4$, PhCOCl, or EtBr at the dinitrogen ligand,[18−20] we and others have very recently observed that treatment of **1** and **3** with HCl or HBF$_4$ in THF or benzene leads to the double protonation at the cyano carbon of the nitrile ligand to give the cationic imido complexes *trans*-[MX(NCH$_2$R)(dppe)$_2$]$^+$ (M = Mo, W; X = Cl, F).[21,22] Furthermore, we have discovered that the reaction of complex **2** with 2 equiv of benzoylacetonitrile at room temperature unexpectedly affords the (nitrido)(nitrile-enolato) complex *trans*-[Mo(N)(NCCHCOPh)(dppe)$_2$] (**4a**) along with 1-phenyl-2-propen-1-one.[21] The latter reaction provides a very rare example of the C≡N triple bond fission of a nitrile ligand to form the metal nitride,[23−25] and its reaction mechanism is of great interest. Now we have succeeded in full characterization of (alkylideneamido)(nitrile-enolato) complexes that are the key intermediates for this reaction and have evaluated the reaction mechanism through the kinetic study.

## Experimental Section

**General Considerations.** All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques unless otherwise specified. Bis(dinitrogen) complex **2**,[26] benzoylmalononitrile,[27] 4-chlorobenzoylacetonitrile,[28] 4-anisoylacetonitrile,[28,29] and isobutyrylacetonitrile[30] were prepared according to the literature methods. Solvents were dried by common procedures and degassed before use. Other reagents were commercially obtained and used as received. $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded on a JEOL JNM-EX270 ($^1$H, 270 MHz; $^{31}$P, 109 MHz) or JEOL JNM-LA400 ($^1$H, 400 MHz; $^{31}$P, 162 MHz) spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by $^1$H NMR spectroscopy.

**Syntheses of (Nitrido)(nitrile-enolato) Complexes *trans*-[Mo(N)(NCCR$^1$COR$^2$)(dppe)$_2$] (4b−j).** The following procedure for the synthesis of *trans*-[Mo(N){NCCHCO(C$_6$H$_4$COOMe-4)}(dppe)$_2$]·0.5C$_6$H$_6$ (**4b**·0.5C$_6$H$_6$) is representative. Dinitrogen complex **2** (104.3 mg, 0.110 mmol) and methyl 4-(cyanoacetyl)benzoate (49.9 mg, 0.246 mmol) were dissolved in benzene (5 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution immediately changed from red to brown and then gradually to green. The mixture was stirred for an additional 2 h, during which time the solution was occasionally degassed to remove the nitrogen gas evolved. The resulting green solution was concentrated to ca. 3 mL under reduced pressure. Addition of hexane (10 mL) to this benzene solution gave **4b**·0.5C$_6$H$_6$ as slightly air-sensitive brownish green needles (117.1 mg, 93% yield), which were collected by filtration, washed twice with ether (5 mL × 2), and dried under vacuum. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 2.3−2.6, 3.0−3.3 (m, 4H each, CH$_2$ of dppe), 3.39 (s, 1H, NCCH), 3.90 (s, 3H, COOMe), 6.9−7.05 (m, 16H, Ph of dppe), 7.17, 7.31 (br t, 4H each, $J$ = 6.8 Hz, Ph of dppe), 7.24 (br t, 8H, $J$ = 6.6 Hz, Ph of dppe), 7.35 (s, 3H, benzene), 7.75 (d, 2H, $J$ = 7.8 Hz, 3-H of C$_6$H$_4$COOMe), 7.86 (br, 8H, Ph of dppe), 7.98 (d, 2H, $J$ = 7.8 Hz, 2-H of C$_6$H$_4$COOMe). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.3 (s). IR (KBr, cm$^{-1}$): 2166 (s, C≡N), 1721 (vs, COOMe), 1522 (m, enolate), 1406 (m, enolate), 976 (m, Mo≡N). Anal. Calcd for C$_{66}$H$_{59}$MoN$_2$O$_3$P$_4$: C, 69.05; H, 5.18; N, 2.44. Found: C, 68.94; H, 5.22; N, 2.39.

***trans*-[Mo(N){NCCHCO(C$_6$H$_4$Cl-4)}(dppe)$_2$]·0.5C$_7$H$_8$ (4c·0.5C$_7$H$_8$).** This compound was obtained in 20% yield as brownish green thick plates or green needles by the reaction of **2** with 4-chlorobenzoylacetonitrile for 3 h followed by recrystallization from toluene−hexane. $^1$H NMR (C$_6$D$_6$): $\delta$ 2.11 (s, 1.5H, Me of toluene), 2.2−2.5, 3.05−3.35 (m, 4H each, CH$_2$ of dppe), 3.75 (s, 1H, NCCH), 6.8−7.2 (m, 34.5H, Ph of dppe and toluene), 7.24, (d, 2H, $J$ = 8.6 Hz, 3-H of C$_6$H$_4$-Cl), 8.06 (br, 8H, Ph of dppe), 8.08 (d, 2H, $J$ = 8.6 Hz, 2-H of C$_6$H$_4$-Cl). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.2 (s). IR (KBr, cm$^{-1}$): 2151 (s, C≡N), 1512 (m, enolate), 1418 (m, enolate), 978 (m, Mo≡N). Anal. Calcd for C$_{64.5}$H$_{57}$ClMoN$_2$OP$_4$: C, 68.47; H, 5.08; N, 2.48. Found: C, 68.50; H, 5.11; N, 2.42.

***trans*-[Mo(N)(NCCHCOTol-4)(dppe)$_2$] (4d).** This compound was obtained in 62% yield as a green powder by the reaction of **2** with 4-toluoylacetonitrile for 3 h followed by recrystallization from benzene−hexane. $^1$H NMR (C$_6$D$_6$): $\delta$ 2.15 (s, 3H, Me), 2.2−2.5, 3.05−3.35 (m, 4H each, CH$_2$ of dppe), 3.93 (s, 1H, NCCH), 6.8−7.1 (m, 32H, Ph of dppe), 7.31 (d, 2H, $J$ = 8.3 Hz, 3-H of Tol), 8.06 (br, 8H, Ph of dppe), 8.29 (d, 2H, $J$ = 8.3 Hz, 2-H of Tol). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.1 (s). IR (KBr, cm$^{-1}$): 2145 (s, C≡N), 1518 (m, enolate), 1422 (m, enolate), 974 (m, Mo≡N). Anal. Calcd for C$_{62}$H$_{56}$MoN$_2$OP$_4$: C, 69.92; H, 5.30; N, 2.63. Found: C, 70.09; H, 5.66; N, 2.67.

***trans*-[Mo(N){NCCHCO(C$_6$H$_4$OMe-4)}(dppe)$_2$] (4e).** This compound was obtained in 54% yield as a green powder by the reaction of **2** with 4-anisoylacetonitrile for 3 h followed by recrystallization from benzene−hexane. $^1$H NMR (C$_6$D$_6$): $\delta$ 2.2−2.5, 3.1−3.4 (m, 4H each, CH$_2$ of dppe), 3.19 (s, 3H, OMe), 3.90 (s, 1H, NCCH), 6.8−7.1 (m, 32H, Ph of dppe), 7.13 (d, 2H, $J$ = 8.6 Hz, 3-H of C$_6$H$_4$OMe), 8.06 (br, 8H, Ph of dppe), 8.31 (d, 2H, $J$ = 8.6 Hz, 2-H of C$_6$H$_4$OMe). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.1 (s). IR (KBr, cm$^{-1}$): 2153 (s, C≡N), 1509 (m, enolate), 1405 (m, enolate), 980 (m, Mo≡N). Anal. Calcd for C$_{62}$H$_{56}$MoN$_2$O$_2$P$_4$: C, 68.89; H, 5.22; N, 2.59. Found: C, 68.56; H, 5.53; N, 2.26.

***trans*-[Mo(N){NCCHCO(C$_4$H$_3$O-2)}(dppe)$_2$]·C$_6$H$_6$ (4f·C$_6$H$_6$).** This compound was obtained in 84% yield as brownish green thick plates or green needles by the reaction of **2** with 2-furoylacetonitrile for 3 h followed by recrystallization from benzene−hexane. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 2.3−2.55, 3.0−3.25 (m, 4H each, CH$_2$ of dppe), 3.38 (s, 1H, NCCH), 6.41 (dd, 1H, $J$ = 3.0, 1.8 Hz, 4-H of furyl), 6.72 (br d, 1H, $J$ = 3.0 Hz, 3-H of furyl), 6.96, 7.21 (br t, 8H each, $J$ = 7.5 Hz, Ph of dppe), 7.16, 7.31 (br t, 4H each, $J$ = 7.3 Hz, Ph of dppe), 7.26 (br d, 1H, $J$ = 1.8 Hz, 5-H of furyl) 7.35 (s, 6H, benzene), 6.93, 7.86 (br, 8H each, Ph of dppe). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.4 (s). IR (KBr, cm$^{-1}$): 2157 (s, C≡N), 1530 (m, enolate), 1418 (m, enolate), 978 (m, Mo≡N). Anal. Calcd for C$_{65}$H$_{58}$MoN$_2$O$_2$P$_4$: C, 69.77; H, 5.22; N, 2.50. Found: C, 69.79; H, 5.28; N, 2.51.

***trans*-[Mo(N){NCCHCO(C$_4$H$_3$S-2)}(dppe)$_2$] (4g).** This compound was obtained in 86% yield as green needles by the reaction of **2** with 2-thenoylacetonitrile for 3 h followed by recrystallization from benzene−hexane. $^1$H NMR (C$_6$D$_6$): $\delta$ 2.25−2.45, 3.0−3.2 (m, 4H each,

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$CH_2$ of dppe), 3.81 (s, 1H, NCCH), 6.77 (dd, 1H, $J$ = 5.1, 1.2 Hz, 5-H of thienyl), 6.84 (dd, 1H, $J$ = 5.1, 3.5 Hz, 4-H of thienyl), 6.85−7.1 (m, 32H, Ph of dppe), 7.58 (dd, 1H, $J$ = 3.5, 1.2 Hz, 3-H of thienyl), 8.03 (br, 8H, Ph of dppe). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 60.1 (s). IR (KBr, cm$^{-1}$): 2151 (s, $C\equiv N$), 1530 (m, enolate), 1412 (m, enolate), 984 (m, $Mo\equiv N$). Anal. Calcd for $C_{59}H_{52}MoN_2OP_4S$: C, 67.04; H, 4.96; N, 2.65. Found: C, 67.19; H, 5.15; N, 2.75.

***trans*-[Mo(N){NCC(CN)COMe}(dppe)$_2$]·0.5$C_7H_8$ (4h·0.5$C_7H_8$).** This compound was obtained in 34% yield as orange prismatic crystals by the reaction of **2** with acetylmalononitrile for 1 h followed by recrystallization from toluene−hexane. $^1H$ NMR ($C_6D_6$): $\delta$ 2.11 (s, 1.5H, Me of toluene), 2.30 (s, 3H, COMe), 2.0−2.3, 2.7−3.0 (m, 4H each, $CH_2$ of dppe), 6.9−7.2 (m, 34.5H, Ph of dppe and toluene), 8.02 (br, 8H, Ph of dppe). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 60.5 (s). IR (KBr, cm$^{-1}$): 2199 (s, uncoordinated $C\equiv N$), 2168 (s, coordinated $C\equiv N$), 1592 (br vs, enolate), 1412 (m, enolate), 990 (m, $Mo\equiv N$). Anal. Calcd for $C_{60.5}H_{55}MoN_3OP_4$: C, 68.56; H, 5.23; N, 3.96. Found: C, 68.54; H, 5.60; N, 4.35.

Orange prismatic crystals of **4h**·1.5$C_2H_4Cl_2$ suitable for crystallographic study were obtained by further recrystallization from 1,2-dichloroethane−hexane. Anal. Calcd for $C_{60}H_{57}Cl_3MoN_3OP_4$: C, 62.00; H, 4.94; N, 3.62. Found: C, 62.40; H, 5.03; N, 3.69.

***trans*-[Mo(N){NCC(CN)COPh}(dppe)$_2$] (4i).** This compound was obtained in 62% yield as orange prismatic crystals or needles by the reaction of **2** with benzoylmalononitrile for 1 h followed by recrystallization from benzene−hexane. $^1H$ NMR ($C_6D_6$): $\delta$ 2.05−2.35, 2.75−3.05 (m, 4H each, $CH_2$ of dppe), 6.9−7.25 (m, 35H, Ph of dppe and COPh), 8.05 (br, 8H, Ph of dppe), 8.36 (br, 2H, COPh). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 60.7 (s). IR (KBr, cm$^{-1}$): 2199 (s, uncoordinated $C\equiv N$), 2155 (s, coordinated $C\equiv N$), 1545 (s, enolate), 1410 (m, enolate), 990 (m, $Mo\equiv N$). Anal. Calcd for $C_{62}H_{53}MoN_3OP_4$: C, 69.21; H, 4.97; N, 3.91. Found: C, 69.32; H, 5.27; N, 3.59.

***trans*-[Mo(N)(NCCHCOPr$^i$)(dppe)$_2$]·0.5$C_6H_6$ (4j·0.5$C_6H_6$).** This compound was obtained in 29% yield as a green powder by the reaction of **2** with isobutyrylacetonitrile for 3 h followed by recrystallization from benzene−hexane. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 1.31 (d, 6H, $J$ = 6.9 Hz, CH*Me*$_2$), 2.35−2.6, 2.65−2.9 (m, 4H each, $CH_2$ of dppe), 2.62 (sep, 1H, $J$ = 6.9 Hz, C*H*Me$_2$), 3.55 (s, 1H, NCCH), 7.01, 7.14 (br t, 8H each, $J$ = 7.6 Hz, Ph of dppe), 7.19, 7.25 (br t, 4H each, $J$ = 7.4 Hz, Ph of dppe), 7.35 (s, 3H, benzene), 7.06, 7.70 (br, 8H each, Ph of dppe). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 60.3 (s). IR (KBr, cm$^{-1}$): 2141 (s, $C\equiv N$), 1538 (m, enolate), 1418 (m, enolate), 980 (m, $Mo\equiv N$). Anal. Calcd for $C_{61}H_{59}MoN_2OP_4$: C, 69.38; H, 5.63; N, 2.65. Found: C, 69.33; H, 5.81; N, 3.07.

**Synthesis of *trans*-[Mo(NCHCH$_2$COBu$^t$)(NCCHCOBu$^t$)(dppe)$_2$] (5k).** Dinitrogen complex **2** (95.0 mg, 0.100 mmol) and pivaloylacetonitrile (25.6 mg, 0.205 mmol) were dissolved in toluene (5 mL) at room temperature. With rapid evolution of nitrogen gas, the yellow suspension of **2** immediately turned to a yellow-green solution. The mixture was stirred for an additional 1 h, during which time the solution was occasionally degassed to remove the nitrogen gas evolved. Addition of hexane (15 mL) to the resultant green solution gave *trans*-[Mo(NCHCH$_2$COBu$^t$)(NCCHCOBu$^t$)(dppe)$_2$] (**5k**) (76.6 mg, 67% yield) as air-sensitive light-green microcrystals, which were collected by filtration, washed twice with hexane (15 mL × 2), and dried under vacuum. $^1H$ NMR ($C_6D_6$): $\delta$ 0.80 (s, 9H, $CH_2$CO*Bu$^t$*), 1.48 (s, 9H, CHCO*Bu$^t$*), 2.3−2.6, 3.05−3.35 (m, 4H each, $CH_2$ of dppe), 3.19 (d, 2H, $J$ = 5.3 Hz, $CH_2$CO), 3.67 (s, 1H, NCCH), 4.36 (qnt of t, 1H, $J_{HP}$ = 5.9 Hz, $J_{HH}$ = 5.3 Hz, NCH), 6.9−7.1 (m, 32H, Ph of dppe), 7.51 (br, 8H, Ph of dppe). The assignment of the Bu$^t$ signals is based on the NOE measurements. $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 61.3 (s). IR (KBr, cm$^{-1}$): 2107 (s, $C\equiv N$), 1703 (m, $C{=}O$), 1530 (m, enolate), 1412 (m, enolate). Anal. Calcd for $C_{66}H_{70}MoN_2O_2P_4$: C, 69.35; H, 6.17; N, 2.45. Found: C, 69.41; H, 6.15; N, 2.34.

Brownish green prismatic crystals of **5k**·$C_6H_6$ suitable for crystallographic study were obtained by further recrystallization from benzene−hexane. Anal. Calcd for $C_{72}H_{76}MoN_2O_2P_4$: C, 70.81; H, 6.27; N, 2.29. Found: C, 70.65; H, 6.23; N, 2.15.

**Syntheses of *trans*-[Mo(N)(NCCHCOBu$^t$)(dppe)$_2$]·$C_7H_8$ (4k·$C_7H_8$). Method 1.** Complex **5k** (42.9 mg, 0.0375 mmol) was dissolved in benzene (5 mL), and the solution was refluxed for 1.5 h. Hexane was added to the resultant solution to precipitate a green powder, which was collected by filtration, washed twice with hexane (5 mL × 2), and dried under vacuum. Recrystallization of the powder from toluene−hexane gave *trans*-[Mo(N)(NCCHCOBu$^t$)(dppe)$_2$]·$C_7H_8$ (**4k**·$C_7H_8$) as brownish green needles (18.1 mg, 43% yield). $^1H$ NMR ($C_6D_6$): $\delta$ 1.54 (s, 9H, Bu$^t$), 2.11 (s, 3H, Me of toluene), 2.2−2.4, 3.05−3.25 (m, 4H each, $CH_2$ of dppe), 3.29 (s, 1H, NCCH), 6.8−7.2 (m, 37H, Ph of dppe and toluene), 8.05 (br, 8H, Ph of dppe). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 60.2 (s). IR (KBr, cm$^{-1}$): 2151 (s, $C\equiv N$), 1518 (m, enolate), 1418 (m, enolate), 978 (m, $Mo\equiv N$). Anal. Calcd for $C_{66}H_{66}MoN_2OP_4$: C, 70.58; H, 5.92; N, 2.49. Found: C, 70.30; H, 5.87; N, 2.34.

In a separate run, a benzene-$d_6$ solution (0.75 mL) of complex **5k** (9.2 mg, 8.0 $\mu$mol, 10.7 mol/m$^3$) was sealed in an NMR tube at −78 °C under vacuum and kept at room temperature for 120 h. The $^{31}P\{^1H\}$ NMR analysis of the resultant solution indicated that 34% of the starting **5k** was converted into the (nitrido)(nitrile-enolato) complex **4k**. No other signal was observed in the $^{31}P\{^1H\}$ NMR spectrum. The $^1H$ NMR spectrum of this solution also showed that **4k** was formed in 35% yield together with 4,4-dimethyl-1-penten-3-one (31% yield, $^1H$ NMR ($C_6D_6$): $\delta$ 0.95 (s, 9H, Bu$^t$), 5.20 (dd, 1H, $J$ = 7.6, 5.0 Hz, CHCO), 6.38 (d, 1H, $J$ = 7.6 Hz, $CH_2$), 6.39 (d, 1 H, $J$ = 5.0 Hz, $CH_2$)).[31]

**Method 2.** Complex **2** (95.5 mg, 0.101 mmol) and pivaloylacetonitrile (26.9 mg, 0.215 mmol) were dissolved in benzene, and the solution was refluxed for 1.5 h. Then hexane was added to the resulting solution to precipitate a green powder, which was collected by filtration, washed twice with hexane (5 mL × 2), and dried under vacuum. Recrystallization of this powder from toluene−hexane gave **4k**·$C_7H_8$ as brownish green needles (53.3 mg, 47% yield).

**Synthesis of *trans*-[Mo{NCH$_2$CH$_2$CO(C$_6$H$_4$Cl-4)}{NCCHCO(C$_6$H$_4$Cl-4)}(dppe)$_2$][OTf] (6c$^+$[OTf]$^-$).** Complex **2** (97.5 mg, 0.103 mmol) and 4-chlorobenzoylacetonitrile (375.4 mg, 2.090 mmol) were dissolved in benzene (7 mL) at room temperature. With rapid evolution of nitrogen gas, the yellow suspension immediately turned dark red. The mixture was stirred for an additional 3 h, during which time the suspension was occasionally degassed to remove the nitrogen gas evolved. Triethylammonium trifluoromethanesulfonate (81.9 mg, 0.326 mmol) was added to the resultant suspension, and the mixture was stirred for an additional 30 min. The mixture was evaporated under vacuum to give a dark brown oil, which was washed twice with ether (10 mL × 2) and extracted with benzene (2 mL × 2). Addition of ether to the benzene solution gave a brown precipitate, which was collected by filtration and dissolved in $CH_2Cl_2$. This solution was passed through a column packed with Sephadex LH-20 (eluent, methanol−$CH_2Cl_2$, 4:1). The first red band eluted was collected and evaporated to dryness, and the residual solid was recrystallized from $CH_2Cl_2$−ether to afford *trans*-[Mo{NCH$_2$CH$_2$CO(C$_6$H$_4$Cl-4)}{NCCHCO(C$_6$H$_4$-Cl-4)}(dppe)$_2$][OTf] (**6c**$^+$[OTf]$^-$; OTf = $OSO_2CF_3$) as dark red prismatic crystals (15.3 mg, 11%). $^1H$ NMR ($CDCl_3$): $\delta$ 2.08 (t, 2H, $J$ = 6.9 Hz, $CH_2$CO), 2.94 (br, 2H, $NCH_2$), 2.95−3.15, 3.25−3.45 (m, 4H each, $CH_2$ of dppe), 3.42 (s, 1H, NCCH), 7.0−7.15 (m, 16H, Ph of dppe), 7.25−7.4 (m, 20H, Ph of dppe and $C_6H_4Cl$), 7.43 (d, 2H, $J$ = 8.5 Hz, $C_6H_4Cl$), 7.45 (br, 8H, Ph of dppe), 7.54 (d, 2H, $J$ = 8.4 Hz, $C_6H_4Cl$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 47.0 (s). IR (KBr, cm$^{-1}$): 2123 (vs, $C\equiv N$), 1684 (m, $C{=}O$), 1534 (m, enolate), 1418 (s, enolate). Anal. Calcd. for $C_{71}H_{61}Cl_2F_3MoN_2O_5P_4S$: C, 60.82; H, 4.39; N, 2.00. Found: C, 60.93; H, 4.31; N, 1.99.

**Synthesis of *trans*-[Mo(NCH$_2$CH$_2$COBu$^t$)(NCCHCOBu$^t$)(dppe)$_2$][OTf]·CH$_2$Cl$_2$ (6k$^+$[OTf]$^-$·CH$_2$Cl$_2$).** To a benzene solution of complex **5k** (79.5 mg, 0.070 mmol) was added trifluoromethanesulfonic acid (20 $\mu$L, 0.23 mmol), and the resulting dark red mixture was stirred at room temperature for 1 h. Then the solvent was removed under reduced pressure, and the residual oil was purified by passing through a column packed with Sephadex LH-20 (eluent, methanol−$CH_2Cl_2$, 4:1). The first brown band was collected and evaporated to dryness, and the red residue was recrystallized from $CH_2Cl_2$−ether to give *trans*-[Mo(NCH$_2$CH$_2$COBu$^t$)(NCCHCOBu$^t$)(dppe)$_2$][OTf]·CH$_2$Cl$_2$ (**6k**$^+$[OTf]$^-$·CH$_2$Cl$_2$) as dark red prismatic crystals (22.2 mg, 23%). $^1H$ NMR ($CDCl_3$): $\delta$

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(31) Overberger, C. G.; Schiller, A. M. *J. Polym. Sci.*, *Part C*: *Polym. Symp.* **1963**, *1*, 325−337.

0.66 (s, 9H, CH$_2$COBu$^t$), 1.09 (s, 9H, CHCOBu$^t$), 1.20 (t, 2H, $J$ = 6.8 Hz, CH$_2$CO), 2.73 (t of qnt, 2H, $J_{HH}$ = 6.8 Hz, $J_{HP}$ = 4.2 Hz, NCH$_2$), 2.8−3.0, 3.25−3.45 (m, 4H each, CH$_2$ of dppe), 3.13 (s, 1H, NCCH), 5.30 (s, 2H, CH$_2$Cl$_2$), 7.0−7.1 (m, 16H, Ph of dppe), 7.34 (br t, 8H, $J$ = 7.4 Hz, Ph of dppe), 7.39 (br, 8H, Ph of dppe), 7.25, 7.46 (br t, 4H each, $J$ = 7.1 Hz, Ph of dppe). The assignment of the Bu$^t$ signals is based on the NOE measurements. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 45.8 (s). IR (KBr, cm$^{-1}$): 2118 (vs, C≡N), 1698 (m, C═O), 1547 (m, enolate), 1408 (s, enolate). Anal. Calcd for $C_{68}H_{73}Cl_2F_3MoN_2O_5P_4S$: C, 59.26; H, 5.34; N, 2.03. Found: C, 58.93; H, 5.49; N, 2.03.

**Characterization of the (Alkylideneamido)(nitrile-enolato) Complexes.** The following (alkylideneamido)(nitrile-enolato) complexes **5a−g** were detected as intermediate species when the reactions of complex **2** and the corresponding $\beta$-ketonitriles were followed by $^1$H NMR, $^{31}$P{$^1$H} NMR, and IR. They were characterized by comparison of the spectroscopic data with those of complex **5k**. Selected spectroscopic data are as follows.

***trans*-[Mo(NCHCH$_2$COPh)(NCCHCOPh)(dppe)$_2$] (5a).** $^1$H NMR (C$_6$D$_6$): $\delta$ 3.25 (d, 2H, $J$ = 5.9 Hz, CH$_2$CO), 4.26 (qnt of t, 1H, $J_{HP}$ = 6.3 Hz, $J_{HH}$ = 5.9 Hz, NCH), 4.39 (br, 1H, NCCH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.3 (s). IR (KBr, cm$^{-1}$): 2118 (s, C≡N), 1682 (m, C═O).

***trans*-[Mo{NCHCH$_2$CO(C$_6$H$_4$COOMe-4)}{NCCHCO(C$_6$H$_4$COOMe-4)}(dppe)$_2$] (5b).** This complex was formed only in low concentration, and the $^1$H NMR data could not be obtained. $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.4 (s). IR (KBr, cm$^{-1}$): 2118 (s, C≡N), 1723 (vs, COOMe) 1688 (m, C═O).

***trans*-[Mo{NCHCH$_2$CO(C$_6$H$_4$Cl-4)}{NCCHCO(C$_6$H$_4$Cl-4)}(dppe)$_2$] (5c).** This complex was formed only in low concentration, and the $^1$H NMR data could not be obtained. $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.4 (s). IR (KBr, cm$^{-1}$): 2116 (s, C≡N), 1684 (m, C═O).

***trans*-[Mo(NCHCH$_2$COTol-4)(NCCHCOTol-4)(dppe)$_2$] (5d).** $^1$H NMR (C$_6$D$_6$): $\delta$ 2.03 (s, 3H, Me), 2.13 (s, 3H, Me), 3.25 (d, 2H, $J$ = 5.9 Hz, CH$_2$CO), 4.32 (qnt of t, 1H, $J_{HP}$ = 6.3 Hz, $J_{HH}$ = 5.9 Hz, NCH), 4.44 (br, 1H, NCCH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.3 (s). IR (KBr, cm$^{-1}$): 2116 (s, C≡N), 1686 (m, C═O).

***trans*-[Mo{NCHCH$_2$CO(C$_6$H$_4$OMe-4)}{NCCHCO(C$_6$H$_4$OMe-4)}(dppe)$_2$] (5e).** $^1$H NMR (C$_6$D$_6$): $\delta$ 3.21 (s, 3H, Me), 3.26 (d, 2H, $J$ = 5.9 Hz, CH$_2$CO), 3.29 (s, 3H, Me), 4.34 (qnt of t, 1H, $J_{HP}$ = 6.3 Hz, $J_{HH}$ = 5.9 Hz, NCH), 4.42 (br, 1H, NCCH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.3 (s). IR (KBr, cm$^{-1}$): 2110 (s, C≡N), 1669 (m, C═O).

***trans*-[Mo{NCHCH$_2$CO(C$_4$H$_3$O-2)}{NCCHCO(C$_4$H$_3$O-2)}(dppe)$_2$] (5f).** $^1$H NMR (C$_6$D$_6$): $\delta$ 3.29 (d, 2H, $J$ = 5.9 Hz, CH$_2$CO), 4.13 (qnt of t, 1H, $J_{HP}$ = 6.3 Hz, $J_{HH}$ = 5.9 Hz, NCH), 4.59 (br, 1H, NCCH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.5 (s). IR (KBr, cm$^{-1}$): 2114 (m, C≡N), 1673 (s, C═O).

***trans*-[Mo{NCHCH$_2$CO(C$_4$H$_3$S-2)}{NCCHCO(C$_4$H$_3$S-2)}(dppe)$_2$] (5g).** $^1$H NMR (C$_6$D$_6$): $\delta$ 3.27 (d, 2H, $J$ = 5.9 Hz, CH$_2$CO), 4.15 (qnt of t, 1H, $J_{HP}$ = 6.3 Hz, $J_{HH}$ = 5.9 Hz, NCH), 4.34 (br, 1H, NCCH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 60.3 (s). IR (KBr, cm$^{-1}$): 2110 (m, C≡N), 1665 (s, C═O).

**Kinetic Study of the Reactions between Complex 2 and $\beta$-Ketonitriles.** The following procedure is representative. A benzene-$d_6$ solution (0.75 mL) of **2** (9.7 mg, 10 $\mu$mol, 14 mol/m$^3$) and ca. 2 equiv of benzoylacetonitrile (3.1 mg, 21 $\mu$mol) was sealed in an NMR tube at −78 °C under vacuum. The sample was quickly warmed to 25 °C, and the reaction was started to be monitored by means of $^{31}$P{$^1$H} NMR. The spectra were obtained every 10 min for 5 h. Throughout the measurement, only three signals were observed, which were assigned as complexes **2** ($\delta$ 65.4), **4a** ($\delta$ 60.2), and **5a** ($\delta$ 60.3). The ratios of these complexes were determined on the basis of the relative intensities of the $^{31}$P{$^1$H} NMR signals. In separate experiments, it was confirmed that complexes **2**, **4**, and **5k** show the $^{31}$P{$^1$H} NMR signals with essentially the same relative intensities. Kinetic constants were calculated by the linear and nonlinear regression programs of Wolfram *Mathematica* 3.0 based on the least-squares and Gauss−Newton methods.

**X-ray Diffraction Studies.** Single crystals of **4h**·1.5C$_2$H$_4$Cl$_2$, **5k**·C$_6$H$_6$, and **6c**$^+$[OTf]$^-$ were sealed in glass capillaries under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer with graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å) at 21 °C using the $\omega$ scan technique for **5k**·C$_6$H$_6$ and the $\omega$-2$\theta$ scan technique for **4h**·1.5C$_2$H$_4$Cl$_2$ and **6c**$^+$[OTf]$^-$ ($5° < 2\theta < 50°$). The orientation matrices and unit cell parameters were determined by least-squares refinement of 23−25 machine-centered reflections with $27.7° < 2\theta < 35.6°$ for **4h**·1.5C$_2$H$_4$Cl$_2$, $29.1° < 2\theta < 35.4°$ for **5k**·C$_6$H$_6$, and $33.3° < 2\theta < 37.5°$ for **6c**$^+$[OTf]$^-$. Intensity data were corrected for Lorentz and polarization effects and for absorption (empirical, $\psi$ scans). For crystals of **5k**·C$_6$H$_6$ and **6c**$^+$[OTf]$^-$, no significant decay was observed for three respective standard reflections monitored every 150 reflections during the data collection. For compound **4h**·1.5C$_2$H$_4$Cl$_2$, slight decay (3.09%) was observed during the data collection, and a correction for decay was applied.

The structure solution and refinements were carried out by using the teXsan Program package.[32] The positions of the non-hydrogen atoms were determined by direct methods (SIR92[33] for **6c**$^+$[OTf]$^-$) or Patterson methods (DIRDIF PATTY[34] for **4h**·1.5C$_2$H$_4$Cl$_2$ and **5k**·C$_6$H$_6$,) and subsequent Fourier syntheses. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic thermal parameters except for the carbon and fluorine atoms of one of the Bu$^t$ groups in **5k**·C$_6$H$_6$ and the triflate anion in **6c**$^+$[OTf]$^-$. The triflate anion in **6c**$^+$[OTf]$^-$ showed signs of disorder, and the carbon and fluorine atoms of this anion could not be refined. These atoms were located on the basis of the difference Fourier map and were included in the refinement as fixed isotropic parameters. The Bu$^t$ group of the nitrile-enolato ligand in **5k**·C$_6$H$_6$ was also found to be disordered, and the three methyl carbons of this Bu$^t$ group were refined with occupancy factors of 0.6/0.4. The carbon atoms of the major structure were refined anisotropically, while those of the minor structure were refined with isotropic parameters. Hydrogen atoms except for those of the disordered Bu$^t$ group in **5k**·C$_6$H$_6$ were placed at the calculated positions and were included in the final stage of refinements with fixed isotropic parameters. The atomic scattering factors were taken from ref 35, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 36. The maximum and minimum residual peaks on the final difference Fourier maps were 0.71/−0.55, 0.58/−0.66, and 0.87/−0.80 e/Å$^3$ for **4h**·1.5C$_2$H$_4$Cl$_2$, **5k**·C$_6$H$_6$, and **6c**$^+$[OTf]$^-$, respectively. Details of the X-ray diffraction study are summarized in Table 1.

## Results and Discussion

**Reactions of Complex 2 with $\beta$-Ketonitriles to Give (Nitrido)(nitrile-enolato) Complexes.** In the previous paper,[21] we proposed that the reaction of dinitrogen complex **2** with benzoylacetonitrile, which results in the C≡N triple bond cleavage to give the (nitrido)(nitrile-enolato) complex **4a**, involves protonation of the coordinated cyano group by the acidic α-CH of benzoylacetonitrile, but no direct evidence for the mechanism was available. To clarify the detailed mechanism, we at first examined reactions of **2** with various $\beta$-ketonitriles. When complex **2** was allowed to react with 2−2.5 equiv of *p*-substituted benzoylacetonitriles (4-RC$_6$H$_4$)COCH$_2$CN (R = MeOCO, Cl, Me, MeO) at room temperature, the (nitrido)(nitrile-enolato) complexes *trans*-[Mo(N){NCCHCO(C$_6$H$_4$R-4)}(dppe)$_2$] (**4b−e**) were obtained in moderate to good yields (Scheme 1). Similarly, other types of $\beta$-ketonitriles such as (2-C$_4$H$_3$X)COCH$_2$CN (X = O, S), RCOCH(CN)$_2$ (R = Me, Ph), and Pr$^i$COCH$_2$CN afforded the corresponding (nitrido)(nitrile-

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[32] *teXsan*: *Crystal Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

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[34] PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system*; Technical Report of the Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1992.

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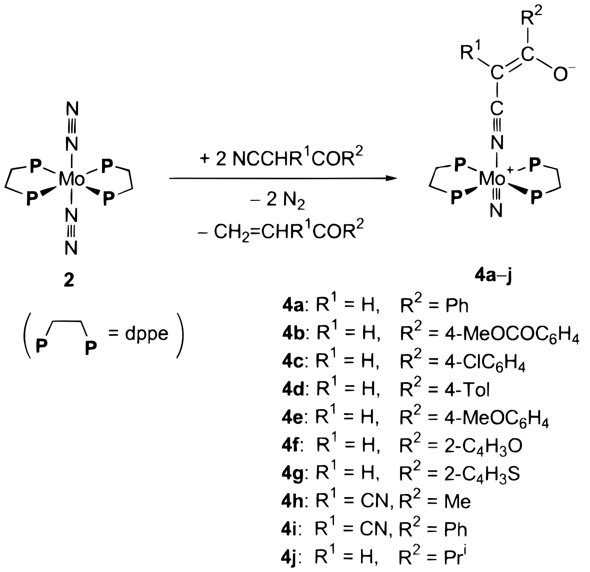
[36] *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C.

**Table 1.** X-ray Crystallographic Data for **4h**·$1.5C_2H_4Cl_2$, **5k**·$C_6H_6$, and **6c**$^+$[OTf]$^-$

| | **4h**·$1.5C_2H_4Cl_2$ | **5k**·$C_6H_6$ | **6c**$^+$[OTf]$^-$ |
|---|---|---|---|
| empirical formula | $C_{60}H_{57}Cl_3MoN_3OP_4$ | $C_{72}H_{76}MoN_2O_2P_4$ | $C_{71}H_{61}Cl_2F_3MoN_2O_5P_4S$ |
| formula weight | 1162.32 | 1221.24 | 1402.07 |
| crystal system | monoclinic | triclinic | triclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ |
| crystal size, mm | 0.75 × 0.30 × 0.05 | 0.80 × 0.40 × 0.15 | 0.50 × 0.25 × 0.15 |
| $a$, Å | 13.982(5) | 9.8581(9) | 14.983(2) |
| $b$, Å | 18.416(4) | 13.628(2) | 15.110(3) |
| $c$, Å | 22.753(4) | 25.851(3) | 16.682(3) |
| α, deg | | 102.97(1) | 107.70(2) |
| $\beta$, deg | 100.19(2) | 96.791(9) | 102.01(1) |
| $\gamma$, deg | | 104.099(9) | 96.98(2) |
| $V$, Å$^3$ | 5766(2) | 3227.2(8) | 3449(1) |
| $Z$ | 4 | 2 | 2 |
| $\mu$(Mo Kα), cm$^{-1}$ | 5.19 | 3.48 | 4.48 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.339 | 1.257 | 1.350 |
| $R^a$ | 0.052 | 0.063 | 0.069 |
| $R_w{}^b$ | 0.035 | 0.041 | 0.056 |
| GOF$^c$ | 1.63 | 1.97 | 2.41 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = [\sigma_c^2(F_0) + p^2F_0^2/4]^{-1}$ [$p$ = 0.002 (**4h**·$1.5C_2H_4Cl_2$), 0.001 (**5k**·$C_6H_6$), 0.003 (**6c**$^+$[OTf]$^-$)]. [c] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

### Scheme 1



**2**

**4a**–**j**

**4a**: $R^1$ = H, $R^2$ = Ph
**4b**: $R^1$ = H, $R^2$ = 4-MeOCOC$_6$H$_4$
**4c**: $R^1$ = H, $R^2$ = 4-ClC$_6$H$_4$
**4d**: $R^1$ = H, $R^2$ = 4-Tol
**4e**: $R^1$ = H, $R^2$ = 4-MeOC$_6$H$_4$
**4f**: $R^1$ = H, $R^2$ = 2-C$_4$H$_3$O
**4g**: $R^1$ = H, $R^2$ = 2-C$_4$H$_3$S
**4h**: $R^1$ = CN, $R^2$ = Me
**4i**: $R^1$ = CN, $R^2$ = Ph
**4j**: $R^1$ = H, $R^2$ = Pr$^i$

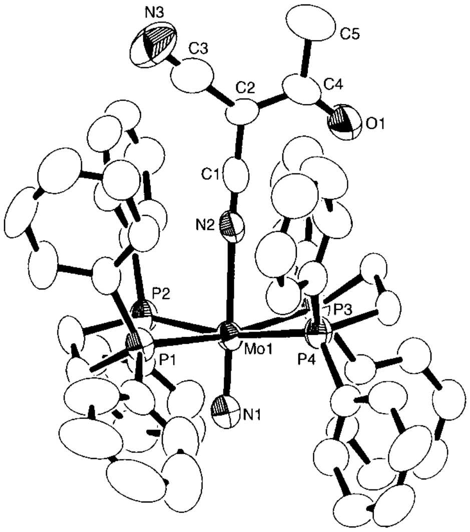


**Figure 1.** Structure of *trans*-[Mo(N){NCC(CN)COMe}(dppe)$_2$]·$1.5C_2H_4Cl_2$ (**4h**·$1.5C_2H_4Cl_2$). Hydrogen atoms and solvating 1,2-dichloroethane are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

enolato) complexes **4f**−**j**, revealing that the C≡N triple bond cleavage reaction occurs with a wide range of $\beta$-ketonitriles. In contrast, no C≡N triple bond fission was observed with less acidic nitriles including methyl cyanoacetate and diphenylacetonitrile. It seems that this reaction requires at least one $\beta$-keto group (or stronger electron-withdrawing group) in the substrate nitrile.

The (nitrido)(nitrile-enolato) complexes **4b**−**j** were characterized by their spectroscopic data as well as an X-ray crystallographic study of **4h**·$1.5C_2H_4Cl_2$. The IR spectra of (nitrido)(nitrile-enolato) complexes **4** showed absorptions with medium intensities at 974−990 cm$^{-1}$ characteristic of the Mo≡N bond.[37,38] The $\nu$(C≡N) band due to the coordinated cyano group in **4** appeared at 2141−2168 cm$^{-1}$. This value is comparable to those reported for the N-bound cyanoenolato (2110−2200 cm$^{-1}$)[39−42] or keteniminato complexes (2120−2190 cm$^{-1}$).[43−47] Two absorptions observed at 1405−1422 and 1509−1592 cm$^{-1}$ are assignable to the enolate group. The $^1$H NMR spectra of **4b**−**g** and **4j** displayed a singlet at $\delta$ 3.38−3.93 with the intensity of 1H, confirming the deprotonated structure of the nitrile-enolato ligands. The $^{31}$P{$^1$H} NMR spectra showing a singlet at $\delta$ 60.1−60.7 clearly indicate the *trans* geometry.

The molecular structure of **4h**·$1.5C_2H_4Cl_2$ established by X-ray diffraction study is given in Figure 1, and selected bond distances and angles are shown in Table 2. The metrical features around the molybdenum center are closely related to those found for **4a**·$0.5C_7H_8$.[21] The C(1)−C(2), C(2)−C(3), and C(2)−C(4)

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**Table 2.** Selected Bond Distances and Angles in **4h**·$1.5C_2H_4Cl_2$

| Distances (Å) | | | |
|---|---|---|---|
| Mo(1)−P(1) | 2.517(2) | Mo(1)−P(2) | 2.511(2) |
| Mo(1)−P(3) | 2.530(2) | Mo(1)−P(4) | 2.532(2) |
| Mo(1)−N(1) | 1.704(6) | Mo(1)−N(2) | 2.406(6) |
| O(1)−C(4) | 1.220(9) | N(2)−C(1) | 1.151(8) |
| N(3)−C(3) | 1.13(1) | C(1)−C(2) | 1.412(10) |
| C(2)−C(3) | 1.43(1) | C(2)−C(4) | 1.43(1) |
| C(4)−C(5) | 1.49(1) | | |
| **Angles (deg)** | | | |
| P(1)−Mo(1)−N(1) | 93.0(2) | P(1)−Mo(1)−N(2) | 85.6(2) |
| P(2)−Mo(1)−N(1) | 88.3(2) | P(2)−Mo(1)−N(2) | 90.9(2) |
| P(3)−Mo(1)−N(1) | 98.7(2) | P(3)−Mo(1)−N(2) | 82.6(2) |
| P(4)−Mo(1)−N(1) | 100.8(2) | P(4)−Mo(1)−N(2) | 79.9(1) |
| N(1)−Mo(1)−N(2) | 178.6(2) | Mo(1)−N(2)−C(1) | 176.9(6) |
| N(2)−C(1)−C(2) | 177.9(9) | C(1)−C(2)−C(3) | 120.4(8) |
| C(1)−C(2)−C(4) | 115.3(8) | C(3)−C(2)−C(4) | 124.3(8) |
| O(1)−C(4)−C(2) | 122.3(8) | | |

distances in the nitrile-enolato ligand are almost the same (1.41−1.43 Å), and this ligand takes an essentially planar conformation. The negative charge is considered to be highly delocalized over the nitrile-enolato ligand. The enolato oxygen atom O(1) is found to be located considerably close to the dppe phenyl (C(13)) and methylene (C(18)) carbons of a neighboring molecule (O(1)···C(13), 3.20(1); O(1)···C(18), 3.327(9) Å). In particular, the O(1)···H(15)−C(18) angle and the O(1)···H(15) distance are estimated to be 151.8° and 2.46 Å, respectively, which strongly suggest that there exists an intermolecular C−H···O hydrogen bond between these atoms.[48−53] We have previously described that complex **4a** also forms a short intermolecular C−H···O contact that can be considered as a hydrogen bond.[21] The fact that the oxygen atoms of the nitrile-enolato ligands in crystals of both **4a** and **4h** are involved in intermolecular hydrogen bondings with weakly acidic CH groups is of special interest. We consider that the formation of such C−H···O hydrogen bonds is favored by the unique zwitterionic structure of **4** where the enolato oxygen atom has no countercation in the vicinity.

**Synthesis and Properties of the (Alkylideneamido)(nitrile-enolato) Complex 5k.** When complex **2** was allowed to react with 2 equiv of pivaloylacetonitrile in toluene at room temperature, the (alkylideneamido)(nitrile-enolato) complex *trans*-[Mo($NCHCH_2COBu^t$)($NCCHCOBu^t$)($(dppe)_2$)] (**5k**) was isolated in 67% yield instead of the (nitrido)(nitrile-enolato) complex *trans*-[Mo(N)($NCCHCOBu^t$)($(dppe)_2$)] (**4k**). Complex **5k** includes two distinct organic ligands derived from pivaloylacetonitrile, one of which is incorporated in its deprotonated form, while the other is in the protonated form at the cyano carbon. The $^1H$ NMR spectrum of **5k** clearly demonstrated the presence of the two types of ligands derived from pivaloylacetonitrile. The singlet signals at $\delta$ 1.48 (9H) and 3.67 (1H) are attributable to the nitrile-enolato ligand ($NCCHCOBu^t$), while the signals at $\delta$ 0.80 (s, 9H), 3.19 (d, 2H), and 4.36 (qnt of t, 1H) are assignable to the alkylideneamido ligand ($NCHCH_2COBu^t$). These assignments are in accord with the IR spectrum, which exhibited the $\nu$(C≡N) band of the nitrile-enolato ligand and the $\nu$(C═O) band of the alkylideneamido ligand at 2107 and 1703 $cm^{-1}$, respectively.

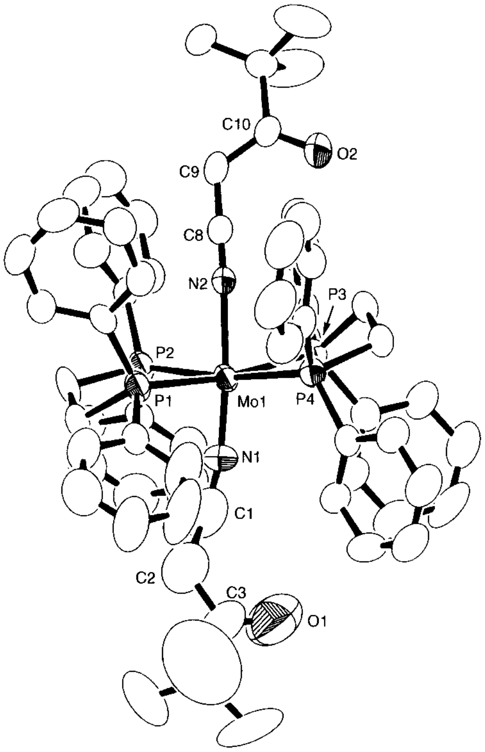

**Figure 2.** Structure of *trans*-[Mo($NCHCH_2COBu^t$)($NCCHCOBu^t$)($(dppe)_2$)]·$C_6H_6$ (**5k**·$C_6H_6$). Hydrogen atoms and solvating benzene are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

**Table 3.** Selected Bond Distances and Angles in **5k**·$C_6H_6$

| Distances (Å) | | | |
|---|---|---|---|
| Mo(1)−P(1) | 2.486(3) | Mo(1)−P(2) | 2.488(2) |
| Mo(1)−P(3) | 2.527(2) | Mo(1)−P(4) | 2.508(3) |
| Mo(1)−N(1) | 1.754(7) | Mo(1)−N(2) | 2.157(7) |
| O(1)−C(3) | 1.26(1) | O(2)−C(10) | 1.242(9) |
| N(1)−C(1) | 1.29(1) | N(2)−C(8) | 1.142(10) |
| C(1)−C(2) | 1.61(2) | C(2)−C(3) | 1.50(2) |
| C(8)−C(9) | 1.41(1) | C(9)−C(10) | 1.41(1) |
| **Angles (deg)** | | | |
| P(1)−Mo(1)−N(1) | 87.4(3) | P(1)−Mo(1)−N(2) | 90.3(2) |
| P(2)−Mo(1)−N(1) | 88.2(3) | P(2)−Mo(1)−N(2) | 86.2(2) |
| P(3)−Mo(1)−N(1) | 100.6(3) | P(3)−Mo(1)−N(2) | 81.5(2) |
| P(4)−Mo(1)−N(1) | 100.4(3) | P(4)−Mo(1)−N(2) | 85.2(2) |
| N(1)−Mo(1)−N(2) | 174.3(3) | Mo(1)−N(1)−C(1) | 167.5(9) |
| Mo(1)−N(2)−C(8) | 168.4(8) | N(1)−C(1)−C(2) | 129(1) |
| C(1)−C(2)−C(3) | 118(1) | O(1)−C(3)−C(2) | 114(1) |
| N(2)−C(8)−C(9) | 175(1) | C(8)−C(9)−C(10) | 123.5(8) |
| O(2)−C(10)−C(9) | 118.3(9) | | |

A crystallographic study of **5k**·$C_6H_6$ provided the final structure assignment of the (alkylideneamido)(nitrile-enolato) complex. An ORTEP view is depicted in Figure 2, and important bond distances and angles are summarized in Table 3. The geometry around the molybdenum center is distorted octahedral with the alkylideneamido and nitrile-enolato ligands *trans* to each other. The Mo(1)−N(1) and N(1)−C(1) bond distances at 1.754(7) and 1.29(1) Å, respectively, as well as the almost linear Mo(1)−N(1)−C(1) arrangement (167.5(9)°) are consistent with the Mo═N and N═C double bond character of the alkylideneamido ligand. Interestingly, significantly longer Mo−N (1.853(8) Å) and shorter N−C (1.224(16) Å) distances are reported for the related molybdenum alkylideneamido complex *trans*-[MoCl(NCHCOOMe)($(dppe)_2$)].[54] On the other hand, the

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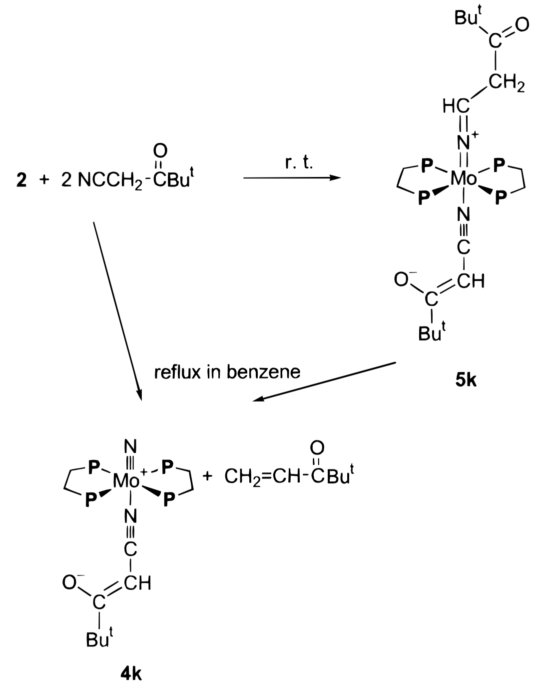
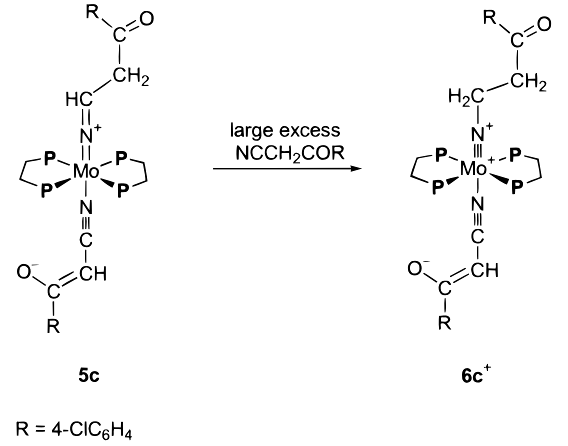
**Scheme 2**



**Scheme 3**



nitrile-enolato ligand is coordinated to the molybdenum center with the Mo−N distance (Mo(1)−N(2), 2.157(7) Å) much shorter than those in complexes **4h**$\cdot$1.5$C_2H_4Cl_2$ (2.406(6) Å) and **4a**$\cdot$0.5$C_7H_8$ (2.386(3) Å), reflecting the smaller *trans* influence of the alkylideneamido ligand than that of the nitrido ligand. Other metrical features within the nitrile-enolato ligand in **5k**$\cdot C_6H_6$ are similar to those of **4h**$\cdot$1.5$C_2H_4Cl_2$. It should also be noted that the enolato oxygen atom O(2) is in contact with one of the dppe phenyl CH (C(22)−H(19)) of a neighboring molecule. The estimated O(2)···H(19) separation and the O(2)···H(19)−C(22) angle are 2.67 Å and 159.2°, respectively, which imply weak intermolecular interaction between these atoms.[48−53]

Importantly, complex **5k** underwent the C═N double bond cleavage of the alkylideneamido ligand on refluxing in benzene to produce the (nitrido)(nitrile-enolato) complex **4k**, which was isolated in moderate yield and characterized spectroscopically (Scheme 2). As expected, **4k** was also obtained directly by the reaction of complex **2** with pivaloylacetonitrile in refluxing benzene. Furthermore, although the C═N double bond cleavage of **5k** was sluggish at room temperature, the $^1H$ and $^{31}P\{^1H\}$ NMR analysis of a benzene-$d_6$ solution of **5k** revealed that ca. 35% of the starting **5k** was transformed into complex **4k** and 4,4-dimethyl-1-penten-3-one after 120 h at room temperature without formation of any detectable amounts of byproducts. These observations clearly indicate that the (alkylideneamido)(nitrile-enolato) complexes similar to **5k** are key intermediates for the C≡N triple bond cleavage of $\beta$-ketonitriles on the molybdenum center.

To obtain preliminary information about the kinetics of the reaction between complex **2** and $\beta$-ketonitriles, the conversion of complex **5k** to **4k** was monitored by $^{31}P\{^1H\}$ NMR at 90 °C in toluene-$d_8$ for 3.5 h. The reaction was clearly shown to be first-order in the concentration of complex **5k** by the double logarithmic plot of the reaction rate and the concentration (the differential method), and the rate constant at this temperature was determined to be $1.08(10) \times 10^{-4}$ $s^{-1}$. Under the same conditions, *trans*-[Mo(NCDCD$_2$COBu$^t$)(NCCDCOBu$^t$)(dppe)$_2$] (**5k**-$d_4$), which was prepared by the H−D exchange reaction of **5k** with $D_2O$ in toluene-$d_8$, was transformed to *trans*-[Mo(N)(NCCDCOBu$^t$)(dppe)$_2$] (**4k**-$d_1$) with the rate constant of $4.1(4) \times 10^{-5}$ $s^{-1}$. Thus, the $k_H/k_D$ value was estimated to be $2.7 \pm 0.4$. The primary kinetic isotope effect observed indicates that the rate-determining step in the reaction includes a C−H bond breaking process.[55]

**Formation of (Imido)(nitrile-enolato) Complexes.** Although the reaction of complex **2** with 2 equiv of 4-chlorobenzoylacetonitrile smoothly gave the corresponding (nitrido)(nitrile-enolato) complex **4c** as described above, use of a large excess (20 equiv) of the nitrile essentially suppressed the C≡N triple bond cleavage reaction (Scheme 3). In this case, anion metathesis of the crude reaction mixture with [NHEt$_3$][OTf] and purification by column chromatography led to isolation of a new cationic complex *trans*-[Mo{NCH$_2$CH$_2$CO(C$_6$H$_4$Cl-4)}{NCCHCO(C$_6$H$_4$Cl-4)}(dppe)$_2$][OTf] (**6c**$^+$[OTf]$^-$). In the $^1H$ NMR, complex **6c**$^+$[OTf]$^-$ showed signals attributable to the $NCH_2CH_2CO$ group ($\delta$ 2.08, t, 2H; 2.94, br, 2H), revealing the presence of the imido ligand generated by the double protonation of a nitrile molecule on the molybdenum center.[21] In addition, the IR absorptions at 2123, 1534, and 1418 $cm^{-1}$ indicate that the complex also contains the nitrile-enolato ligand.

The molecular structure of **6c**$^+$[OTf]$^-$ was unambiguously determined by X-ray diffraction study. An ORTEP view is illustrated in Figure 3, and important bond distances and angles are given in Table 4. The Mo(1)−N(1) and N(1)−C(1) bond distances at 1.704(9) and 1.46(1) Å, respectively, and the linear Mo(1)−N(1)−C(1) linkage (178.3(8)°) confirm that the C(1) atom, which was originally a cyano carbon, has been doubly protonated to form the imido ligand.[21,54,56] On the other hand, the nitrile-enolato ligand shows structural characteristics similar to those observed for **5k**$\cdot C_6H_6$.

The cation **6c**$^+$ is considered to be formed by the protonation of the initially formed (alkylideneamido)(nitrile-enolato) complex *trans*-[Mo{NCHCH$_2$CO(C$_6$H$_4$Cl-4)}{NCCHCO(C$_6$H$_4$Cl-4)}(dppe)$_2$] (**5c**) with an excess of the acidic free nitrile. In fact, protonation of complex **5k** with HOTf also provided the (imido)(nitrile-enolato) complex *trans*-[Mo(NCH$_2$CH$_2$COBu$^t$)(NCCHCOBu$^t$)(dppe)$_2$][OTf] (**6k**$^+$[OTf]$^-$). It is interesting to note that, in both cations **6c**$^+$ and **6k**$^+$, the protonation has occurred not at the negatively charged nitrile-enolato ligand but at the alkylideneamido ligand. On the other hand, it was

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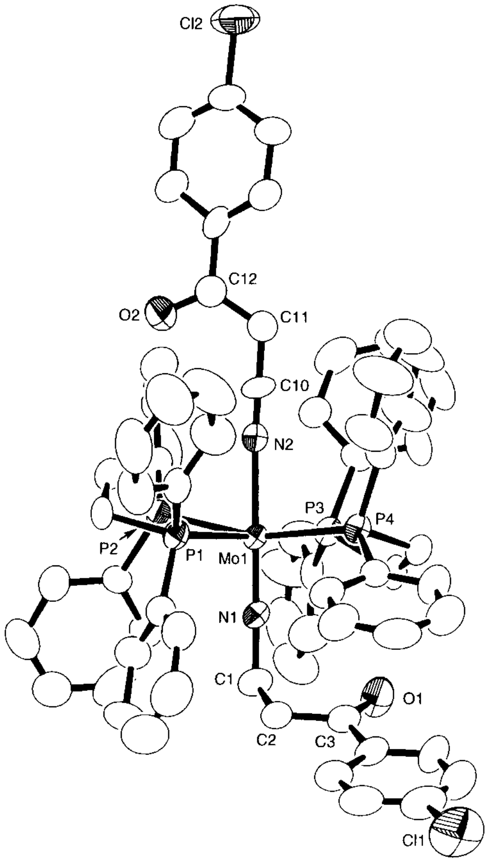


**Figure 3.** Structure of the cationic part in *trans*-[Mo{$NCH_2CH_2CO$-($C_6H_4Cl$-4)}{$NCCHCO(C_6H_4Cl$-4)}$(dppe)_2$][OTf] ($6c^+[OTf]^-$). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

**Table 4.** Selected Bond Distances and Angles in **6c**$^+$[OTf]$^-$

| | | | |
|---|---|---|---|
| Distances (Å) | | | |
| Mo(1)−P(1) | 2.601(3) | Mo(1)−P(2) | 2.550(3) |
| Mo(1)−P(3) | 2.518(3) | Mo(1)−P(4) | 2.552(3) |
| Mo(1)−N(1) | 1.704(9) | Mo(1)−N(2) | 2.188(10) |
| O(1)−C(3) | 1.21(1) | O(2)−C(12) | 1.23(1) |
| N(1)−C(1) | 1.46(1) | N(2)−C(10) | 1.12(1) |
| C(1)−C(2) | 1.53(1) | C(2)−C(3) | 1.49(1) |
| C(10)−C(11) | 1.36(2) | C(11)−C(12) | 1.39(2) |
| Angles (deg) | | | |
| P(1)−Mo(1)−N(1) | 93.4(3) | P(1)−Mo(1)−N(2) | 87.1(3) |
| P(2)−Mo(1)−N(1) | 101.5(3) | P(2)−Mo(1)−N(2) | 78.7(2) |
| P(3)−Mo(1)−N(1) | 90.4(3) | P(3)−Mo(1)−N(2) | 89.2(3) |
| P(4)−Mo(1)−N(1) | 94.6(3) | P(4)−Mo(1)−N(2) | 85.2(2) |
| N(1)−Mo(1)−N(2) | 179.5(4) | Mo(1)−N(1)−C(1) | 178.3(8) |
| Mo(1)−N(2)−C(10) | 174(1) | N(1)−C(1)−C(2) | 114.4(10) |
| C(1)−C(2)−C(3) | 114(1) | O(1)−C(3)−C(2) | 120(1) |
| N(2)−C(10)−C(11) | 179(1) | C(10)−C(11)−C(12) | 120(1) |
| O(2)−C(12)−C(11) | 122(1) | | |

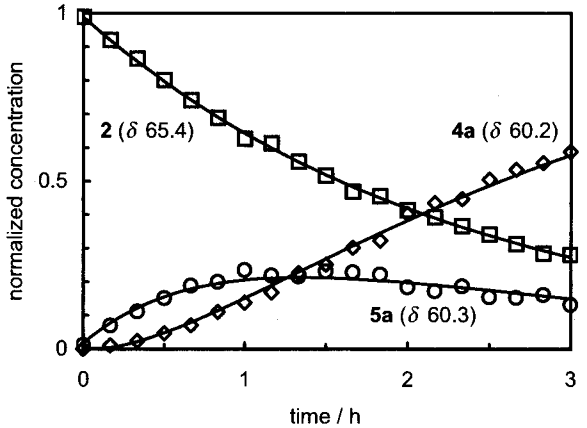


**Figure 4.** Typical time-course for the reaction of complex **2** (14 mol $m^{-3}$ in $C_6D_6$) with benzoylacetonitrile (2 equiv, 25 °C). The solid lines are theoretical and are obtained by using eqs 1−3 ($k_1 = 1.2 \times 10^{-4}$ $s^{-1}$, $k_2 = 3.1 \times 10^{-4}$ $s^{-1}$).

demonstrated by the $^1$H NMR analysis that the nitrile-enolato ligand in **5k** underwent fast H−D exchange of the α-CH on treatment with $D_2O$ in $CD_2Cl_2$ (100% conversion within 5 min). At the same time, slower H−D exchange at the N═CH and $CH_2CO$ groups in the alkylideneamido ligand ($t_{1/2} \geq 20$ min) and the formation of *trans*-[Mo($NCD_2CD_2COBu^t$)($NCCDCOBu^t$)-$(dppe)_2]^+$ (**6k**$^+$-$d_5$) were observed. Noteworthy is that the H−D exchange was also observed in toluene-$d_8$; however, only **5k**-$d_4$ was formed and further protonation leading to **6k**$^+$-$d_5$ did not take place (vide supra). These results suggest that the kinetically favorable site for the protonation of complex **5k** (and probably complex **5c**) is the nitrile-enolato ligand, while the isolated cations **6c**$^+$ and **6k**$^+$ are the thermodynamic products.

It should also be mentioned that, unlike the (alkylideneamido)(nitrile-enolato) complex **5k**, the (imido)(nitrile-enolato) complexes **6c**$^+$[OTf]$^-$ and **6k**$^+$[OTf]$^-$ showed no sign of the C−N bond breaking at room temperature. We consider that the (imido)(nitrile-enolato) complexes are not the direct intermediate for the nitrido complex formation but are "dead-end" species in the conversions of β-ketonitriles.

**Kinetics of the Reaction between Complex 2 and β-Ketonitriles. Evaluation of the C≡N Triple Bond Cleavage Mechanism.** Aiming at evaluating the reaction mechanism of the C≡N triple bond cleavage on the Mo(0) center, kinetics of the reaction between complex **2** and some aroylacetonitriles was investigated by means of $^{31}P\{^1H\}$ NMR. In each case, only three molybdenum species, the starting dinitrogen complex **2**, the final nitrido complex **4**, and the intermediary (alkylideneamido)-(nitrile-enolato) complex **5** were observed. Complexes **5a**−**g** could not be isolated in a pure form but were characterized by comparing their spectroscopic data with those of the fully characterized analogue **5k**. Essentially no signal attributable to the (imido)(nitrile-enolato) species similar to complex **6c**$^+$ was detected. Since only one intermediate **5** was observed for this reaction, the total reaction process should include two relatively slow steps, which correspond to conversion of complex **2** to **5** and that of **5** to **4**.

At first, the reaction of complex **2** with benzoylacetonitrile was examined under different conditions. A typical reaction-course is depicted in Figure 4. In experiments with varying concentrations of benzoylacetonitrile, the time-course of the normalized concentrations of complexes **2**, **4a**, and **5a** showed essentially no dependence on the concentration of the nitrile. In addition, the consumption rate of **2** was clearly shown to be first-order in the concentration of **2** by the differential method. Considering the preliminary information that the conversion of complex **5k** to **4k** obeys first-order kinetics (vide supra), the total rate for the conversion of complex **2** into **4** is assumed to be analyzed as two successive reactions where the first and second rate-determining steps are first-order in the concentrations of **2** and **5**, respectively, but zero-order in the concentration of the nitrile. In this case, the concentrations of complexes **2**, **4**, and **5** are given by eqs 1−3, where $k_1$, $k_2$, $[\mathbf{2}]_0$, $[\mathbf{5}]_0$, and $[\mathbf{4}]_0$ are the first-order rate constants for the consumption of **2** and **5** and the initial concentrations of **2**, **5**, and **4**,

**Table 5.** Kinetic Data for the Reaction of Complex **2** with $\beta$-Ketonitriles ($RCOCH_2CN$) in Benzene-$d_6$

| R | $T$<br>°C | $C$<br>mol $m^{-3}$ [a] | equiv[b] | $k_1$<br>$10^{-4}$ $s^{-1}$ | $k_2$<br>$10^{-4}$ $s^{-1}$ | $\sigma_p$ or $\sigma_a$[c] |
|---|---|---|---|---|---|---|
| Ph | 25 | 6 | 8 | 1.3(1) | 2.9(3) | 0 |
| | 25 | 7 | 6 | 1.2(2) | 2.6(3) | |
| | 25 | 6 | 4 | 1.1(1) | 2.7(3) | |
| | 25 | 14 | 2 | 1.2(1) | 3.1(3) | |
| | 20 | 11 | 4 | 0.51(6) | 1.6(1) | |
| | 30 | 14 | 4 | 2.9(3) | 4.6(4) | |
| | 35 | 16 | 4 | 5.4(7) | 7.2(7) | |
| | 50 | 16 | 3 | 40(5) | 30(5) | |
| 4-$MeOC_6H_4$ | 25 | 14 | 3 | 1.3(1) | 1.00(9) | −0.288 |
| 4-Tol | 25 | 13 | 4 | 1.1(1) | 1.5(1) | −0.165 |
| 4-$ClC_6H_4$ | 25 | 14 | 2 | 0.9(1) | 6.0(6) | +0.221 |
| 4-$MeOCOC_6H_4$ | 25 | 12 | 3 | 1.0(1) | 11(2) | +0.445 |
| 2-$C_4H_3S$ | 25 | 12 | 4 | 1.1(1) | 5.5(5) | +0.71 |
| 2-$C_4H_3O$ | 25 | 14 | 4 | 1.0(1) | 7.6(8) | +1.08 |

[a] Initial concentration of complex **2**. [b] Amount of $RCOCH_2CN$ used per complex **2**. [c] The $\sigma$ values were taken from refs 58 and 59.

respectively ($[\mathbf{5}]_0$, $[\mathbf{4}]_0 \cong 0$).

$$[\mathbf{2}] = [\mathbf{2}]_0^{-k_1 t} \tag{1}$$

$$[\mathbf{5}] = [\mathbf{2}]_0 \frac{k_1(e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1} + [\mathbf{5}]_0 e^{-k_2 t} \tag{2}$$

$$[\mathbf{4}] = [\mathbf{2}]_0 \frac{k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})}{k_2 - k_1} + [\mathbf{5}]_0(1 - e^{-k_2 t}) + [\mathbf{4}]_0 \tag{3}$$

The observed time-course plots of the normalized concentrations of complexes **2**, **5a**, and **4a** fit the theoretical curves calculated by using eqs 1−3 fairly well. The $k_1$ and $k_2$ values obtained are listed in Table 5. In agreement with the above assumption, both $k_1$ and $k_2$ values are independent of the concentration of benzoylacetonitrile. In addition, based on the $k_1$ and $k_2$ values estimated at 20−50 °C, the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the first rate-determining step (conversion of **2**) are 112 ± 3 kJ $mol^{-1}$ and 56 ± 12 J $mol^{-1}$ $K^{-1}$, respectively, while those for the second rate-determining step (conversion of **5a**) are 73 ± 3 kJ $mol^{-1}$ and −69 ± 9 J $mol^{-1}$ $K^{-1}$, respectively. It was previously reported that the rate-determining step for the reaction of complex **2** with RCN (R = Me, Ph, 4-Tol) to give the (dinitrogen)(nitrile) complex *trans*-$[Mo(N_2)(NCR)(dppe)_2]$ is the dissociation of one dinitrogen ligand from complex **2**, and the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for such reactions were determined to be 110−114 kJ $mol^{-1}$ and 51−69 J $mol^{-1}$ $K^{-1}$, respectively.[57] The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ obtained from the $k_1$ data are in good agreement with the reported values, indicating that the first slow step of the present reaction is also the dissociation of a dinitrogen ligand from **2**. It should be pointed out that the loss of dinitrogen ligand is known to be accelerated by irradiation with a tungsten lump.[20] In fact, when a control experiment with complex **2** and benzoylacetonitrile was conducted under room light, the consumption of complex **2** was about eight times as fast as that in the dark, while the $k_2$ value was little affected by the light.

To gain further information about the conversion of **5** to **4**, the rate constants ($k_1$ and $k_2$) for the reactions of **2** with various $\beta$-ketonitriles were determined (Table 5). As expected, the $k_1$ values are almost constant regardless of the nitriles used. In contrast, the $k_2$ values showed strong dependence on the nitrile; introduction of the electron-withdrawing groups enhanced the rate for the conversion of **5** to **4**. The $k_2$ values obtained with *p*-substituted benzoylacetonitriles and heteroaroylacetonitriles displayed good correlations with the original Hammett substituent constants ($\sigma_p$) and the replacement substituent constants for heteroaryl groups ($\sigma_a$), respectively (the $\sigma_p$ and $\sigma_a$ values are those derived from the ionization constants of the substituted benzoic acids in water).[58,59] Thus, linear relationships between log $k_2$ and $\sigma_p$ or $\sigma_a$ were observed, where the $\rho_p$ and $\rho_a$ values (reaction constants) are 1.42 ± 0.07 and 0.41 ± 0.05, respectively (Figure 5). These positive $\rho$ values imply that a (partial) negative charge is developed on the side chain of the aromatic ring during the rate-determining step.

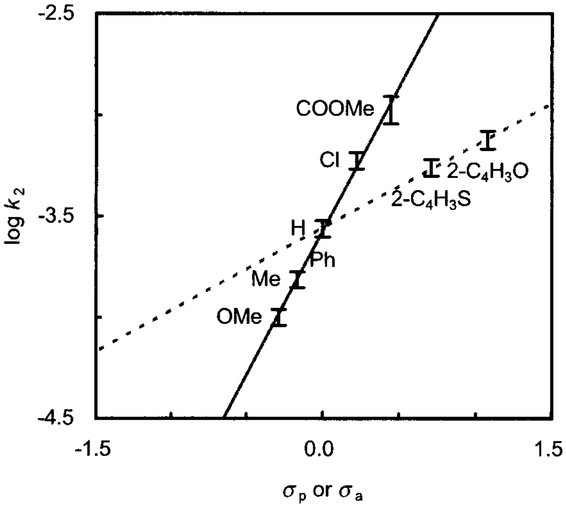
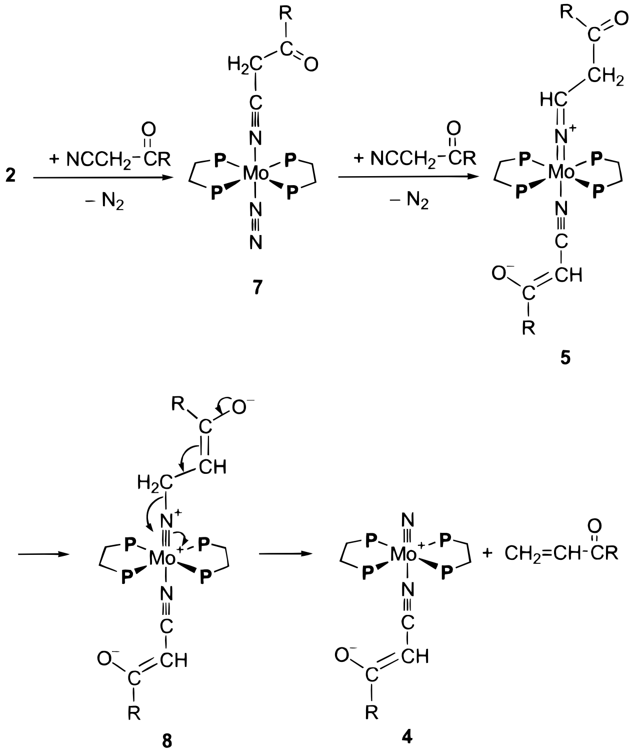


**Figure 5.** Hammett plot for the $k_2$ values of the reactions of complex **2** with *p*-substituted benzoylacetonitriles (solid line) and heteroaroylacetonitriles (broken line). The $\rho_p$ value for the solid line and the $\rho_a$ value for the broken line are 1.42 and 0.41, respectively.

**Scheme 4**



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On the basis of these facts, we have concluded that the rate-determining step for the conversion of **5** to **4** is the 1,2-proton shift from the α-CH of the carbonyl group to the amido carbon in the alkylideneamido ligand to form an anionic enolate-imido ligand (Scheme 4). The high susceptibility of the amido carbon in complex **5** to protonation, which is substantiated by the facile formation of complexes **6c**$^+$ and **6k**$^+$ from **5c** and **5k**, supports this hypothesis. Furthermore, the primary isotope effect observed for the reaction of **5k** to **4k** and the negative $\Delta S^{\ddagger}$ value estimated for the reaction with benzoylacetonitrile are also in accord with the intramolecular proton shift mechanism.

Now we propose the total reaction mechanism depicted in Scheme 4. The reaction is initiated by the relatively slow loss of dinitrogen ligand from complex **2** to form a coordinatively unsaturated species, which binds a *β*-ketonitrile molecule to give a (dinitrogen)(nitrile) complex **7**. The cyano carbon in complex **7** is immediately protonated by a second molecule of the *β*-ketonitrile, and the following substitution of the dinitrogen ligand with the enolate anion of the *β*-ketonitrile yields the (alkylideneamido)(nitrile-enolato) complex **5**, which is observed as an intermediate. The proton shift from the α-position of the carbonyl group to the amido carbon in the alkylideneamido ligand leads to the formation of the (imido)(nitrile-enolato) type complex **8**, and this step is the second slow step. Complex **8** undergoes a fast C−N bond cleavage at the imido ligand to form the final products, the nitrido complex **4** and the ketone.

The mechanism for the C≡N triple bond cleavage uncovered in the present study is unprecedented and unique. It has been reported that the tungsten alkoxides $[W_2(OR)_6]$ (R = Bu$^t$, CMe$_2$CF$_3$) are transformed into nitrido complexes by reaction with nitriles,[23−25] where a metathesis-type mechanism has been postulated, which is completely different from that of the present reaction. In the mechanism depicted in Scheme 4, the double protonation of the cyano carbon of the coordinated nitrile molecule is crucial for the C≡N triple bond cleavage, and such reactivity is obviously attributed to the highly *π*-donating nature of the Mo(0) center. This type of activation of nitriles not only provides a promising method for the chemical transformation of nitriles but also opens a new route to metal nitrides.

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**Supporting Information Available:** Tables of crystallographic data, positional and thermal parameters, and bond lengths and angles for complexes **4h**·1.5$C_2H_4Cl_2$, **5k**·$C_6H_6$, and **6c**$^+$[OTf]$^-$ (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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