

Preliminary communication

THE FORMATION OF *N*-(ETHOXYCARBONYLMETHYL)DIAZENIDO (C₂H₅COOCH₂N₂) DERIVATIVES OF MOLYBDENUM. THE 1,3-ADDITION OF C—X (X = Cl, Br AND I) TO THE Mo—N₂ MOIETY OF BIS-(DINITROGEN)BIS(1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)MOLYBDENUM

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Summary

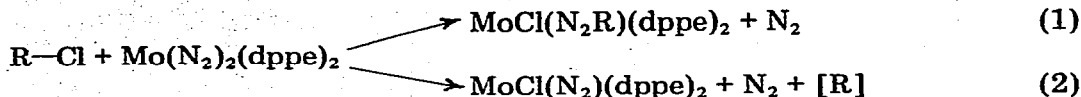
The reactions of ethyl haloacetates with Mo(N₂)₂(dppe)₂ (where dppe = 1,2-bis(diphenylphosphino)ethane) to form MoX(N₂CH₂COOC₂H₅)(dppe)₂ (where X = Cl, Br and I) are reported. These stable compounds are readily protonated with aqueous fluoroboric acid to form [MoX(N₂HCH₂COOC₂H₅)(dppe)₂]BF₄, the *N*-(ethoxycarbonylmethyl)hydrazido derivatives.

We wish to report the first example of the (formal) addition of an alkyl carbon—chlorine bond to a metal—N₂ moiety, namely Mo—N₂ in Mo(N₂)₂(dppe)₂ (I), (where dppe = 1,2-bis(diphenylphosphino)ethane). Ethyl chloroacetate in benzene reacts with I (5 h ambient temperature) to yield the *N*-(ethoxycarbonylmethyl)diazenido derivative MoCl(N₂CH₂COOC₂H₅)(dppe)₂. Generally small amounts of unreacted I, and considerable amounts of MoCl₂(dppe)₂ are also obtained.

N-Alkyl-, *N*-acyl- and *N*-aroyl-diazenido derivatives have been reported as products from the reaction of I (or the tungsten analogue) with alkyl bromides and iodides [1–3], acyl chlorides [4] and aroyl chlorides [4,5], respectively. We previously reported that the reaction of methyl chloride with I forms MoCl(N₂)(dppe)₂ [2]. Clearly, the presence of the ester group α to chlorine in ethyl chloroacetate is favoring the 1,3-addition of the carbon—chlorine bond (eq. 1) against direct substitution of dinitrogen by a chlorine atom (eq. 2). Interestingly, ethyl 4-chlorobutyrate does not react with I to form an alkyldiazenido derivative at ambient temperature.

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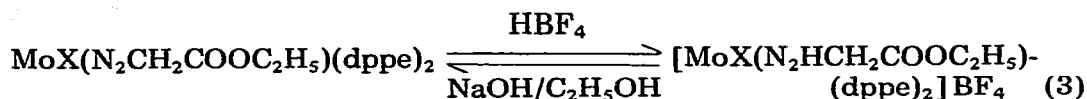
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In a typical reaction, 0.7363 g (0.776 mmol) of I and three-fold excess of ethyl chloroacetate were magnetically stirred in 165 ml of thoroughly deoxygenated benzene for 5 h under ordinary fluorescent lighting. An excess of an (originally) 48% aqueous HBF_4 solution and 250 ml of deoxygenated ethanol were then added. After 0.25 h of stirring, the solution was concentrated to 100 ml and filtered to remove $\text{MoCl}_2(\text{dppe})_2$ (0.0885 g). The red filtrate was evaporated to dryness and then extracted with benzene* (275 ml) giving a pink-tan solution and leaving an uncharacterized pink solid (0.3659 g). Addition of 90 ml of heptane to the solution precipitated the remaining pink impurity. Concentration of the yellow filtrate to 50 ml and addition of 150 ml of heptane precipitated the tan product, $[\text{MoCl}(\text{NNHCH}_2\text{COOC}_2\text{H}_5)(\text{dppe})_2]\text{-}[\text{BF}_4]$ (0.3195 g, 0.283 mmol, 36%). Found: C, 59.10; H, 5.06; N, 2.62; Halogen, 9.50. Calcd.: C, 59.46; H, 4.99; N, 2.48; Halogen, 9.85%.

$[\text{MoCl}(\text{NNHCH}_2\text{COOC}_2\text{H}_5)(\text{dppe})_2]\text{-}[\text{BF}_4]$ can be readily deprotonated with NaOH in ethanol to give the neutral alkyldiazenido compound. In a typical reaction, addition of ca. two equivalents of NaOH dissolved in ethanol to an ethanol solution of 0.5627 g (0.498 mmol) of $[\text{MoCl}(\text{NNHCH}_2\text{COOC}_2\text{H}_5)(\text{dppe})_2]\text{-}[\text{BF}_4]$ produced an immediate color change from tan to orange and rapid precipitation of the orange product, $\text{MoCl}(\text{NNCH}_2\text{COOC}_2\text{H}_5)(\text{dppe})_2$ (0.3658 g, 0.351 mmol, 70%). Found: C, 63.55; H, 5.23; N, 2.50; Cl, 3.48. Calcd.: C, 64.47; H, 5.31; N, 2.68; Cl, 3.40%.

Ethyl bromo- and iodoacetates and ethyl 4-iodobutyrate react analogously with I in benzene to yield the corresponding alkyldiazenido derivatives which can be reversibly protonated with HBF_4 (e.g. eq. 3).



The neutral ethoxycarbonylmethyldiazenido derivatives exhibit $\nu(\text{NN})$ at ca. 1508 cm^{-1} and $\nu(\text{CO})$ at ca. 1736 cm^{-1} (KBr pellet). Upon protonation, $\nu(\text{NN})$ is moved (but the new $\nu(\text{NN})$ has not been identified) and $\nu(\text{CO})$ remains essentially unchanged (ca. 1740 cm^{-1}) while $\nu(\text{NH})$ appears at ca. 3290 cm^{-1} (nujol). In the PMR spectra** of the *N*-(ethoxycarbonylmethyl)-hydrazido derivatives, the N—H resonance varies as the *trans* halogen changes; τ 3.9 (Cl), 4.0 (Br), and 4.6 ppm (I). The resonance of the protons of the methylene group attached to nitrogen occurs at ca. τ 7.9 ppm and is split by the N—H proton (J 4.5 Hz). Addition of D_2O causes the disappearance of the N—H resonance and the methylene doublet collapses to a singlet.

*Chromatography using a silica gel column and eluting with an ethanol-Skelly solve B solvent mixture may also be used for purification, but the yields are lower.

** CDCl_3 solution; internal reference TMS (τ 10 ppm).

Protonation of the (ethoxycarbonylmethyl)diazenido ligand may occur at either of the nitrogen atoms, in theory. Protonation of the nitrogen atom attached to the metal of related aryldiazenido complexes has been reported and supported by single-crystal X-ray diffraction studies; [PtCl(P(C₂H₅)₃)₂(HN₂C₆H₄F)]ClO₄ (II) [6] and [RuCl(GO)₂(HN₂C₆H₅)₃]₂ClO₄ (III) [7]. In the PMR spectra the N—H resonances for II and III occur at τ - 5.1 [8]* and τ - 1.75 ppm [7], respectively. On the other hand, those compounds that have been shown to be protonated at the other nitrogen atom, [MoI-(N₂HC₈H₁₇)(dppe)₂]I (IV) [2]**, exhibit an N—H resonance at much higher field; τ 6.10 ppm for IV. The closely related cationic hydrazido (N₂H₂) complexes exhibit N—H₂ PMR resonances at higher field, e.g., τ 6.98 ppm in [WCl(N₂H₂)(dppe)₂]B(C₆H₅)₄ [9]. A crystal structure determination [10] of the latter compound shows both protons attached to the terminal nitrogen atom.

Based upon the PMR spectral data (τ (N—H) and J (H—NC—H)), we propose that protonation of the (ethoxycarbonylmethyl)diazenido ligand occurs at the carbon-bound nitrogen. We also believe based upon ν (NN), that the (ethoxycarbonylmethyl)diazenido ligand is bonded in a singly-bent fashion to molybdenum.

We are presently studying the chemistry of these functionally-substituted aryldiazenido derivatives.

Acknowledgements

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*BF₄⁻ salt.

**Other compounds of this type have been structurally characterized (see references in [2] but no PMR data have been given).