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Preliminary communication

Organotransition-metal complexes of multidentate ligands

XIII *. Is $AgNO_3$ a nitrosylation reagent?

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Abstract

Silver nitrate reacted at room temperature within minutes with [M(bdmpam)$(CO)_3$] to give cations, [M(bdmpam)$(CO)_2$(NO)]$^+$, in acetonitrile, where M is Mo or W and bdmpam is *N,N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethane. The yield of the nitrosyl product is comparable to that obtained via a solvent containing [NO]BF_4 or [NO_2]BF_4.

Probably due to the considerable diversity of their chemical, physical, and structural properties, much recent research attention has been focused on metal-nitrosyl complexes [2]. External sources such as NO, NO^+, NOX (X = halides), *N*-nitrosoamides, NH_2OH, NO_2^-, RONO, or HNO_3 can introduce a nitrosyl group into the coordination sphere of transition-metal atoms [3]. Following our success in preparation of the air-stable, 17-electron complexes, $(HBPz'_3)Mo(CO)_3$ (Pz′ = 3,5-dimethylpyrazol-1-yl), by oxidation of their precursor, $(HBPz'_3)Mo(CO)_3^-$, with $AgBF_4$ or $[Cp_2Fe]PF_6$ [4], and [Cr(bdmpam)(NO)$(NCMe)_2$]$[BF_4]_2$ by oxidative nitrosylation of [Cr(bdmpam)$(CO)_3$] with excess [NO]BF_4 in MeCN [5] (bdmpam = *N,N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethane), we accidently found that $AgNO_3$ is able to nitrosylate [M(bdmpam)$(CO)_3$] (M = Mo, W).

Exactly two equivalents of $AgNO_3$ in MeCN are required, as determined by measuring and comparing IR spectra after addition of some $AgNO_3$ solution, to nitrosylate one equivalent of [M(bdmpam)$(CO)_3$]. Nitrosylation is complete at room temperature within minutes, to give [M(bdmpam)$(CO)_2$(NO)]NO_3, which can be

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* For part XII, see ref. 1.

isolated as [M(bdmpam)(CO)$_2$(NO)]Y (Y = BF_4, PF_6) [*]. The yield of 35–40% is comparable to that obtained in a solvent containing [NO]BF_4 or [NO_2]BF_4. The 17-electron dication, [M(bdmpam)(NO)(NCMe)$_2$]$^{2+}$, could not be isolated from the reaction with $AgNO_3$, [NO]BF_4, or [NO_2]BF_4. The process of transformation of one equivalent of NO_3^- into NO in the reaction is not known at the present stage of investigation.

By comparing the coupling constants, the four doublets observed for the methylene groups in the ^{1}H NMR spectrum [**] of either [Mo(bdmpam)(CO)$_2$(NO)]$^+$ (**1**) or [W(bdmpam)(CO)$_2$(NO)]$^+$ (**2**) can be grouped into two sets of resonances. Like the assignments of the ^{1}H NMR spectra of [M(bdmpam)(CO)$_2$(π-allyl)]PF_6 [6], the two sets can be assigned to the two unequivalent methylene groups in **1** or **2**. Thus, the nitrosyl group adopts an unsymmetrical position with respect to the bdmpam ligand and this ligand assumes a facial arrangement rather a meridional one around the metal atom in a structure similar to that of [Cr(bdmpam)(NO)(NCMe)$_2$][BF_4]$_2$ [5], Further, the nitrosyl complexes are stereochemically rigid in solution at room temperature on the NMR time scale. This geometry can be supported by observing the two carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum [***] of **1** and the two intense carbonyl stretching frequencies [†] with comparable intensity, which indicate the presence of two *cis*-carbonyls [7].

Nitrosylation of neutral and cationic metal carbonyl derivatives of multidentate ligands (especially phosphorus ligands [8]) and isolation and subsequent reactions of the cationic intermediates [9] following silver oxidation in the reaction are currently under investigation, in order to delineate the scope and the mechanism of the reaction.

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[*] The synthesis of [Mo(bdmpam)(CO)$_2$(NO)]PF_6 is as follows. A solution of [Mo(bdmpam)(CO)$_3$] (0.43 g, 1.0 mmol) in 30 ml of MeCN was stirred and added slowly to a solution of $AgNO_3$ (0.34 g, 2.0 mmol) in 20 ml of MeCN. A dark solution soon developed with formation of gas bubbles and a dark gray precipitate. KPF_6 (0.52 g, 2.8 mmol) dissolved in 5 ml of deaerated water was added to the suspension and the solvents were then removed under vacuum to give a solid residue. A yellow product was extracted from the residue with CH_2Cl_2. Removal of CH_2Cl_2 from the extract gave a crystalline solid (0.20 g, 35%). Anal. Found: C, 31.13; H, 3.71; N, 14.59. $C_{15}H_{21}F_6MoN_6O_3P$, calcd.: C, 31.37; H, 3.69; N, 14.63%. [Mo(bdmpam)(CO)$_2$(NO)]BF_4 and [W(bdmpam)(CO)$_2$(NO)]BF_4 were prepared similarly from the corresponding [M(bdmpam)(CO)$_3$] complexes using excess $AgNO_3$/KBF_4, [NO]BF_4, or [NO_2]BF_4. [Mo(bdmpam)(CO)$_2$(NO)]BF_4, Anal. Found: C, 34.63; H, 4.09; N, 16.26. $C_{15}H_{21}BF_4MoN_6O_3$, calcd.: C, 34.91; H, 4.10; N, 16.28%. [W(bdmpam)(CO)$_2$(NO)]BF_4, Anal. Found: C, 29.77; H, 3.59; N, 13.75. $C_{15}H_{21}BF_4N_6O_3W$, calcd.: C, 29.82; H, 3.50; N, 13.92%.

[**] **1** (acetone-d_6, 296 K, 100 MHz): methyl groups on the ring 3,5-positions, δ 2.30 (3H, s), 2.35 (3H, s), 2.42 (6H, s); N–CH_3, 3.54 (3H, s); N–CH_2–N, 5.32 (1H, d, J = 12.1 Hz), 5.38 (1H, d, J = 12.4 Hz), 5.57 (1H, d, J = 12.4 Hz), 5.60 (1H, d, J = 12.1 Hz); hydrogens on ring 4-position, 6.09 (1H, s), 6.17 (1H, s) ppm. **2** (CD_3CN, 296 K, 100 MHz): methyl groups on the ring 3,5-positions, δ 2.24 (3H, s), 2.25 (3H, s), 2.33 (3H, s), 2.40 (3H, s); N–CH_3, 3.49 (3H, s); N–CH_2–N, 5.03 (1H, d, J = 12.0 Hz), 5.06 (1H, d, J = 12.2 Hz), 5.25 (1H, d, J = 12.0 Hz), 5.39 (1H, d, J = 12.2 Hz); hydrogens on ring 4-position, 5.99 (1H, s), 6.11 (1H, s) ppm.

[***] [Mo(bdmpam)(CO)$_2$(NO)]PF_6 (CD_3CN, 296 K, 25.2 MHz): methyl groups on ring 3,5-positions, δ 11.8 (2C), 13.2 (1C), 15.8 (2C); N–CH_3, 49.5 (1C); N–CH_2–N, 72.0 (2C); carbons on ring 4-position, 109.4 (2C); carbons on ring 3,5-positions, 145.4 (1C), 146.2 (1C), 154.5 (1C), 155.0 (1C); CO, 219.6 (1C), 225.8 (1C) ppm.

[†] IR (CH_2Cl_2): ν(CO), 2033, 1956 for **1** and 2009, 1923 for **2**; ν(NO), 1668 for **1** and 1662 cm^{-1} for **2**.

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