Letters to the Editor

Metathetical imidation of dioxobis(dimethyldithiocarbamato)molybdenum with o-substituted N-sulfinylanilines

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The chemistry of transition metal imido complexes [M]=NR, which are promising reagents for the transfer of the imido groups, has been extensively developed in recent years.¹ In this connection, a search for new versatile procedures for their synthesis is an urgent problem. Earlier, one of the main procedures, *viz.*, the thermaly induced metathetical replacement of the oxo ligands by the imide ligands, has been widely used in reactions of transition metal oxo complexes with amines,² silyl-amines,³ phosphine imines,⁴ and isocyanates.^{5,6} However, these imidating reagents are of limited usefulness. In particular, these reagents proved to be inefficient in imidation of thermally labile metal-containing substrates, such as transition metal oxo dithiocarbamate complexes.⁶

Previously, we have reported that *N*-sulfinylamines are very promising imidating reagents, particularly, in the synthesis of transition metal imido complexes, which are inaccessible by other procedures.⁷ In the present study, we demonstrated that the reaction of $MoO_2(S_2CNMe_2)_2$ with 2 equiv. of *N*-sulfinyl derivatives of polyhalogenoanilines ArNSO (Ar = 2,4,6-Cl₃C₆H₂ or 2,4,6-Br₃C₆H₂) in boiling toluene proceeded smoothly to give the corresponding bis(arylimido) complexes **1a,b** (Scheme 1).

Analogous reactions with polyalkyl-substituted *N*-sulfinylanilines ArNSO (Ar = $2,6-Pr_{2}^{i}C_{6}H_{3}$ or Scheme 1

$$MoO_2(S_2CNMe_2)_2 \xrightarrow{ArNSO} (ArN=)_2Mo(S_2CNMe_2)_2$$

1a,b

Ar = 2,4,6-Cl₃C₆H₂ (**a**), 2,4,6-Br₃C₆H₂ (**b**) *i*. Toluene, 110 °C, 4 h.

2,4,6-Me₃C₆H₂) proceeded more slowly to produce mixtures of products **2**–4 (Scheme 2). Along with the expected bis(imido) complexes **2a,b**, mixed oxo imido complexes **3a,b** and binuclear complexes **4a,b** were formed in 15–20% yields (¹H NMR). This set of the reaction products is, apparently, attributed to the low rate of formation of the target bis(imido) complexes **2a,b**, so that the side process giving rise to binuclear complexes **4a,b** becomes quite competitive. In the latter complexes, the μ -S atoms are formed through the partial transformation of the dithiocarbamate ligands.

The results obtained in the present study demonstrate that deoxoimidation with the use of *o*-halogenand alkyl-substituted *N*-sulfinylanilines shows considerable promise for the synthesis of imidobis(dimethyldithiocarbamato)molybdenum complexes.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 6, pp. 987–988, June, 2002.

1066-5285/02/5106-1075 \$27.00 © 2002 Plenum Publishing Corporation

Scheme 2

$$MoO_2(S_2CNMe_2)_2 \xrightarrow{ArNSO} (ArN=)_2Mo(S_2CNMe_2)_2 + 2a,b$$

+
$$(Me_2NCS_2)MO S MO(S_2CNMe_2)$$

4a,b

Ar = 2,6-Prⁱ₂C₆H₃ (**a**), 2,4,6-Me₃C₆H₂ (**b**) *i*. Toluene, 5 h, 110 °C.

The $MoO_2(S_2CNMe_2)_2$ complex was prepared analogously to $MoO_2(S_2CNEt_2)_2$.⁸ *N*-Sulfinylanilines ArNSO (Ar = 2,4,6-Cl_3C_6H_2 or 2,4,6-Br_3C_6H_2) were synthesized according to a known procedure.⁹

The ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-400 instrument. The mass spectra were measured on a Finnigan MAT SSQ-710 instrument.

Bis(2,4,6-trichlorophenylimido)bis(dimethyldithiocarbamato)molybdenum (1a). A solution of $MoO_2(S_2CNMe_2)_2$ (0.59 g, 1.6 mmol) and 2,4,6- $Cl_3C_6H_2NSO$ (0.8 g, 3.3 mmol) in toluene (50 mL) was refluxed for 4 h, the solvent was evaporated, and the product was extracted with CH_2Cl_2 (10 mL). After recrystallization from a CH_2Cl_2 —hexane mixture at -20 °C, the analytically pure dark-brown product was obtained in a yield of 1.16 g (86%). Found (%): C, 29.80; H, 2.03; N, 7.65; Cl, 29.12. $C_{18}H_{16}Cl_6N_4MoS_4$. Calculated (%): C, 29.81; H, 2.22; N, 7.73; Cl, 29.33. ¹H NMR (400 MHz, CDCl₃), δ : 7.15 (s, 4 H, CH_{arom}); 3.37 (s 12 H, CH₃). ¹³C NMR (100 MHz, CDCl₃), δ : 202.8 (CS₂); 150.28, 128.47, 127.9, 127.1 (C_{arom}); 40.58 (CH₃). MS (EI, 70 eV), m/z (I_{rel} (%)): 726 [M]⁺ (100), 638 (54), 606 (62), 531 (20), 120 (23).

Bis(2,4,6-tribromophenylimido)bis(dimethyldithiocarbamato)molybdenum (1b) was prepared analogously from MoO₂(S₂CNMe₂)₂ (0.59 g, 1.6 mmol) and Br₃C₆H₂NSO (1.2 g, 3.2 mmol) in a yield of 1.14 g (72%). Found (%): C, 21.77; H, 1.6; N, 5.6; Br, 50.2. C₁₈H₁₆Br₆N₄MoS₄. Calculated (%): C, 21.77; H, 1.6; N, 5.44; Br, 48.4. ¹H NMR (400 MHz, CDCl₃), δ : 7.53 (s, 4 H, CH_{arom}); 3.37 (s, 12 H, CH₃). ¹³C NMR (100 MHz, CDCl₃), δ : 202.63 (CS₂); 152.65, 133.7, 117.8, 115.2 (C_{arom}); 41.06 (CH₃). MS (EI, 70 eV), *m/z* (*I*_{rel} (%)): 992 [M]⁺ (100), 951 (67), 909 (10), 869 (95), 665 (12), 577 (28), 329 (31), 120 (37).

This study was financially supported by the International Science and Technology Center (ISTC, Grant 1577).

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Received March 18, 2002; in revised form May 29, 2002