

# Reactions of Metalated Amidines With Carbon Disulphide and Tricarbonyl(chloro)- $\eta$ -cyclopentadienylmolybdenum†

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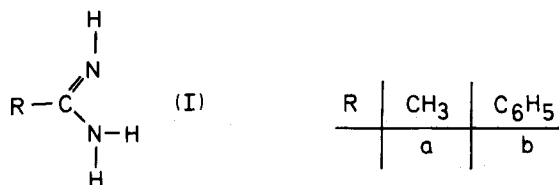
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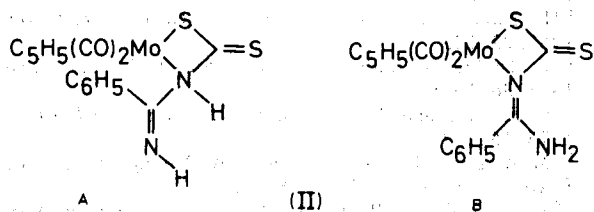
Metalated  $N,N'$ -dialkylamidines,  $[C_6H_5C(NR)_2]^- [R = CH_3, CH(CH_3)_2, \text{ or } CH_2C_6H_5]$ , give insertion products with  $CS_2$  which can be stabilized by reaction with  $C_5H_5Mo(CO)_3Cl$  to give  $N$ -imidoyldithiocarbamate complexes  $[R = CH(CH_3)_2 \text{ or } CH_2C_6H_5]$  or can undergo cleavage of one C–N bond with subsequent addition of  $CS_2$  and oxygen ( $R = CH_3$ ).<sup>1</sup> Both types of product complex are  $C_5H_5Mo(CO)_2$  derivatives. This paper deals with the corresponding reactions of unsubstituted benz- and acet-amidines  $[RC(NH)_2]^- (R = C_6H_5 \text{ or } CH_3)$ .

## Results and Discussion

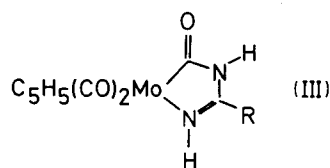
The metalation of amidines (Ia, b) is carried out with  $C_4H_9Li$  in THF and is followed by the addition of  $CS_2$  and  $C_5H_5Mo(CO)_3Cl$ . As the main products the  $C_5H_5(CO)_2Mo$   $N$ -imidoylcarbamoyl complexes (IIIa, b) were isolated. They exhibit spectroscopic properties (Tables 1 and 2) similar to those of the  $N,N'$ -dialkyl and -diaryl  $N$ -imidoylcarbamoyl complexes derived from  $C_5H_5Mo(CO)_3Cl$  and  $Mn(CO)_5Cl$ .<sup>1,2</sup>



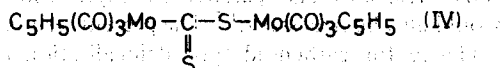
A product containing the amidine ligand together with  $CS_2$  could be isolated only from the reaction with benzamidine (Ib) (as proven by C, H, N analysis and the field desorption mass spectrum). Because of the deep violet colour of the product (II) we assign a structure different from that of the brown-coloured  $C_5H_5(CO)_2Mo$  dithiocarbamates.<sup>1,3</sup>



Coordination by sulphur and nitrogen as shown in structures (II) is supported by i.r. and  $^1H$  n.m.r. spectra (Table 1). The  $\nu_{NH}$  bands at 3396 and 3291  $cm^{-1}$  are 100  $cm^{-1}$  to lower frequency than in the free amidines,<sup>4</sup> and the  $\nu_{CN}$  band at 1611  $cm^{-1}$  is characteristic of a co-ordinated CN double bond. Thus we favour structure (IIB), as in  $N$ -phenylamidines where the tautomeric form  $RC(NC_6H_5)NH_2$  is preferred.<sup>5</sup> The  $^1H$  n.m.r. spectrum shows only one  $C_5H_5$  singlet, excluding the presence of *cis/trans* isomers with respect to the CN double bond. The NH protons give only one broad singlet, consistent with formulation B. In contrast, the two NH protons of (IIIa, b) exhibit two different multiplets.



As a by-product, the new binuclear  $CS_2$ -bridged complex  $[C_5H_5Mo(CO)_3]_2CS_2$  (IV) was formed from both amidines (Ia) and (Ib). The presence of six CO groups is demonstrated by the molecular ion in the field desorption mass spectrum, and the i.r. spectrum (Table 1). As expected, the  $^1H$  n.m.r. spectrum shows two different singlets for the two  $C_5H_5$  groups. Similar bridged dithiocarbonyl complexes of Mn, Re, and Fe are known.<sup>6,7</sup>



## Procedure

Metalation of the amidines (Ia, b) was carried out by literature methods.<sup>1</sup> Use of THF instead of ether increases the extent of formation of  $[C_5H_5Mo(CO)_3]_2CS_2$  (IV).

To 3.6 mmol of a solution of the metalated amidine, 4.0 mmol of  $CS_2$  are added at 0°C, followed by 1.0 g (3.6 mmol) of  $C_5H_5Mo(CO)_3Cl$  at -35°C. The mixture is warmed slowly to room temperature and agitated for 12 h. A brown precipitate, of (IIIa) or (IIIb), is filtered off and recrystallized from acetone-ether 2 : 1. The concentrated filtrate is chromatographed on  $SiO_2$ . Elution with benzene gives a broad dark red band, which is rechromatographed three times in order to separate the red-violet product (IV) from the dark red  $[C_5H_5Mo(CO)_3]_2$ . Product (II) is eluted with benzene-ether 1 : 1 and rechromatographed with benzene. Compounds (II) and (IV) are recrystallized from ether-pentane 2 : 1.

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Table 1  $^1\text{H}$  N.m.r. spectra of the complexes (II)–(IV) ( $\delta$  values and multiplicities)

	$\text{CH}_3$	$\text{C}_5\text{H}_5$	$\text{C}_6\text{H}_5$	NH	Solvent <sup>a</sup>
(II)		5.54(s)	7.38(m), 7.93(m)	8.23(m)	$\text{CDCl}_3 - (\text{CD}_3)_2\text{CO}$ (1 : 1)
(IIIa)	2.31(d) <sup>b</sup>	5.29(s)		8.25(m), 9.59(m)	$(\text{CD}_3)_2\text{CO}^c$
(IIIb)		5.37(s)	7.56(m), 7.92(m)	9.09(m), 10.39(m)	$(\text{CD}_3)_2\text{CO}^c$
(IV)		5.40(s), 5.70(s)			$\text{CDCl}_3$

<sup>a</sup> $\text{Me}_4\text{Si}$  as internal standard, Varian T-60 instrument, temp. 33 °C.<sup>b</sup> $J(\text{CH}_3 - \text{NH})$  0.75 Hz.<sup>c</sup>Bruker WH90 instrument, temp. 25 °C.

Table 2 Properties of compounds (II)–(IV)

Colour	Yield (%)	M.p. (° C) (decomp.)	Mol. wt. <sup>e</sup>	Infrared <sup>f</sup>				
				$\nu_{\text{NH}}$ ( $\nu_{\text{ND}}$ )	$\nu_{\text{C}\equiv\text{O}}$	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{CN,NCS}}$	$\nu_{\text{CS}}$
(II) <sup>a</sup> Black-violet	7	155	Calc. 412.3 Found 414	3396, 3291m (2545, 2400)	1962, 1880vs <sup>g</sup>		1611, 1514s	
(IIIa) <sup>b</sup> Brown	20	212	Calc. 302.1 Found 304	3380s, 3157m	1960, 1868vs <sup>g</sup>	1569vs	1628w	
(IIIb) <sup>c</sup> Yellow-brown	32	206	Calc. 364.2 Found 366	3375s, 3155w	1960, 1872vs <sup>g</sup>	1578s	1610w	
(IV) <sup>d</sup> Violet-red	7	150	Calc. 566.2 Found 568		2032s, 1945vs, 1862s			972, 941mw

<sup>a</sup>Found: C, 43.66; H, 2.95; N, 6.7.  $\text{C}_{15}\text{H}_{12}\text{MoN}_2\text{O}_3\text{S}_2$  requires C, 43.7; H, 2.95; N, 6.8%.<sup>b</sup>Found: C, 39.7; H, 3.35; N, 9.3.  $\text{C}_{10}\text{H}_{10}\text{MoN}_2\text{O}_3$  requires C, 39.75; H, 3.35; N, 9.25%.<sup>c</sup>Found: C, 49.3; H, 3.3; N, 7.45.  $\text{C}_{15}\text{H}_{12}\text{MoN}_2\text{O}_3$  requires C, 49.45; H, 3.3; N, 7.7%.<sup>d</sup>Found: C, 35.3; H, 2.0.  $\text{C}_{17}\text{H}_{10}\text{Mo}_2\text{O}_6\text{S}_2$  requires C, 36.05; H, 1.8%.<sup>e</sup>Determination by mass spectrometry (related to  $^{98}\text{Mo}$ ).<sup>f</sup>Determined for KBr discs.<sup>g</sup>Solvent  $\text{CH}_2\text{Cl}_2$ .

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