

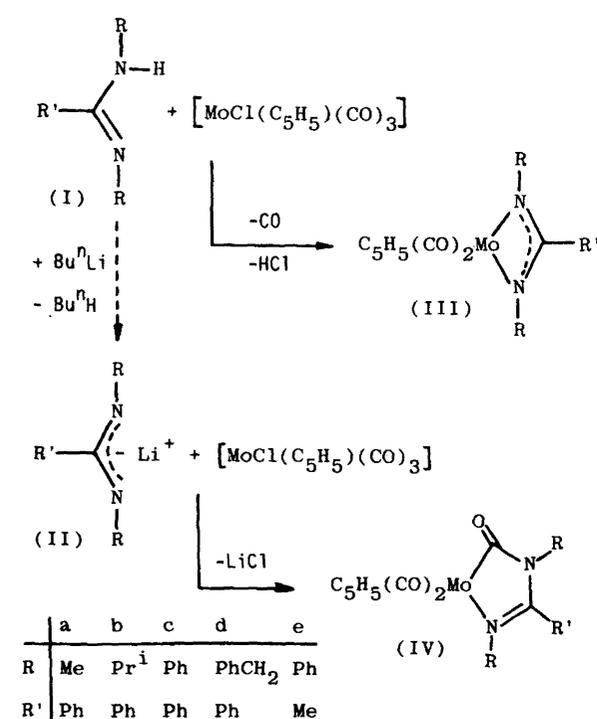
Reactions of Amidines and Metallated Amidines with Tricarbonyl-(chloro)cyclopentadienylmolybdenum

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The reactions of tricarbonyl(chloro)cyclopentadienylmolybdenum, $[\text{MoCl}(\text{C}_5\text{H}_5)(\text{CO})_3]$, with thioamides are of a different type from those with metallated thioamides. Whereas in the reaction with thioamides complexes with four-membered chelate rings are formed,^{1,2} the reaction with lithiated thioamides leads to carbonyl insertion products with five-membered chelate rings.³ In this paper the reactions of amidines and metallated amidines with $[\text{MoCl}(\text{C}_5\text{H}_5)(\text{CO})_3]$ are described.



Treatment of $[\text{MoCl}(\text{C}_5\text{H}_5)(\text{CO})_3]$ with the amidines (Ia-e) in pyridine at 100 °C gives the red amidinato complexes (IIIa-e) in 10-85% yields. In the reaction of $[\text{MoCl}(\text{C}_5\text{H}_5)(\text{CO})_3]$ with the lithioamidines (IIa-e) in ether at -78 °C, yellow carbonyl insertion products (IVa-e) are obtained in 20-40% yields. In cases c-e these are accompanied by compounds (III) [(IIIc) in 33% yield; traces of (III d) and (IIIe)].

The i.r. spectra (KBr) of the complexes (IIIa-e) contain two characteristic $\text{C}\equiv\text{O}$ bands at ca. 1950 and 1850 cm^{-1} . Those of the complexes (IVa-e) show in addition to the $\text{C}\equiv\text{O}$ bands at 1950 and 1860 cm^{-1} a band at 1608-1626 cm^{-1} for the carbamoyl $\text{C}=\text{O}$ bond.^{5,6,10-12}

In the mass spectrometer the molecular ions successively lose two CO groups in the case of the complexes (IIIa-e) and three CO groups in the case of the complexes (IVa-e); these processes are followed by substituent-dependent ligand fragmentation.

In the ¹H n.m.r. spectra of all the complexes (III) and (IV) the C_5H_5 protons give sharp singlets. In the complexes (IIIa-e) the two *N*-substituents R are chemically equivalent. The reduction in symmetry associated with the incorporation of an additional CO group into the chelate ring in the complexes (IVa-e) results in separation of the resonances for the two *N*-alkyl groups.

Formamidinato complexes of type (III) have been reported previously.^{6,7} Also, CO-insertion products of type (IV) have been observed,⁴⁻⁶ although in ref. 4 they were not formulated as such.

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Techniques used: I.r., ¹H n.m.r., mass spec.

References: 14

Table 1: Characteristic i.r. absorptions of the complexes (IIIa-e) and (IVa-e)

Table 2: Mass spectra (70 eV) of the complexes (IIIa-e) and (IVa-e)

Table 4: Characteristic properties, yields, and analytical data of the complexes (IIIa-e) and (IVa-e)

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Table 3 ^1H Nmr spectra of the complexes (IIIa – e) and (IVa – e)^a (τ values and multiplicities)

| | CH ₃ | N-CH ₃ | CH | C ₅ H ₅ | C ₆ H ₅ |
|--------|---|-----------------------|--|-------------------------------|-------------------------------|
| (IIIa) | | 7.10(s) | | 4.50(s) | 2.60(m) |
| (IIIb) | 9.07(d), 9.12(d) ^b | | 6.66(m) ^b | 4.43(s) | 2.76(m) |
| (IIIc) | | | | 4.44(s) | 3.07(m) |
| (IIId) | | | 5.61(d), 5.95(d) ^c | 5.23(s) | 2.75(m) |
| (IIIe) | 8.19(s) | | | 4.39(s) | 3.00(m) |
| (IVa) | | { 6.80(s), 7.21(s) | | 4.64(s) | 2.69(m) |
| (IVb) | { 8.97(d) ^b 8.73(d), 8.70(d) ^b | | { 6.69(m) ^b 6.13(m) ^b | 4.71(s) | 2.68(m) |
| (IVc) | | | | 4.63(s) | 3.08(m) |
| (IVd) | | | { 5.26(m) ^{c,d} 5.42(m) ^{c,d} | 5.07(s) | 2.81(m) |
| (IVe) | 8.19(s) | | | 4.39(s) | 3.00(m) |

^aSolvent CDCl₃; Me₄Si as internal standard; Varian T-60 instrument, temp. 33 °C.

^b(CH₃)₂CH, J 6.5–7 Hz.

^cC₆H₅CH₂; J_{gem} 14 Hz.

^dBecause of partial overlap by the C₅H₅ signal only the τ value is listed at which both AB systems are centred.

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