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Preliminary communication

MONONUCLEAR BENZO[*c*]CINNOLINE, AND PHENANTHRIDINE PENTACARBONYL COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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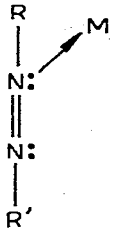
Summary

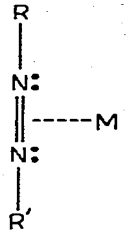
Complexes of the type $M(CO)_5L$ (L = benzo[*c*]cinnoline; M = Cr, Mo, W; L = phenanthridine; M = W) have been prepared.

There is current interest [1, 2] in the coordination chemistry of compounds containing the azo linkage $(-\ddot{N}=\ddot{N}-)$ in view of the possibility that a diimide (diazene HN=NH)—transition metal complex might be an intermediate in the enzymatic fixation of dinitrogen [3, 4].

Examples of the structural types I—IV are now known [1, 2], the azo linkage being bonded to the metal through a nitrogen lone pair or via the N=N double bond. Very recently a nickel—lithium complex containing π-bonded dinitrogen has been described [5, 6].



(I)



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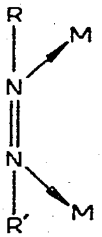

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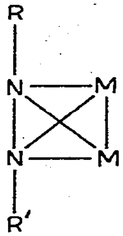


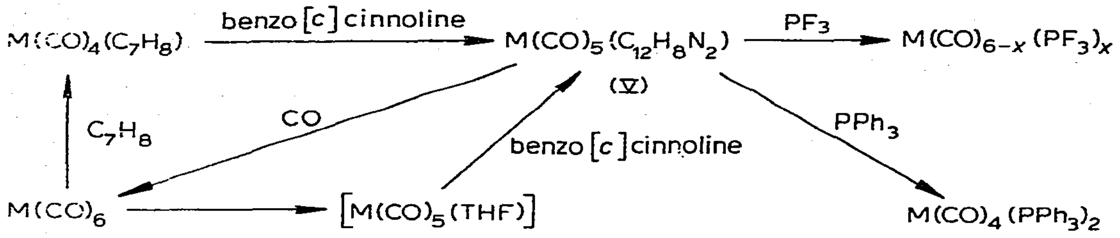
(IV)

Bennett [7] has reported that benzo[*c*]cinnoline reacts with iron carbonyls to afford a complex of type IV, $[M = Fe(CO)_3]$, but attempts to form analogous complexes with other metal carbonyls (e.g. Cr, Mo, W, Co and Ni) were all unsuccessful. We now describe two different synthetic routes to mononuclear benzo[*c*]-

cinnoline complexes of chromium, molybdenum, and tungsten pentacarbonyls, $M(CO)_5(C_{12}H_8N_2)$, (M = Cr, Mo, W), (Va) or (Vb), using much milder reaction conditions. These red crystalline complexes* are readily obtained by ligand displacement reactions (see Scheme 1) as follows:

(a) from the corresponding norbornadienemetal tetracarbonyl complexes, $M(CO)_4(C_7H_8)$ [M = Cr, m.p. 136° (dec.), 83% yield; M = Mo, m.p. 115° (dec.), 81% yield; M = W, m.p. 155° (dec.), 85% yield];

(b) from the tetrahydrofuran metal pentacarbonyl complexes $M(CO)_5(THF)$ generated in situ from $M(CO)_6$.

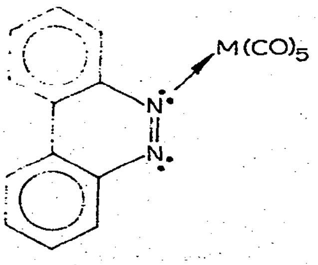


(M = Cr, Mo, W)

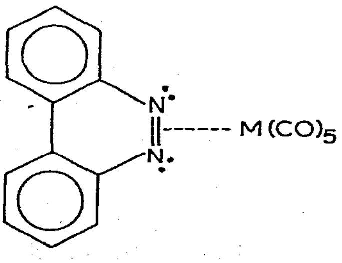
SCHEME 1

All the benzo[*c*]cinnolinemetal pentacarbonyl complexes are rather air sensitive in solution, but much less so in the solid state (Mo < Cr < W). Their mass spectra exhibit peaks corresponding to the parent ions and peaks indicating successive loss of all five carbonyl groups. Benzo[*c*]cinnoline can be displaced from the complexes by treatment with either triphenylphosphine or carbon monoxide (M = Cr) and trifluorophosphine (M = Mo).

The infrared spectra of all the benzo[*c*]cinnoline complexes in the carbonyl stretching region show the characteristic four band pattern expected for a pentacarbonyl complex. The band positions [e.g., M = Mo, ν(CO) at 2074m, 1984w, 1938s, 1896(sh) cm^{-1}] are very similar to those previously reported by Kraihanzel and Cotton [8] for the pyridine complex $Mo(CO)_5(py)$ suggesting that the most likely structure involves coordination via the lone pair of one of



(Va)



(Vb)

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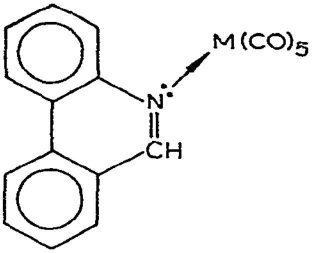
*Satisfactory elemental analyses have been obtained for all new complexes.

the nitrogen atoms (Va) rather than through the N=N double bond (Vb). This type of bonding has been observed previously in metal carbonyl complexes of 2,3-diazabicyclo[2.2.1]hept-2-ene [9]. The UV spectra of the benzo[*c*]cinnoline complexes show absorption maxima at 568 nm, (M = Cr), 525 nm, (M = Mo), and 540 nm, (M = W), which are assigned to $n \rightarrow \pi^*$ transitions. The observed shift to lower wavelength from the free ligand value (415 nm) is rather more pronounced than that observed on azobenzene—nickel(0) phosphine complexes [10], [11]. In the absence of any metal 'shuttling' an unambiguous distinction between Va and Vb should be possible by a detailed ^{13}C NMR study and this is currently underway.

Using method (b) described above, we have also synthesised the analogous phenanthridinemetal pentacarbonyl complex (VI)* (M = W).



(VI)

Acknowledgements

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*Professor M. Herberhold (personal communication) has also independently obtained complexes V and also analogous azobenzene complexes using this synthetic approach.