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SYNTHESIS, REACTIONS AND FLUXIONAL BEHAVIOUR OF SOME BENZO[*c*] CINNOLINE AND PHENANTHRIDINE PENTACARBONYL COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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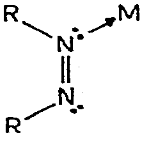
Summary

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

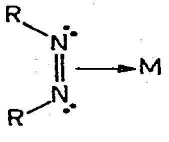
Introduction

The coordination chemistry of azo-compounds is currently of interest [1,2] in view of the possibility that a diazene (HN=NH)-transition metal complex might be an intermediate in the enzymatic fixation of dinitrogen [3,4].

The azo- ligand can bond to transition metals in a number of ways and examples of all of the structural types A—D are now known [5—35].



(A)



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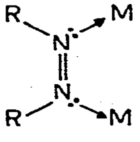

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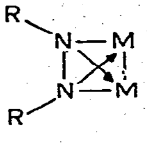

(D)

Bennett [20] has reported a benzo[*c*] cinnoline iron carbonyl complex of type D [M = $Fe(CO)_3$], but attempts to form a related series of compounds by the direct reaction of benzo[*c*] cinnoline with other metal carbonyls (e.g., Cr, Mo, W, Co, or Ni) proved unsuccessful.

We felt that this type of complex might be obtained via alternative synthetic routes under milder conditions involving displacement of other coordinated ligands and we now report on a series of benzo[*c*] cinnoline Group VIB metal pentacarbonyl complexes and their phenanthridine analogues *.

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* A preliminary report of part of this work has appeared [52].

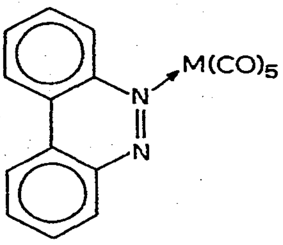
Results and discussion

As expected, benzo[*c*]cinnoline reacts readily with the norbornadiene complexes $M(C_7H_8)(CO)_4$ (M = Cr, Mo, W) under mild conditions to afford the wine-red crystalline benzo[*c*]cinnoline metal pentacarbonyl complexes (I) via disproportionation reactions:

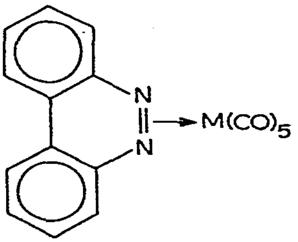
$$M(C_7H_8)(CO)_4 + C_{12}H_8N_2 \xrightarrow[-M(CO)_6]{-C_7H_8} \underset{(I)}{M(C_{12}H_8N_2)(CO)_5}$$

(M = Cr, Mo, W)

All the benzo[*c*]cinnoline pentacarbonyl complexes obtained are soluble in aromatic and chlorinated solvents and rather air-sensitive in solution, but much less so in the solid state (Mo < Cr < W). Although only the tungsten complex exhibits the parent peak ion in the mass spectrum, the common feature of the mass spectra of all these complexes is the appearance of peaks indicating the successive loss of all five carbonyl groups from the parent compound. The infrared spectra of the benzo[*c*]cinnoline pentacarbonyl complexes show the characteristic four band pattern in the ν(CO) stretching frequency region expected for pentacarbonyl species [36] and the data are listed in Table 1. The positions and intensities of the carbonyl stretching bands are very similar to those previously reported by Cotton and Kraihanzel [37] for the analogous pyridine complexes $M(py)(CO)_5$ (M = Cr, Mo, W), suggesting that the most likely structure for the benzo[*c*]cinnoline complexes is Ia involving coordination via the lone pair of one nitrogen atom rather than the alternative Ib involving π-bonding through the —N=N— double bond.



(I a)



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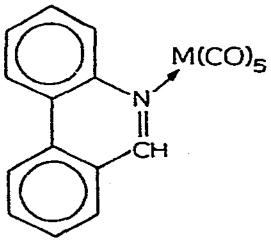
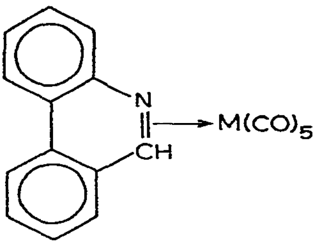


(II a)



(II b)

TABLE 1

CARBONYL STRETCHING FREQUENCIES OF SOME GROUP VIB PENTACARBONYL COMPLEXES [a]

Compound [c]	A_1^1 (cm^{-1})	B_1 [b] (cm^{-1})	E (cm^{-1})	A_1^2 (cm^{-1})	Ref.
$Cr(cinn)(CO)_5$	2068	1980	1936	1892	This work
$Mo(cinn)(CO)_5$	2074	1984	1938	1896	This work
$W(cinn)(CO)_5$	2072	1977	1930	1892	This work
$Cr(phend)(CO)_5$	2068	1980	1932	1896	This work
$Mo(phend)(CO)_5$	2078	1982	1943	1900	This work
$W(phend)(CO)_5$	2072	1972	1934	1894	This work
$Cr(py)(CO)_5$	2073	1986	1936	1905	37
$Mo(py)(CO)_5$	2079	1987	1944	1890	37
$W(py)(CO)_5$	2076	1980	1933	1895	37

[a] In $CHCl_3$ solution. [b] Raman active only in strictly C_{4v} symmetry. [c] cinn = benzo[*c*]cinnoline; phend = phenanthridine; py = pyridine.

The benzo[*c*]cinnoline metal pentacarbonyl complexes are also readily obtained by the displacement of tetrahydrofuran from the appropriate metal pentacarbonyl tetrahydrofuran compounds [38], $M(CO)_5(THF)$, generated in situ via ultra-violet irradiation of a mixture of $M(CO)_6$ and tetrahydrofuran.

$$\begin{tikzcd} M(CO)_6 \arrow[r, "THF", "UV"'] & {[M(CO)_5(THF)]} \arrow[r, "C_{12}H_8N_2"] \arrow[dr, "C_{13}H_9N"'] & (I) \\ & & M(CO)_5(\text{phenanthridine}) \end{tikzcd}$$

(II)

Since the completion of this work Heberhold et al. [35] have described the preparation of a variety of related chromium pentacarbonyl azo- complexes $Cr(CO)_5L$ (L = 2,3-diazabicyclo[2.2.1]hept-2-ene, 5-phenyl-3,4,5-triaza-tricyclo-[$5.2.1.0^{2,6\ exo}$]dec-3-ene, pyridazine and dispiro[cyclohexane-2-[1.3.4]thiadiazoline-5′-cyclohexane) using the photolysis reaction. This type of reaction can be extended to the synthesis of other azometal pentacarbonyl complexes, for example we have synthesised the phenanthridine metal pentacarbonyl complexes (II) in a similar fasion.

Compounds II (M = Cr, W) form yellow crystals, but the molybdenum compound, which is much more soluble, could not be isolated in a pure form from small amounts of phenanthridine. All the phenanthridine pentacarbonyl complexes are more soluble in common solvents than their benzo[*c*]cinnoline analogues and since their IR spectra are very similar in the carbonyl stretching region we propose structure IIa rather than IIb.

Further information on the nature of the bonding in I and II comes from ^1H and ^{13}C NMR studies. Three distinct patterns of lines in the ratio 1:1:2 are observed in the ^1H NMR spectrum of free benzo[*c*]cinnoline which can be assigned to the pairs of equivalent protons (H^2, $H^{2'}$, H^3, $H^{3'}$) and (H^4, $H^{4'}$, H^5, $H^{5'}$) respectively *. In the tungsten benzo[*c*]cinnoline complex the low field pattern

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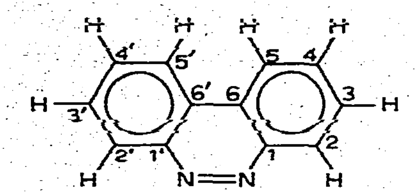
* The protons have the same numbers as their corresponding carbons.



for the H^2 and $H^{2'}$ protons in the ^{1}H-NMR spectrum is broader and more complex, suggesting that in the coordinated benzo[*c*]cinnoline the protons H^2 and $H^{2'}$ are non-equivalent and the azo-ligand is coordinated through the lone pair of one nitrogen atom. Since the (H^3, $H^{3'}$) and (H^4, $H^{4'}$, H^5, $H^{5'}$) resonances are

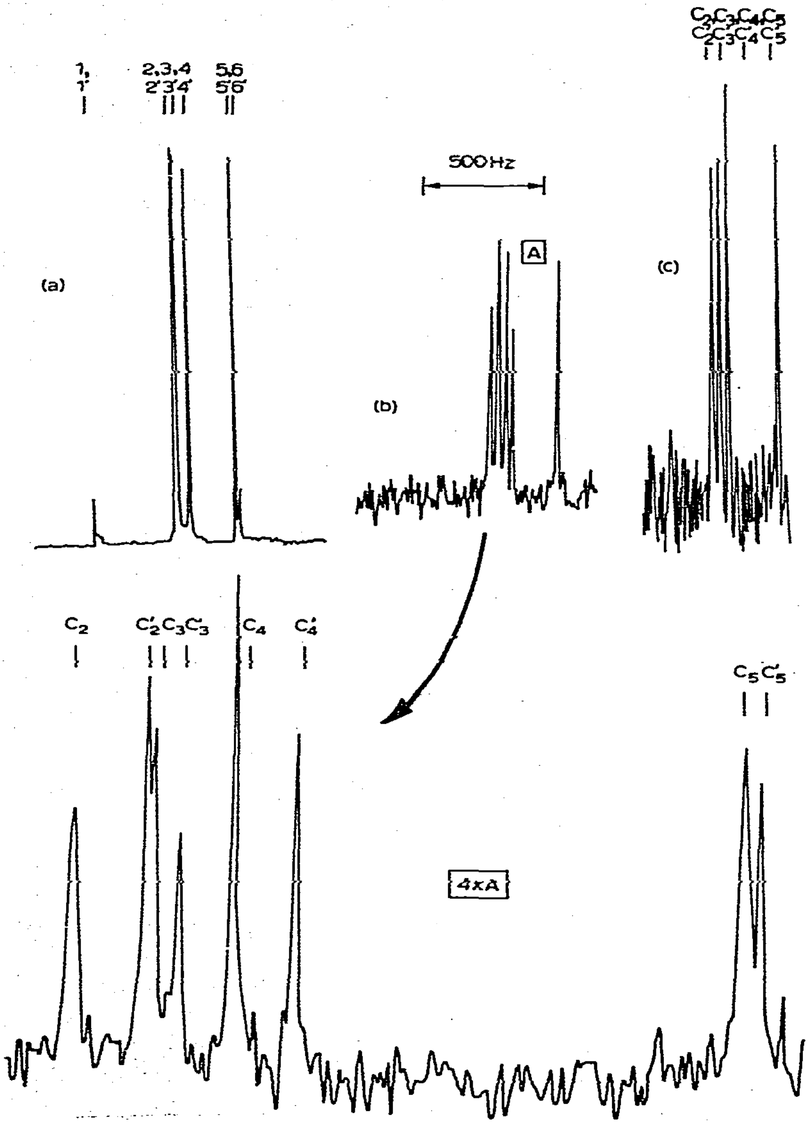


Fig. 1. a: ^{1}H decoupled ^{13}C NMR spectrum (at 25.15 MHz) of benzo[*c*]cinnoline; b: ^{1}H decoupled ^{13}C NMR spectrum (at 25.15 MHz) of benzo[*c*]cinnoline tungsten pentacarbonyl; c: ^{1}H decoupled ^{13}C NMR spectrum (at 25.15 MHz) of benzo[*c*]cinnoline pentacarbonyl chromium.

TABLE 2

^{13}C-CHEMICAL SHIFTS FOR BENZO[*c*] CINNOLINE METAL PENTACARBONYL COMPLEXES [a]

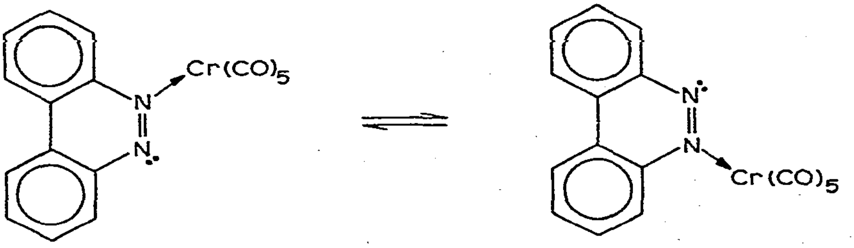
Compound	$\delta(C_1, C_1')$ (ppm)	$\delta(C_2, C_2')$ (ppm)	$\delta(C_3, C_3')$ (ppm)	$\delta(C_4, C_4')$ (ppm)	$\delta(C_5, C_5')$ (ppm)	$\delta(C_6, C_6')$ (ppm)
benzo[*c*] cinnoline	145.3	131.3	131.0	129	121.2	120.5
$Cr(cinn)(CO)_5$		133.1	132.0	130.5	121.8	
$Mo(cinn)(CO)_5$	145.3	131.4	130.1	129.2	121.4	120.9
$W(cinn)(CO)_5$		133.0	131.7	130.4	121.7	
		131.8	131.3	129.4	121.5	

[a] δ in ppm from TMS, in $CDCl_3$ solution.

sharp, this complex is believed to be rigid in solution at room temperature. The ^{1}H NMR spectrum of the chromium pentacarbonyl benzo[*c*] cinnoline complex, on the other hand, shows three broad patterns which suggest that the chromium may be 'shuttling' between the two nitrogen atoms. The separation between the two low field resonances is smaller than that of the free benzo[*c*] cinnoline. The resonances in the ^{1}H NMR spectrum of the molybdenum complex are also broadened.

Further confirmation of the nitrogen bonded structure Ia comes from ^{13}C NMR spectroscopic studies. The proton decoupled ^{13}C NMR spectrum of free benzo[*c*] cinnoline (Fig. 1a) and Table 2 contains four strong and two weak resonances. The strong lines are assigned to the four equivalent pairs of carbon atoms of the rings (2—5 and 2′—5′)and the weak resonances correspond to the equivalent pairs of tertiary carbons (1, 1′) and (6, 6′). The proton decoupled ^{13}C NMR spectrum of the rather insoluble benzo[*c*] cinnoline tungsten complex I (M = W) exhibits eight distinct resonances for the carbon atoms (2—5 and 2′—5′) while the resonances for (1, 1′) and (6, 6′) are too weak to be seen (Fig. 1b). These results imply that the carbon atoms in the two rings of benzo[*c*] cinnoline are non-equivalent in the tungsten complex, again consistent only with structure Ia.

Interestingly the ^{13}C NMR spectrum of I (M = Cr) is much simpler in appearance than that of the tungsten analogue exhibiting only four resonances in different positions than benzo[*c*] cinnoline itself (see Table 2 and Fig. 1c) which presumably implies that the metal is 'shuttling' between the two nitrogen atoms at room temperature.



This type of fluxional behaviour has also been reported to occur in the recently reported $ArCr(CO)_2L$ (L = 2,3-diazabicyclo[2.2.1]hept-2-ene) compound [39] and certain pyrazollyl metal complexes [40,41]. The ^{13}C NMR

TABLE 3

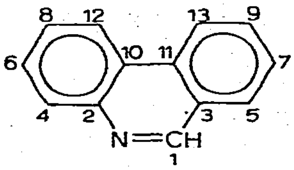
^{13}C-CHEMICAL SHIFTS FOR PHENANTHRIDINE METAL PENTACARBONYL COMPLEXES [a]

Compound	$\delta(C^1)$ (ppm)	$\delta(C^2)$ (ppm)	$\delta(C^3)$ (ppm)	$\delta(C^4, C^5)$ (ppm)	$\delta(C^6, C^7)$ (ppm)	$\delta(C^8, C^9)$ (ppm)	$\delta(C^{10}, C^{11})$ (ppm)	$\delta(C^{12}, C^{13})$ (ppm)
phenanthridine	153.1	144.1	132.0	130.4	128.3	127.0	126.6	121.0
				129.8	128.2	126.6	123.7	121.3
Cr(phend)(CO)$_5$	162.0	145		133.1	129.3	128.5	125.4	122.8
				130.7		127.8		121.7
W(phend)(CO)$_5$	163.5	144.3		133.5	132.5	128.6	122.8	122.4
				133.1	129.5	128.1		121.8

[a] δ in ppm from TMS in CDCl$_3$ solution.

spectrum of I (M = Mo) is very similar to that of the free benzo[*c*]cinnoline and this is consistent with its much greater instability in solution compared with the chromium and tungsten complexes.

In the case of phenanthridine and its coordination complexes the ^{13}C NMR spectra cannot, of course, differentiate between IIa and IIb owing to the lower symmetry of the ligand. The ^{13}C NMR spectra of phenanthridine and its pentacarbonyl complexes show a pattern of lines assignable to the 13 non-equivalent carbon atoms of the ligand (Table 3).



It is interesting to compare our results with recent papers of Herberhold et al. [35,39,42], mentioned earlier, which were published since completion of our work. Using the photolysis reaction discussed above, several chromium pentacarbonyl azo-complexes of the type $Cr(CO)_5L$ (L = azo-ligand) have also been prepared. The reaction of $Cr(C_7H_8)(CO)_4$ with pyridazine afforded the disubstituted product $Cr(CO)_4(pyradazine)_2$ which could be converted to the thermally unstable pentacarbonyl complex $Cr(CO)_5(pyridazine)$ on treatment with carbon monoxide and to the dinuclear bridged complex $Cr_2(CO)_6(pyridazine)_2$ on further reaction with $Cr(C_7H_8)(CO)_5$. The diazabicycloheptene chromium pentacarbonyl complex is also reported to give a dinuclear complex on heating, but we find no analogous reaction with the benzo[*c*]cinnoline series of complexes.

TABLE 4

SOME $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ BANDS IN THE ABSORPTION SPECTRA OF BENZO[*c*]CINNOLINE AND PHENANTHRIDINE COMPLEXES

Compound	λ_{max} $\pi \rightarrow \pi^*$ (nm)	λ_{max} $n \rightarrow \pi^*$ (nm)	Ref.
Benzo[*c*]cinnoline	380	405	43
$Cr(cinn)(CO)_5$	565	394	This work
$Mo(cinn)(CO)_5$	526	362	This work
$W(cinn)(CO)_5$	540	382	This work
phenanthridine	345		43
$Cr(phend)(CO)_5$	415		This work
$Mo(phend)(CO)_5$	390		This work
$W(phend)(CO)_5$	400		This work
$PhN{=}NPh$	321	440	44
$(PhN{=}NPh)^-H^+$	410		44
$SbCl_5(PhN{=}NPh)$	420		45
$PtCl_2(PhN{=}NPh)AsPh_3$	418	318	46
$PdBr_2(PhN{=}NPh)_2$	395	316	46

Electronic absorption spectra

The bands observed in the UV spectrum of benzo[*c*]cinnoline in hexane at 380 and 405 nm have been assigned to $\pi \rightarrow \pi^*$ transitions respectively [43] (see Table 4). In all the three benzo[*c*]cinnoline metal pentacarbonyl complexes the UV spectra show a band which is shifted towards longer wavelength and is increased in intensity compared with the free ligand. We assign this band to the $\pi \rightarrow \pi^*$ transition while a weaker band at slightly shorter wavelength than that of the free ligand is assigned to the $n \rightarrow \pi^*$ transition. The chromium complex shows the largest $\pi \rightarrow \pi^*$ shift and molybdenum the lowest. Similar results are obtained for the phenanthridine metal pentacarbonyl complexes (Table 4), but in this case the $n \rightarrow \pi^*$ transitions have not been assigned with certainty either in the free ligand [44] or in the complexes.

These observations are in line with those previously observed for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands of azobenzene and its conjugate acid [44] and several coordination complexes listed in Table 4 [45,46].

Reactions

As mentioned above, we found no evidence for any dinuclear benzo[*c*]-cinnoline or phenanthridine metal carbonyl complexes when the metal pentacarbonyl azo-compounds are heated. Neither benzo[*c*]cinnoline nor phenanthridine are readily displaced from the pentacarbonyl complexes under mild conditions, however, heating I (M = Mo) with an excess of trifluorophosphine gives a mixture of products of the type $Mo(CO)_{6-x}(PF_3)_x$ (x = 1—3) [47]. Compound I (M = Cr) reacts with carbon monoxide in refluxing benzene to give $Cr(CO)_6$, while prolonged treatment with an excess of triphenylphosphine yields the known complex *cis*-$Cr(CO)_4(PPh_3)_2$ [48]. Similarly, phenanthridine is displaced from II (M = Cr) by triphenylphosphine in refluxing benzene.

Experimental

Reactions were carried out and complexes handled either under an atmosphere of dry nitrogen gas or in vacuo. Solvents were dried by standard methods and freshly distilled under dry nitrogen prior to use.

IR spectra were recorded in the range 4000—400 cm^{-1} on either a Perkin—Elmer 457 or 125 grating spectrometer. UV spectra were recorded on a Unicam SP800 spectrophotometer. ^1H NMR spectra were recorded using a Varian HA100 spectrometer operating at 100 MHz. ^{13}C NMR spectra were recorded on a JEOL PFT100 Fourier Transform NMR spectrometer operating at 25.15 MHz with noise decoupling. Mass spectra were obtained using either an AEI MS9 or a Hitachi Perkin—Elmer RMU6E spectrometer. Elemental analyses were carried out by Mr. and Mrs. A.G. Olney of this department.

Benzo[*c*]cinnoline (Ralph N. Emanuel Ltd.) and phenanthridine (Fluka) were used as supplied. Trifluorophosphine (Ozark—Mahoning Company) was dried by passage through P_2O_5 and purified by trap to trap fractionation in the high vacuum line. The norbornadiene tetracarbonyl complexes were prepared by literature methods [49—51] and sublimed in vacuo before use.

Reaction of bicycloheptadienechromiumtetracarbonyl with benzo[c] cinnoline

Bicycloheptadienechromiumtetracarbonyl (0.512 g, 2 mmol) reacted slowly with benzo[*c*]cinnoline (0.360 g, 2 mmol) in benzene (30 ml) at room temperature, giving a light-red solution after stirring for 3 h. Several weak new bands appeared in the carbonyl stretching region of the infrared spectrum of the solution. On refluxing the mixture for 3 h under dinitrogen the colour of the solution changed to dark-red and the new bands in the infrared spectrum increased in intensity. The reaction mixture was filtered through celite and after removal of solvent the resulting solid was recrystallised from chloroform and hexane to give dark-red crystals of benzo[*c*]cinnoline chromiumpentacarbonyl (0.310 g, 80% based on half the starting chromium), m.p. 136°C (dec.) (Found: C, 54.5; H, 2.2; N, 7.5. $C_{17}H_8CrN_2O_5$ calcd.: C, 54.83; H, 2.15; N, 7.52%). IR spectrum: 3080w, 3050vw, 2068 *, 1980 *, 1936vs *, 1892(sh) *, 1607w, 1576m, 1545s, 1472m, 1457s, 1432m, 1377m, 1345m, 1287w, 1246w, 1188m, 1168m, 1146s, 1127s, 1099vs, 1025w, 1006w, 995w, 962s, 944s, 912w, 863m, 844w, 760vs, 718vs, 620s, 615m, 602vs, 586s, 575(sh), 552m, 481m, 467m, 408s, cm^{-1} (KBr disc). ^1H NMR spectrum: τ 1.24 (2H), 1.43 (2H), 2.06 (4H) ($CDCl_3$ solution). The ^{13}C NMR spectrum is discussed in the text and data listed in Table 2. The UV spectrum showed two bands at 565 and 394 nm (hexane solution) and the mass spectrum exhibited a peak at *m/e* 220 due to $[Cr(CO)_6]^+$ and other peaks indicating the subsequent loss of all five carbonyls from the $Cr(C_{12}H_8N_2)(CO)_5$ compound. The colourless filtrate after isolating the complex showed a very strong band at 1985 cm^{-1} in the infrared spectrum suggesting the formation of $Cr(CO)_6$.

Reaction of bicycloheptadienemolybdenumtetracarbonyl with benzo[c] cinnoline

To a solution of freshly sublimed bicycloheptadienemolybdenumtetracarbonyl (0.300 g, 1 mmol) in benzene (25 ml) was added benzo[*c*]cinnoline (0.270 g, 1.5 mmol). The colour of the solution instantly changed from yellow to violet and the mixture was stirred at room temperature for a further 2 h under dinitrogen. After filtration through a sinter packed with celite and washing with benzene (5 ml), the solvent was reduced in volume (5 ml) under vacuum and addition of hexane gave a red powder identified as benzo[*c*]cinnoline molybdenumpentacarbonyl (0.168 g, 81% based on half of the molybdenum). Well-formed red needles were obtained by recrystallisation from $CHCl_3$/hexane and the complex was further purified by recrystallisation from chloroform only [m.p. 115°C (dec.)] (Found: C, 49.5; H, 2.3; N, 6.9. $C_{17}H_8MoN_2O_5$ calcd.: C, 49.03; H, 1.92; N, 6.73%). IR spectrum: 2074m *, 1984w, 1938vs *, 1896(sh) *, 1606w, 1577m, 1545m, 1344(sh), 1282w, 1247w, 1185w, 1166s, 1142s, 1139s, 1098vs, 976m(br), 960s, 930m, 860w, 759vs, 718s, 713(sh), 624s, 612vs, 594s cm^{-1} (Nujol mull). ^1H NMR τ 1.20 (2H), 1.40 (2H), 2.0 (4H), ($CDCl_3$ solution). The UV spectrum shows two absorptions at 526 and 362 nm. The mass spectrum exhibits a parent ion at *m/e* 264 for $[Mo(CO)_6]^+$ and peaks showing the successive loss of carbon monoxide from $Mo(C_{12}H_8N_2)(CO)_5$. The complex is very air-sensitive in solution but much less so in the solid. A solid sample darkened when it was left under dinitrogen for a prolonged period (~one month) and is

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* $CHCl_3$ solution using Perkin—Elmer 125 spectrometer.

probably light-sensitive. The reaction was accompanied by decomposition. The presence of $Mo(CO)_6$ in the filtrate was detected by infrared spectroscopy, indicating that disproportionation of the starting molybdenumtetracarbonyl complex had occurred.

Reaction of bicycloheptadienetungstentetracarbonyl with benzo[c]cinnoline

Bicycloheptadienetungstentetracarbonyl (0.388 g, 1 mmol) was refluxed with benzo[*c*]cinnoline (0.180 g, 1 mmol) in benzene (20 ml) for 4 h under an atmosphere of dinitrogen. After removal of solvent the product was recrystallised from chloroform/hexane to yield benzo[*c*]cinnoline tungstenpentacarbonyl as dark-red crystals (0.125 g, 85% based on half of the initial tungsten), m.p. 155°C (dec.) (Found: C, 40.2; H, 1.9; N, 5.9. $C_{17}H_8N_2O_5W$ calcd.: C, 40.47; H, 1.58; N, 5.55%). IR spectrum: 2072m *, 1977w *, 1930vs *, 1892(sh), 1608w, 1576m, 1542m, 1341w, 1284w, 1245w, 1187w, 1167m, 1141m, 1127s, 1096s, 1027w, 990w, 960s, 927s, 860m, 840m, 754vs, 716vs, 660vs, 620s, 552s, cm^{-1} (Nujol mull). ^1H NMR spectrum: τ 1.15 (2H), 1.64 (2H), 2.04 (4H). ^{13}C NMR spectrum is fully discussed in the text and the data are listed in Table 2. The UV spectrum consists of two bands at 540 and 382 nm (hexane solution). The mass spectrum shows a peak due to the parent ion at *m/e* 504 and other peaks expected for stepwise losses of five carbon monoxide molecules from $W(C_{12}H_8N_2)(CO)_5$. The IR spectrum of the filtrate also shows the presence of $W(CO)_6$. The benzo[*c*]cinnolinetungstenpentacarbonyl complex is more stable in air than its chromium and molybdenum analogues.

Reaction of tetrahydrofuranchromiumpentacarbonyl with benzo[c]cinnoline

Chromium hexacarbonyl (0.660 g, 3 mmol) in tetrahydrofuran (40 ml) was irradiated with ultraviolet light under dinitrogen for 36 h. The original colourless solution became orange, indicating the formation of tetrahydrofuranchromiumpentacarbonyl. The colour of the solution changed to red on addition of benzo[*c*]cinnoline (0.540 g, 3 mmol). After stirring the reaction mixture at room temperature for 24 h, removal of the volatiles led to the recovery of solvent and unreacted chromiumhexacarbonyl (0.300 g, 50% of original). The residue was recrystallised from chloroform/hexane to afford burgundy-red crystals of benzo[*c*]cinnolinechromiumpentacarbonyl (0.340 g, 34%), m.p. 137—138°C (dec.) (Found: C, 54.5; H, 2.1; N, 7.6. $C_{17}H_8CrN_2O_5$ calcd.: C, 54.83; H, 2.15; N, 7.52%). The compound is identical with that prepared from the norbornadienechromiumtetracarbonyl complex. The yield can be increased to 50% by irradiating the mixture after addition of benzo[*c*]cinnoline for 24 h. Unreacted benzo[*c*]cinnoline was recovered from the filtrate by recrystallation from hexane after allowing the red solution to be open to air until the red colour disappeared.

Reaction of tetrahydrofuranmolybdenumpentacarbonyl with benzo[c]cinnoline

In a similar fashion to that described above, tetrahydrofuranmolybdenumpentacarbonyl [38] was prepared by UV irradiation of a tetrahydrofuran (30 ml) solution of molybdenumhexacarbonyl (0.792 g, 3 mmol) for 48 h under an at-

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* $CHCl_3$ solution using Perkin—Elmer 125 spectrometer.

mosphere of nitrogen gas. Benzo[*c*]cinnoline (0.540 g, 3 mmol) was added to the resulting tetrahydrofuranmolybdenumpentacarbonyl complex and the mixture was stirred at reflux temperature for 5 h. After removal of solvent, sublimation gave unreacted molybdenumhexacarbonyl (0.480 g, 60%). The solid remaining was extracted with chloroform and recrystallised from $CHCl_3$/hexane to give red crystals of benzo[*c*]cinnoline molybdenumpentacarbonyl (0.353 g, 28%) (Found: C, 50.6; H, 2.2; N, 7.6. $C_{17}H_8MoN_2O_5$ calcd.: C, 49.03; H, 1.92; N, 6.73%). The IR spectrum and melting point are identical with a sample obtained by the alternative route described above. Unreacted benzo[*c*]cinnoline was recovered from the filtrate.

Reaction of tetrahydrofurantungstenpentacarbonyl with benzo[c] cinnoline

Tetrahydrofurantungstenpentacarbonyl [38] was made by UV irradiation of hexacarbonyl (0.708 g, 2 mmol) in tetrahydrofuran (40 ml) for 24 h. Benzo[*c*]cinnoline (0.360 g, 2 mmol) was then added to the solution and the mixture agitated under dinitrogen for 24 h at room temperature. The solvent was removed under vacuum; unreacted tungstenhexacarbonyl was sublimed off (0.255 g, 35%) and the product was recrystallised from chloroform/hexane to yield long red needles of benzo[*c*]cinnoline tungstenpentacarbonyl (0.400 g, 39%) which can be further purified by recrystallisation from a chloroform solution (Found: C, 40.4; H, 1.9; N, 5.8. $C_{17}H_8N_2O_5W$ calcd.: C, 40.47; H, 1.58; N, 5.55%). The yield was increased to 47% on refluxing the reaction mixture for 2—3 h and to 65% by UV irradiation of the solution. The infrared and ultraviolet spectra are identical with those prepared by an alternative method.

Reaction of tetrahydrofuranchromiumpentacarbonyl with phenanthridine

Phenanthridine (0.716 g, 4 mmol) was added to a solution of tetrahydrofuranchromiumpentacarbonyl obtained as described above from chromiumhexacarbonyl (0.880 g, 4 mmol) and tetrahydrofuran (40 ml). The mixture was subjected to further UV irradiation for another 24 h under dinitrogen. After removal of solvent and unreacted chromiumhexacarbonyl (0.400 g, 45%) the residue was recrystallised from a concentrated chloroform solution by cooling below room temperature to afford yellow crystals of phenanthridinechromiumpentacarbonyl (0.470 g, 32%), m.p. 123—125°C (dec.) (Found: C, 58.1; H, 2.8; N, 3.9. $C_{18}H_9CrNO_5$ calcd.: C, 58.25; H, 2.42; N, 3.77%). IR spectrum: 3085vw, 3060vw, 2068s *, 1980w *, 1932vs *, 1966(sh) *, 1618m, 1587w, 1528m, 1495s, 1460s, 1446s, 1387s, 1347m, 1251s, 1188w, 1167m, 1151(sh), 1144m, 1108m, 1050m, 962w, 938m, 921(sh), 913m, 815vs, 791m, 753vs, 725vs, 652vs(br), 619s, 558m, 539(sh), 500m, 450vs cm^{-1} (KBr disc). ^1H NMR spectrum shows one singlet and two multiplets at τ 0.4 (1H), 1.4 (3H) and 2.1 (5H). ^{13}C NMR spectrum is similar to the free phenanthridine and discussed in the text. The UV spectrum shows a band at 415 nm in addition to those of the free ligand. The mass spectrum exhibits a parent ion for $[Cr(CO)_6]^+$ and peaks corresponding to stepwise loss of all the CO molecules from $Cr(C_{13}H_9N)(CO)_5$. The compound is soluble in all common solvents and although very air-sensitive in solution, it is rather stable in the solid state.

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* $CHCl_3$ solution obtained on a Perkin—Elmer 125 spectrometer.

Reaction of tetrahydrofuranmolybdenumpentacarbonyl with phenanthridine

A mixture of molybdenumhexacarbonyl (0.530 g, 2 mmol) and phenanthridine (0.358 g, 2 mmol) in tetrahydrofuran (25 ml) was stirred for 48 h with simultaneous UV irradiation gave only a very small quantity of product. It was not possible to isolate a pure product from the reaction mixture, but the existence of the desired phenanthridinemolybdenumpentacarbonyl complex was established by the IR spectrum of the solution which showed the expected carbonyl stretching bands at 2078m, 1982w, 1943vs, 1900(sh) cm^{-1} ($CHCl_3$ solution) and a maxima at 390 nm in the UV spectrum. After removing the solvent, unreacted molybdenumhexacarbonyl was collected by sublimation (0.350 g, 70%).

Reaction of tetrahydrofurantungstenpentacarbonyl with phenanthridine

Tungstenhexacarbonyl (0.704 g, 2 mmol) and phenanthridine (0.358 g, 2 mmol) were dissolved in tetrahydrofuran (30 ml) in a Schlenk-tube flushed with dinitrogen. The mixture was irradiated with UV light for 48 h, the solvent removed under vacuum, and unreacted tungstenhexacarbonyl was recovered by sublimation. The residue was extracted with chloroform and recrystallised to yield phenanthridine tungstenpentacarbonyl as yellow crystals (0.520 g, 50%), m.p. 140—142°C (dec.) (Found: C, 42.9; H, 1.8; N, 2.8. $C_{18}H_9NO_5W$ calcd.: C, 42.46; H, 1.92; N, 2.78%). IR spectrum: 3080vw, 3060vw, 2072m *, 1972w *, 1934vs *, 1892(sh) *, 1614m, 1585w, 1526m, 1494m, 1468m, 1445s, 1386s, 1346m, 1257vs, 1197w, 1186w, 1167w, 1162w, 1143w, 1116m, 1057w, 1008w, 914w, 865s, 790m, 770s, 752vs, 736w, 724s, 616vs, 591vs, 557s, 528w, 431m, 410m, 371vs cm^{-1} (KBr disc). ^{1}H NMR spectrum consists of three resonances at τ 0.3 (1H), 1.5 (3H), and 2.18 (5H). ^{13}C NMR spectrum, which is discussed in the text shows similar patterns to those of the free ligand, data are listed in Table 3. The UV spectrum contains a band at 400 nm (hexane solution), and the mass spectrum exhibits peaks showing a parent ion for $W(CO)_6$ and a fragmentation pattern corresponding to successive loss of CO groups from the $W(C_{13}H_9N)(CO)_5$ compound. The phenanthridinetungstenpentacarbonyl is more stable in air than the chromium analogue.

Reaction of benzo[c] cinnoline chromiumpentacarbonyl with triphenylphosphine

A mixture of benzo[*c*] cinnoline chromiumpentacarbonyl (0.185 g, 0.5 mmol) and triphenylphosphine (0.600 g, 2.4 mmol) was stirred in chloroform (15 ml) for 15 h at room temperature to give *trans*-bis(triphenylphosphine)-chromiumtetracarbonyl (0.580 g, 72%), m.p. 250°C (lit. [48], 250—252°C) after recrystallisation from chloroform/hexane (Found: C, 68.8; H, 4.5. $C_{40}H_{30}CrO_4P_2$ calcd.: C, 69.7; H, 4.31%). The IR spectrum of the complex is identical with a genuine sample [49]. Benzo[*c*] cinnoline was recovered from the filtrate as yellow crystals (0.075 g, 80%) after recrystallisation from hexane.

Reaction of benzo[c] cinnoline molybdenumpentacarbonyl with trifluorophosphine

Benzo[*c*] cinnoline molybdenumpentacarbonyl (0.100 g, 0.25 mmol) was sealed off with trifluorophosphine (0.142 g, 1.5 mmol) and the mixture heated

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* $CHCl_3$ solution recorded on a Perkin—Elmer 125 spectrometer.

at 60°C for 48 h. The red solid became yellow and some white crystals also formed on the side of the ampoule. The ampoule was opened in vacuo, the non-condensable carbon monoxide pumped away and excess trifluorophosphine (0.028 g, 20%) was collected in a trap at liquid nitrogen temperature. The solid residue was sublimed (25°C/10^{-4} mmHg) and white crystals which collected at —78°C were identified as a mixture of complexes of the type $Mo(CO)_{6-x}(PF_3)_x$ (0.075 g) by their infrared and ^{19}F NMR spectra [47]. The involatile solid left in the ampoule was extracted with hexane to afford benzo[*c*]cinnoline, (0.035 g, 77%), identified by its infrared spectrum and melting point.

Reaction of benzo[c]cinnoline chromiumpentacarbonyl with carbon monoxide

A stream of carbon monoxide was bubbled through a solution of benzo[*c*]-cinnoline chromiumpentacarbonyl (0.075 g, 0.02 mmol) in benzene at reflux temperature for 5 h. The colour of the solution changed from red to yellow. After removal of solvent under vacuum the resulting solid was sublimed at room temperature/10^{-4} mmHg and collected on a water cooled probe to afford $Cr(CO)_6$ (0.025 g, 57%) identified by its IR spectrum. The yellow solid residue gave benzo[*c*]cinnoline (0.030 g, 55%) after extracting and recrystallising from hexane.

Reaction of phenanthridine chromiumpentacarbonyl with triphenylphosphine

Phenanthridine chromiumpentacarbonyl (0.180 g, 0.5 mmol) did not react with triphenylphosphine (0.520 g, 2 mmol) in benzene at room temperature. However, on refluxing the mixture for 5 h under nitrogen gas the product was *trans*-bis(triphenylphosphine)chromiumtetracarbonyl (0.460 g, 69%) after recrystallisation from chloroform and hexane. The complex was identified by comparison of its m.p. 248°C (lit. [48], 250—252°C) and IR spectrum with an authentic sample.

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