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CYCLOMETALLATION REACTIONS

VII*. REACTIONS OF BENZO[*h*]QUINOLINE

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SUMMARY

Reactions between benzo[*h*]quinoline (BqH) and $M(CO)_5Me$ (M = Mn, Re), $M_3(CO)_{12}$ (M = Ru, Os) and $[Rh(CO)_2Cl]_2$ have given the complexes $M(CO)_4Bq$ (M = Mn, Re), $M(CO)_2Bq_2$ (M = Ru, Os), and $Bq_2RhCl_2Rh(CO)_2$, respectively; $Cr(CO)_3(\pi\text{-}BqH)$ is metallated on reaction with $Mn(CO)_5Me$, affording $[\pi\text{-}BqMn(CO)_4]Cr(CO)_3$. Spectroscopic evidence was obtained for the formation of $Mo(CO)_2Bq(\pi\text{-}C_5H_5)$. Reactions of some complexes to give bi(benzo[*h*]quinolyl) are also reported. Characteristic changes in the IR and NMR spectra which occur as a result of metallation of the ligand are reported.

RESULTS AND DISCUSSION

We have previously described reactions of azobenzenes[2-4], benzylideneaniline and benzylidenemethylamine[5] with a variety of transition metal compounds, from which complexes containing the transition metal σ-bonded to an *ortho*-carbon of the aromatic ring were obtained. In an extension of these studies, we have found that benzo[*h*]quinoline(I) is metallated with extreme ease in similar reactions. An earlier paper[6] describes the palladation of (I) by means of palladium(II) chloride.

Subsequent halogen-bridge cleavage reactions of this palladium complex have also been reported[7] and a brief description of some rhodium(III) complexes has also appeared[8].

Benzo[*h*]quinoline (BqH) reacts very cleanly with $Mn(CO)_5Me$ to give the complex $Mn(CO)_4Bq$ (II) in virtually quantitative yield, fully characterised by analytical and spectroscopic methods. Thus, the ν(CO) region of the IR spectrum contains four bands, with an intensity pattern similar to that found for $Mn(CO)_4Azb$[2]; the mass spectrum contains a parent ion, and other ions formed by loss of carbonyl groups. These data, together with the ^1H NMR spectrum (discussed in more detail below), enable structure (II) to be assigned to this complex. Substitution of the carbonyl

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[*] For Part VI, see ref. 1. The title of this series has been changed to allow incorporation of studies on other organic systems, which afford complexes which are not properly described as "*ortho*-metallated".

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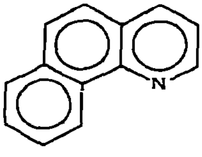
groups by phosphine ligands proceeds readily, and refluxing the complex with $PMePh_2$, for example, gives initially the tricarbonyl, $Mn(CO)_3Bq(PMePh_2)$ (III), and on continued heating, the dicarbonyl, $Mn(CO)_2Bq(PMePh_2)_2$. The latter was identified only spectroscopically, however. The analogous rhenium complex, $Re(CO)_4Bq$, (IV), was also prepared, although in this case, only a 30% yield was obtained, decomposition occurring during reaction.

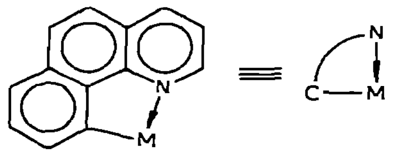
An amusing variant of the reaction described above involved metallation of the tricarbonylchromium π-complex of benzo[*h*]quinoline by heating with $Mn(CO)_5Me$ to give complex (V). In this derivative, there is no evident interaction between the two metal carbonyl groups, the IR spectrum in the ν(CO) region being virtually a superposition of those of the $Cr(CO)_3$ and $Mn(CO)_4$ derivatives of the ligand.

Reaction of the trinuclear carbonyls $M_3(CO)_{12}$ (M=Ru, Os) with benzo[*h*]quinoline rapidly gave the mononuclear complexes $M(CO)_2Bq_2$, [(VI), M=Ru; (VII), M=Os] although in the case of the osmium complex, reaction was incomplete even after 230 h reflux. The IR spectra in the carbonyl region contain the two strong bands characteristic of a *cis*-$M(CO)_2$ group, and other spectroscopic properties confirmed the presence of two metallated ligands attached to the metal atom. Although the osmium compound, which is the first example of this type of complex to be reported for this element, showed a parent ion, the highest ion in the mass spectrum of the ruthenium analogue was $[P-CO]^+$ (at *m/e* 486). In addition to complexes (VI) and (VII), the respective reaction mixtures also afforded the polynuclear hydrides $H_4M_4(CO)_{12}$ (M=Ru or Os) identified by comparison of their IR spectra with authentic samples.

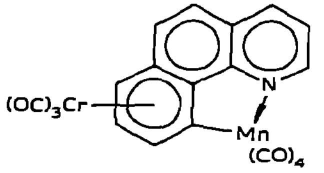
With $[Rh(CO)_2Cl]_2$, the complex $[BqRh(CO)Cl]_2$ was formed, which is assigned structure (VIII) by analogy with similar products obtained in reactions between $[Rh(CO)_2Cl]_2$ and azobenzene[4] or benzylideneaniline[5]. This structure is supported by the presence of two strong ν(CO) bands, and its behaviour with PPh_3, which afforded the known complexes $RhCl(CO)(PPh_3)_2$ and $[Bq_2RhCl]_2$[8]. The latter



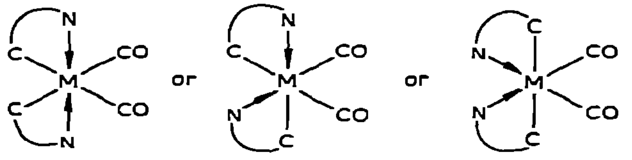
(I)



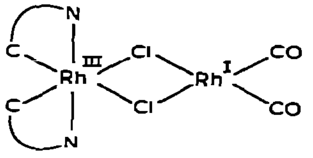
M = $Mn(CO)_4$ (II)
$Mn(CO)_3(PMePh_2)$ (III)
$Re(CO)_4$ (IV)
$Mo(CO)_2(\pi\text{-}C_5H_5)$ (IX)



(V)



M = Ru (VI) ; Os (VII)



(VIII)
[or isomers]

formed a solvate on crystallisation from mixtures containing chlorinated solvents.

In the reaction between (I) and $Mo(CO)_3(\pi\text{-}C_5H_5)Me$, only a small amount of black, air-sensitive crystals were isolated, which exhibited two strong $\nu(CO)$ bands in IR spectrum. No further characterisation was possible, but it seems likely that the product was the expected $Mo(CO)_2Bq(\pi\text{-}C_5H_5)$ (IX). Most of the molybdenum precursor was converted to $[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$ in this reaction.

Several other reactions were examined to extend the range of benzoquinoline complexes obtained, although without success. Thus the reaction between (I) and nickelocene afforded a deep red reaction mixture, which decomposed on attempted isolation of the complex. The prolonged reaction of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ with benzo-[*h*]quinoline afforded only a 20% yield of tetrameric $[Fe(CO)(\pi\text{-}C_5H_5)]_4$.

The reaction between $(BqPdCl)_2$ and thallium cyclopentadienide afforded a yellow oil, which on sublimation gave a white crystalline material. The mass spectrum contained a parent ion at *m/e* 356, and the ^1H NMR spectrum indicated substitution at the 10-position. This material is probably bi(benzo[*h*]quinolyl), and is also obtained in small amounts by pyrolysis of the manganese complex (II).

TABLE 1

CARBONYL STRETCHING FREQUENCIES

Complex		*Solvent*	*$\nu(CO)(cm^{-1})$*
(II)	$Mn(CO)_4Bq$	$CHCl_3$	2075 ms, 1994 vs, 1977 s, 1934 ms
(V)	$[BqMn(CO)_4]Cr(CO)_3$	$CHCl_3$	2089 m, 2010 s, 1992 ms, 1971 m, 1954 vs, 1888.ms
(III)	$Mn(CO)_3Bq(PMePh_2)$	C_6H_{12}	2009 s, 1932 s, 1896 s
(X)	$Mn(CO)_2Bq(PMePh_2)_2$[a]	C_6H_{12}	1913 s, 1844 s
(IV)	$Re(CO)_4Bq$	$CHCl_3$	2094 ms, 1994 vs, 1975 s, 1928 ms
(VI)	$Ru(CO)_2Bq_2$	$CHCl_3$	2020 vs, 1953 s
(VII)	$Os(CO)_2Bq_2$	$CHCl_3$	2001 s, 1928 s
(VIII)	$Bq_2RhCl_2Rh(CO)_2$	$CHCl_3$	2090 s, 2020 s
(IX)	$Mo(CO)_2Bq(\pi\text{-}C_5H_5)$[a]	$CHCl_3$	1961 s, 1917 s

[a] Only identified spectroscopically.

An important feature observed in two of the reactions described above is the isolation of the polynuclear hydrides $H_4M_4(CO)_{12}$ (M = Ru, Os) from reactions involving the corresponding trinuclear carbonyls. We have previously reported the isolation of substituted hydrides of this type during intramolecular metallation reactions of some ruthenium–phosphite complexes[1]. These observations suggest that the displaced hydrogen (from the ligand) is readily attached to the cluster, which may then disproportionate further to the mononuclear complexes and the tetranuclear hydrides:

$$M_3(CO)_{12} + BqH \rightarrow BqM_3(CO)_{12}H + BqH \rightarrow Bq_2M(CO)_2 + \tfrac{1}{2}H_4M_4(CO)_{12} + 4CO$$

Using $Mn(CO)_5Me$, we have been able to metallate a π-complexed ligand for the first time. The $Cr(CO)_3$ derivative of (I) reacted rapidly with $Mn(CO)_5Me$ to give a deep red solution, which also contained $Mn(CO)_4Bq$ (IR spectrum) and complex (V), both of which were subsequently isolated. It is of some interest that we could not effect the complementary reaction: complex (II) did not react with $Cr(CO)_6$, $Cr(CO)_3$-

$(MeCN)_3$, nor $Mo(CO)_3(\pi\text{-}C_6H_3Me_3)$, either in refluxing light petroleum (b.p. 100–120°) or di-n-butyl ether.

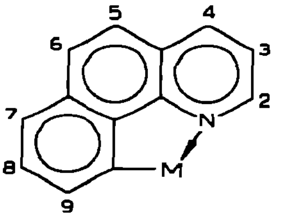
A product which may be a bi(benzo[*h*]quinolyl) was obtained from several reactions. That between $(BqPdCl)_2$ and TlC_5H_5 has been described above. Controlled pyrolysis of the manganese complex (II) in decalin also gave an almost colourless oil. These products give an apparent molecular ion at *m/e* 356, also found in the mass spectrum of complex (II) itself.

IR spectra

We have compared the "fingerprint" regions of the spectra of benzo[*h*]quinoline, and complexes (II) and (IV). The major differences (the larger are italicised) are as follows: on metallation, bands at *1510 m*, *1495 m*, 1014 w, 953 w, *803 s*, 785 w, and 705 w, cm^{-1} in the ligand spectrum do not appear in the spectra of the complexes, and new bands at 1197 mw, 1102 w, 960–980 w, 915 mw, *822 m*, and *760 s*, cm^{-1} are present in the complex spectra. Alterations in intensity are found as follows: the ligand bands at *1592 m*, 878 m, and 743 s, decrease in intensity. Examination of the spectra of the other complexes reported herein have shown that the major differences reported above are also found in these spectra, and are thus characteristic of the presence of a metallated benzoquinoline ligand in these complexes. They are similar to other changes reported in the spectra of metallated aryl phosphine and phosphite complexes, and can be related to the bands found on further substitution of an aromatic nucleus.

TABLE 2

^1H NMR DATA[a]



M	*Complex*	*Chemical shifts (τ, ppm)*								
		H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}
	H_{10}	1.03 dd	2.07 m	1.73 dd			2.20–2.52 m			0.66 dd
	H_{10}[b]	0.91	2.37	1.68			2.13			0.53
(II)	$Mn(CO)_4$	0.83 dd	1.80 dd	1.44 dd			2.2 m			
(III)	$Mn(CO)_3(PMePh_2)$[c]	1.28 dt	2.23 dt	1.76 dt			2.6 m			
(IV)	$Re(CO)_4$	0.69 dd	1.81 dd	1.37 dd			2.25 m			
(VI)	$Bq_2Ru(CO)_2$	1.52	2.86	1.72			2.2			
(V)	$[BqMn(CO)_4]Cr(CO)_3$	0.80 d	1.42 t		2.3 m		3.49 q	4.36 t	3.49 q	
	$(BqH)Cr(CO)_3$[b]	0.94	2.33	1.63	2.33	2.33	3.53	4.06	4.06	2.33
	$(Bq)_2$[a]	0.78 dd	2.16 d	1.24 dd			2.24–2.86 m,	3.28 q		

[a] In acetone-d_6. [b] Data from ref. 9. [c] In CS_2.

^1H NMR spectra (Table 2)

The spectrum of benzo[*h*]quinoline consists of three double doublets at τ 0.66 (H_{10}), 1.03 (H_2) and 1.73 (H_4), a multiplet at τ 2.07 (H_3), and a complex multiplet extending between τ 2.20–2.52 ppm (H_{5-9}). Coordination and metallation, as found in complex (IV) for example, result in changes in the region τ 2.2–2.5 ppm, now of relative intensity 4. Double irradiation experiments enable resonances occurring at τ 0.69, 1.81 and 1.37 ppm to be assigned to H_2, H_3 and H_4, respectively.

Coordination of a $Cr(CO)_3$ group to the ligand results in the usual upfield shift of the resonances associated with the protons of the coordinated ring, and these now resonate nearly 2 ppm to higher field[9]. In the metallated complex (V), the protons in the π-complexed ring are found at τ 3.49 (H_7 and H_9) and at 4.36 ppm (H_8).

*Mass Spectra**

Major ions in the spectra of complexes (II) and (IV) arise by loss of CO groups from the parent ions; subsequent breakdown involves loss of the metal atom to give $[BqH]^+$ and $[Bq]^+$, and ions derived from these species. As expected metal-containing ions are more abundant in the spectrum of the rhenium complex, in keeping with the more stable metal–carbon band. Of interest is the loss of a C_2H_3 fragment from $[C_{13}H_8NRe]^+$ to give ions at *m/e* 336/338. In the spectrum of complex (II), strong doubly-charged ions are found corresponding to $[Mn(CO)Bq]^{2+}$ and $[MnBq]^{2+}$, and also to $[BqH]^{2+}$ and $[Bq]^{2+}$. These are undoubtedly stabilised by the polycyclic nature of the ligand, and weak triply charged $[BqH]^{3+}$ and $[Bq]^{3+}$ are also present.

In the spectrum of the phosphine derivative (III) only a very weak (0.4%) parent ion is found, together with the expected $[P\text{–}3CO]^+$; intermediate ions formed by loss of one or two CO groups were not observed. Other strong ions included $[Bq_2]^+$ (probably formed by thermal decomposition), $[MnBq]^+$ (resulting from loss of the phosphine ligand), and the usual series of ions found in the spectra of compounds containing two phenyl groups attached to a phosphorus atom. The base peak was the phosphine ligand parent ion, $[PMePh_2]^+$.

The spectrum of $Os(CO)_2Bq_2$ showed a parent ion and $[P-nCO]^+$ (n=1,2), together with intense ions corresponding to $[BqH]^+$, $[Bq]^+$, and $[Bq-H]^+$. Surprisingly, no ions were found around *m/e* 356, *i.e.* the parent ion of bi(benzo[*h*]-quinolyl), although the spectrum did contain a complex series of ions formed by break up of the ligands while still attached to osmium.

In these spectra, the presence of both ions $[BqH]^+$ and $[Bq]^+$ is notable, indicating that the presence or absence of these ions is not a relaible indication of the presence of a metallated ligand. We have previously noted[5] similar results with benzylidene-aniline and -methylamine complexes. The tendency for polycyclic hydrocarbons to form $[P+1]^+$ ions by proton capture is well known.

EXPERIMENTAL

Reactions of benzo[h]quinoline

(*a*). *With $Mn(CO)_5Me$.* A mixture of benzo[*h*]quinoline (500 mg, 2.79 mmol) and $Mn(CO)_5Me$ (500 mg, 2.38 mmol) was heated for 3 h in refluxing light petroleum

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* Full mass spectral data may be obtained from the authors upon request.

(50 ml). Removal of solvent, followed by chromatography afforded yellow $Mn(CO)_4Bq$ (II) (800 mg, 90 %), eluted with 4/1 light petroleum/ether, and purified by recrystallisation from a light petroleum/ether mixture.

(*b*). *With* $Re(CO)_5Me$. A similar reaction using benzo[*h*]quinoline (200 mg, 1.12 mmol) and $Re(CO)_5Me$ (250 mg, 0.73 mmol) was stopped after 28 h. At this point, decomposition to a black material had commenced, although there was still some $Re(CO)_5Me$ present. Chromatography afforded white $Re(CO)_4Bq$ (IV) (110 mg, 30 %), eluted with 1/1 light petroleum/ether, and recrystallised from a similar solvent mixture.

(*c*). *With* $Ru_3(CO)_{12}$. Large yellow-green crystals of $Ru(CO)_2Bq_2$ (VI) suddenly separated from the refluxing orange solution of $Ru_3(CO)_{12}$ (500 mg, 0.78 mmol) and benzo[*h*]quinoline (2.0 g, 11.1 mmol) after 2 h. These were filtered from the hot solution, washed with light petroleum, and recrystallised from an ether/dichloromethane mixture to give the pure complex (445 mg, 27 %). On cooling, the mother liquor afforded $H_4Ru_4(CO)_{12}$ (40 mg, 7 %), and several other yellow carbonyl-containing products, present in minor amount, were only partially separated on chromatography.

TABLE 3

ANALYTICAL AND M.P. DATA FOR METALLATED BENZOQUINOLINE COMPLEXES

Complex		*M.p.* (°*C*)	*Analysis found (calcd.) (%)*			*Mol. wt. Found*[a] *(calcd.)*
			C	*H*	*N*	
(II)	$BqMn(CO)_4$	158–159 (dec.)	59.5 (59.1)	2.6 (2.3)	4.1 (4.05)	345 (345)
(III)	$BqMn(CO)_3(PMePh_2)$	160–162	67.4 (67.3)	4.3 (4.05)	2.8 (2.7)	517 (517)
(IV)	$BqRe(CO)_4$	145–148 (dec.)	43.2 (42.8)	1.75 (1.7)	2.9 (2.95)	476 (476)
(V)	$[BqMn(CO)_4]Cr(CO)_3$	158–160 (dec.)	49.9 (50.0)	1.7 (1.65)	2.8 (2.9)	
(VI)	$Bq_2Ru(CO)_2$	257–261 (dec.)	65.5 (65.5)	3.2 (3.1)	5.2 (5.45)	486[b] (514)
(VII)	$Bq_2Os(CO)_2$	315–318 (dec.)	55.9 (55.8)	2.7 (2.65)	4.65 (4.65)	602 (602)
(VIII)	$[BqRh(CO)Cl]_2$	268–270 (dec.)	49.1 (48.9)	2.45 (2.3)	4.75 (4.05)	

[a] Mass spectrometry. [b] $[P-CO]^+$.

(*d*). *With* $Os_3(CO)_{12}$. A similar reaction with $Os_3(CO)_{12}$ (250 mg, 0.28 mmol) and benzo[*h*]quinoline (600 mg, 3.36 mmol) was not complete after 226 h. After filtration, the reaction mixture deposited large golden orange crystals of $Os(CO)_2Bq_2$ (VII) (79 mg, 33 %); the mother liquor afforded $H_4Os_4(CO)_{12}$ (17 mg, 6 %) on further evaporation.

(*e*). *With* $[Rh(CO)_2Cl]_2$. After 2 h, a refluxing light petroleum solution of $[Rh(CO)_2Cl]_2$ (400 mg, 1.03 mmol) and benzo[*h*]quinoline (400 mg, 2.24 mmol) deposited a yellow-green precipitate. Recrystallisation from ether–acetone mixtures gave pure $Bq_2RhCl_2Rh(CO)_2$ (VIII) (200 mg, 28 %) as bright yellow plates.

Reaction between $Cr(CO)_3(\pi\text{-}BqH)$ and $Mn(CO)_5Me$

The chromium complex (250 mg, 0.79 mmol) and $Mn(CO)_5Me$ (350 mg, 1.66 mmol) were heated in toluene for 50 min. The original yellow-orange solution rapidly turned deep red, and exhibited the bands of $Mn(CO)_4Bq$. Chromatography afforded the latter complex (eluted with benzene), and deep red π-$[BqMn(CO)_4]Cr(CO)_3$ (V) (eluted with 1/1 benzene/ether). Recrystallisation of the latter (ether/dichloromethane) gave scarlet crystals of the product (160 mg, 35 %).

Reaction between $Mn(CO)_4Bq$ and $PMePh_2$

A 10 min reflux of a mixture of complex (II) and $PMePh_2$ in light petroleum, followed by evaporation, and recrystallisation (light petroleum/ether) afforded orange crystals of $Mn(CO)_3Bq(PMePh_2)$ (III). If excess phosphine is present, the three-band ν(CO) spectrum of complex (III) rapidly changes to a two-band spectrum [ν(CO), 1913 s, 1844 s cm^{-1}], probably due to the dicarbonyl, $Mn(CO)_2Bq(PMePh_2)_2$ (X).

Bi(benzo[h]quinolyl)

Refluxing a mixture of $(BqPdCl)_2$ and TlC_5H_5 in tetrahydrofuran for 3 h, followed by removal of solvent and chromatography, afforded a pale yellow oil. Sublimation (50°/0.1 mmHg) gave a small amount of white solid, showing a parent ion at *m/e* 356.

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REFERENCES

1 M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, (1973) 1667.
2 M. I. Bruce, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc. A*, (1970) 3204.
3 M. I. Bruce, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc. A*, (1971) 2820.
4 M. I. Bruce, M. Z. Iqbal and F. G. A. Stone, *J. Organometal. Chem.*, 40 (1972) 393.
5 R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc., Dalton. Trans.*, (1972) 1787.
6 M. Nonayama, K. Suzuki and K. Yamasaki, *Proc. Jap. Acad.*, 45 (1969) 605.
7 M. Nonoyama and K. Yamasaki, *Nippon Kagaku Zasshi*, 91 (1970) 1058.
8 M. Nonoyama and K. Yamasaki, *Inorg. Nuclear Chem. Lett.*, 7 (1971) 943.
9 E. O. Fischer, H. A. Goodwin, C. G. Kreiter, H. D. Simmons, K. Sonogashira and S. B. Wild, *J. Organometal. Chem.*, 14 (1968) 359.