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COORDINATION SITE OF $Cr(CO)_3$ IN POLYAROMATIC COMPOUNDS

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Summary

The coordination site of $Cr(CO)_3$ in diarylimines derived from aromatic aldehydes or ketones and aromatic amines has been studied. The results show that electron density is not a unique determining factor. It is suggested that consideration of the three ligand π levels (energy, symmetry, representativity) can account for the results.

Introduction

There has been much interest in the nature of the bonding between the $Cr(CO)_3$ moiety and benzenoid rings but question is still open about the various relevant factors and the extent to which they operate. It should be possible to get insight into that problem by studying effects of substituents on complexation.

It is known that the energy of the metal—ligand π-bond is larger for C_6Me_6 (137 kcal/mol) than for C_6H_6 (120 kcal/mol) [1]. If one accepts the Dewar—Chatt MO description of this bonding, this fact is in agreement with the known π-donor ability of methyl groups. For substituted naphthalene it has been observed that the position of the methyl groups on the ring affects the site of complexation. On the other hand it has been shown that complexation can be disfavoured by electron-releasing groups as well as by electron-withdrawing groups [2], and so factors other than electron-density appear to determine the position of attachment of the $Cr(CO)_3$ moiety.

Attempts to compare electron-withdrawing and -releasing groups and to study the effects of methyl substituents on complexation are described below.

Results

Imines of type I have been converted into complexes as in Scheme 1. The results are listed in Tables 1 and 2.

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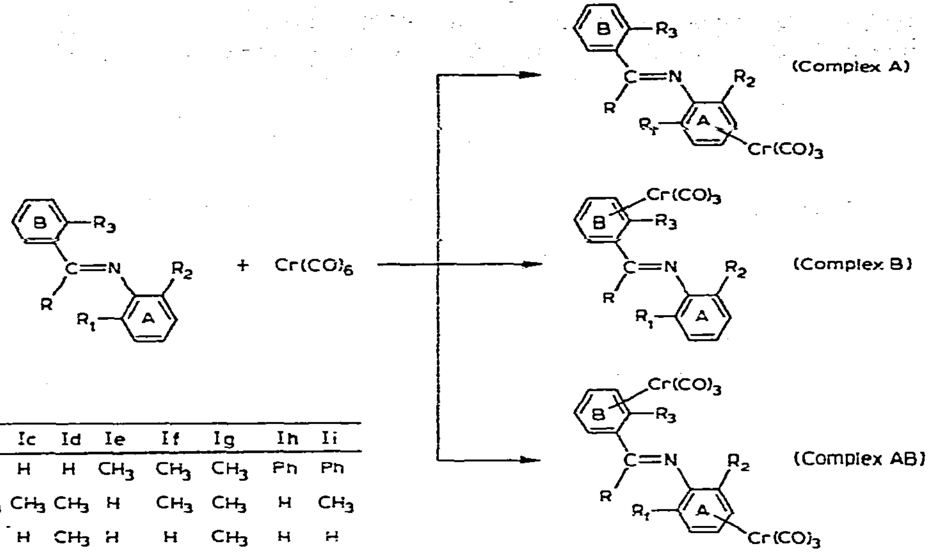
SCHEME 1

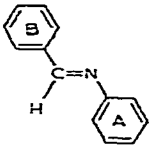
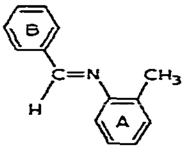
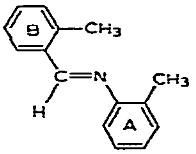
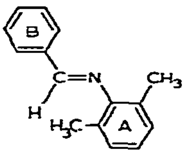


		Ia	Ib	Ic	Id	Ie	If	Ig	Ih	Ii
R	=	H	H	H	H	CH_3	CH_3	CH_3	Ph	Ph
R^1	=	H	CH_3	CH_3	CH_3	H	CH_3	CH_3	H	CH_3
R^2	=	H	H	H	CH_3	H	H	CH_3	H	H
R^3	=	H	H	CH_3	H	H	H	H	H	H

Conformations and electronic interactions in these aromatic imines have been much studied [3,4] and it is accepted that ring A (with $n\pi$ interaction) is electron rich, whereas ring B (with $\pi\pi$ interaction is electron deficient [5,6]. Thus these aromatic imines are good models for comparing effects of electron-withdrawing and -releasing groups. As we are dealing with unfused multiring systems, formation of binuclear complexes (Complex AB) is not exceptional [7], but these binuclear complexes may be formed via either of the mononuclear complexes (Complex A or Complex B) or via both depending on the relative magnitudes of the constants k_3 and k_4 in Scheme 2.

TABLE 1

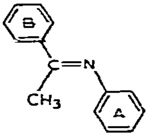
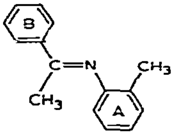
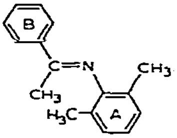
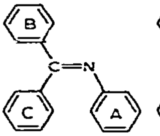
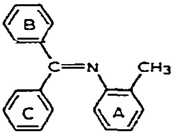
COMPLEXATION SITE IN ALDIMINES

	 (Ia)	 (Ib)	 (Ic)	 (Id)
Method [a]	a	b	b	a
Yield of products [b]	28	58	62	45
Unreacted imine [b]	70			55
Yield of Complex A [c]	0	81	77	100
Yield of Complex B [c]	0	10	16	0
Yield of Complex AB [c]	100	9	7	0
Preferred site	?	Ring A	Ring A	Ring A

[a] See Experimental. [b] Yields (%) are calculated with respect to the starting imine. [c] See Scheme 1.

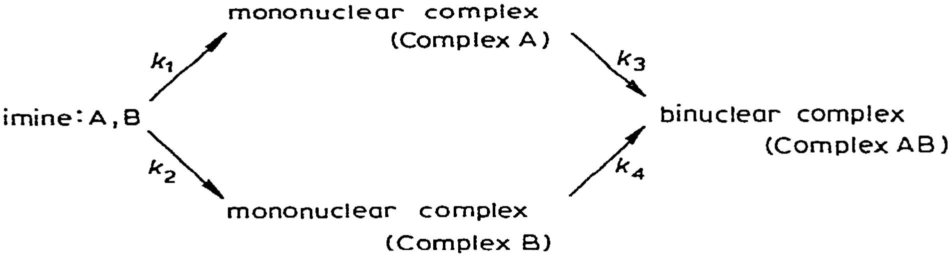
TABLE 2

COMPLEXATION SITE IN KETIMINES

	 (Ie)	 (If)	 (Ig)	 (Ih)	 (Ii)
Method[a]	a	a	b	a	b
Yields of products[b]	68	43	83	59	75
Unreacted imine[b]	32	57		41	7
Yield of Complex A[c]	8	38	100	43	62
Yield of Complex B[c]	81	0	0	57	15
Yield of Complex AB[c]	11	62	0	0	22
Preferred site	Ring B	Ring A[d]	Ring A	Ring B	Ring A

[a] See experimental. [b] Yield (%) are calculated with respect to the starting imine. [c] See Scheme 1. [d] Because Complex AB comes from Complex A (see Table 3).

SCHEME 2



Since the proportions of Complex AB formed are important for establishing the preferred site of complexation in the case of imines Ia (Table 1) and If (Table 2), we have examined the variation with time of the amounts of the several complexes present, the results are shown in Table 3. During complexation of benzalaniline, even at the very beginning of the reaction no mononuclear complexes are detected, NMR spectroscopy shows that Complex AB [14] is the only complexed species formed. As the reaction was conducted with equimolecular quantities of ligand and chromium hexacarbonyl, this behaviour requires that the constants k_3 and/or k_4 are much larger than k_1 and/or k_2. This unexpected result requires further investigation.

For complexation of imines If we note that at the beginning of the reaction (the first 20%) Complex A is the only complexed species formed, then Complex AB appears and becomes the major product. This result indicates that Complex AB may be formed from Complex A, and not from Complex B, which is not detected by ^{1}H NMR.

While no conclusion can be drawn from the behaviour of imine Ia we note that the presence of one methyl group on the azomethine carbon (Ie) or on ring A (Ib) leads to more expected behaviour, that is formation of mixtures of Com-

TABLE 3

COMPLEXATION OF IMINES Ia AND If AS A FUNCTION OF TIME [b]

Starting complex	Products [c]	Time of sampling [a]			
		2	4	6	8
Ia	Imine (%)	100	86	84	80
	Complex A or B(%)	0	0	0	0
	Complex AB(%)	0	14	16	20
		Time of sampling [a]			
		0.45	2.45	4.15	8
If	Imine (%)	100	81	61	35
	Complex A(%)	0	13	15	19
	Complex B(%)	0	0	0	0
	Complex AB(%)	0	6	23	46

[a] The time is given in hours after the beginning of the reaction. [b] Conditions: 5×10^{-3} mol of ligand + 5×10^{-3} mol of $Cr(CO)_6$ in 40 ml diglyme/heptane (1/1). [c] Determined by NMR titration.

plex A, Complex B and Complex AB. It appears that in the absence of methyl substituents on ring A, the electron-deficient ring B is preferred as the site of complexation (Ie and Ih), but introduction of one or two methyl groups on ring A restores this ring as site of complexation (Ib, Id, If, Ig and Ii). Introduction of a methyl group on ring B does not much change the results (compare Ic to Ib, Table 1), but the variation is in the expected way. It is noteworthy that introduction of a methyl group on ring B perturbs the conformation of the compound more than an extra methyl group on ring A, which is already twisted, and variations in the electronic factors are accompanied by variations in the steric factors,

Conclusion

These results confirm that electron-density is not in itself a determining factor, since ring B is preferred in cases Ie and Ih. They confirm also the influence of a methyl group, one *ortho*-methyl group sufficing to restore ring A as the complexation site.

Very little is known about the mechanism of these reactions, but it seems likely that a complicated series of equilibria is involved [8]. Thus, rigorously, final products rather than intermediates must be considered and at first sight, it seems difficult to detect correlations between the properties of the ligands and the types of complexes formed. However, it is known [9] that the metal—ligand bond in benchrotrene comes essentially from interactions between its $4p_\pi$, $3d_\pi$ metal orbitals and the $2p_\pi$ ligand orbitals; such interactions lead to stabilisation (Fig. 1) [10], and the closer the initial levels, the larger the stabilisation. So, it should be possible to account for the results by considering the three ligand π orbitals representative of a ring *, which, in our opinion must fulfil the following conditions

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* This is correct in so far as orbital interactions are indicative of the stability. Strictly one should also consider other factors, such as steric interactions. However, since the ligands are planar and methyl groups are relatively small, steric factors can be assumed to be constant in the series.

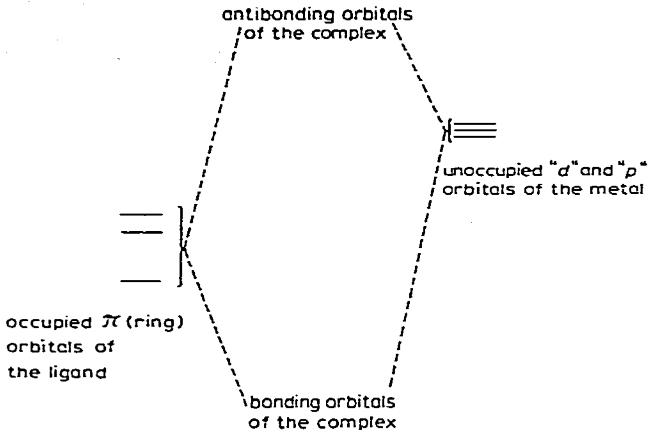


Fig. 1. Qualitative interaction diagram for the occupied π-ligand orbitals and the unoccupied metal orbitals.

to give good bonding and thus stable compounds: (a) energy (the ligands' energy level must be as close as possible to those of the vacant metal orbitals), (b) representativity (the larger coefficients must be in the ring carbon atoms); and (c) symmetry (this must correctly match the metal orbitals).

Thus it is possible to understand why the electron-rich ring A is not always preferred. We assume that in such aromatic imines the fragment (ring A + nitrogen lone pair) is independent of the rest of the molecule (ring B + C=N double bond), and then build up (qualitatively) the energy level diagrams as usually [11—13] (Figs. 2 and 3), it is obvious that depending on the position of the π(C=N) level with respect to the π(ring) levels in Fig. 2, the π orbitals representative of ring B

(continued on p. 191)

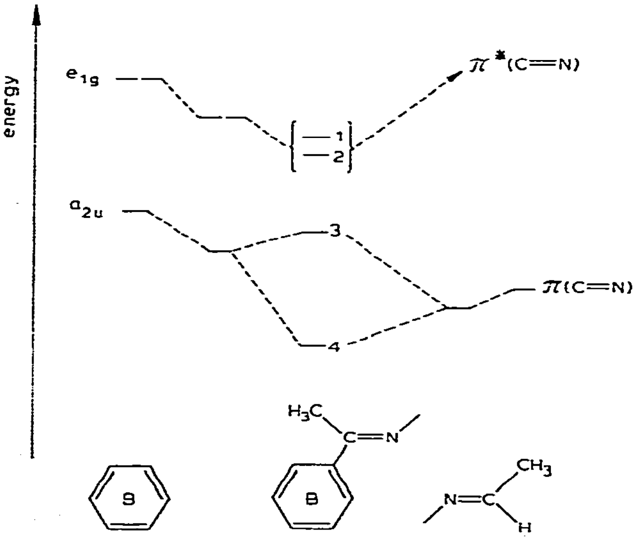
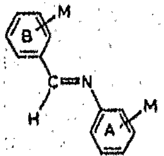
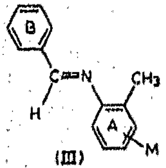
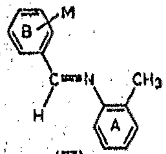
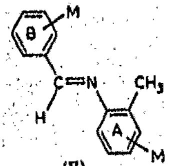
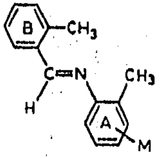
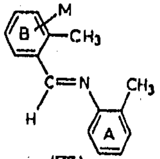
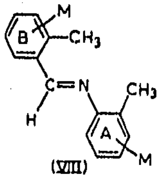
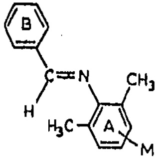


Fig. 2. Qualitative interaction diagram; case where orbitals 1, 2 and 3 are representative of ring B.

TABLE 4

CARACTERISTICS OF COMPLEXES A, COMPLEXES B AND COMPLEXES AB OBTAINED FROM IMINES Ia TO Id

Complexes	^{1}H NMR (δ, ppm)				IR (cm^{-1})		M.p. (°C) (colour)	Elemental analysis (found (calcd.) (%))		
	H_a	ring A	ring B	CH_3 (A) [CH_3 (B)]	ν(C=N)	ν(C≡O)		C	H	N
 (II)	7.85 s	5,40 m, 5H	5,9 m, 2H 5.45 m, 3H		1630 w	1975 (sh) 1970 s 1900 s	dec. (red)			
 (III)	8,85 s	5,25 m, 4H	7.85 m, 2H 7.45 m, 3H	2.1 s	1630 w	1960 s 1885 s	91–92 (red)	61,56 (61,63)	4,13 (3,93)	4,37 (4,23)
 (IV)	7.9	7.15 m, 4H	5.95 m 2H 5.4, 3H	2,3 s	a					
 (V)	7.92 s	5,35 m, 4H	5.95 m, 2H 5.35 m, 3H	2,15 s	1625 w	1985 (sh) 1965 s 1895 s	sublimes (red)			

 (VI)	8.66 s	5.25 m, 4H	7.85 m, 1H 7.25 m, 3H	2.15 s [2.6 s]	1630 w	1960 s 1890 s	*b*			
 (VII)	8.15 s	6.9 7.2 m, 4H	6.38 m, 4H	2.35 s [2.45 s]	1630 w	1960 s 1890 s	*b*			
 (VIII)	8.32 s	6.25 m, 1H 5.55 m, 3H	5.25 m, 4H	2.15 s [2.45 s]	1620 w	1975 (sh) 1965 s 1895 s	152—153 (red)			
 (IX)	8.30 s	7.90 m, 2H 7.55 m, 3H	5.45 m, 1H 5.05 d, 2H	2.0 s	1640 w	1960 s 1880 s	91—94 (orange)	62.70 (62.61)	4.35 (4.35)	4.21 (4.06)

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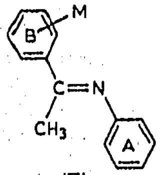
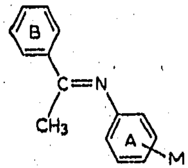
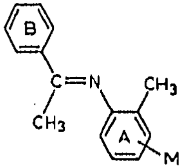
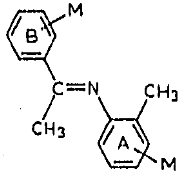
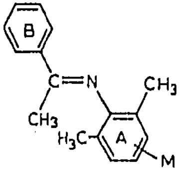
[a] Not isolated but detected in a mixture of complexes III and IV. [b] Mixture of VI and VII.

TABLE 5

CARACTERISTICS OF COMPLEXES A, COMPLEXES B AND COMPLEXES AB OBTAINED FROM IMINES Ic TO Ig

Complexes	^{1}H NMR (δ, ppm)				IR (cm^{-1})		M.p. (°C) (colour)	Elemental analysis (found (calcd.) (%)		
	CH_3	ring A	ring B	CH_3 (A) [CH_3 (B)]	ν(C=N)	ν(C≡O)		C	H	N
 (X)	2.0 s	7.27 m, 3H 6.73 m, 2H	6.05 m, 2H 5.40 m, 3H		1640 w	1975 s 1900 s	115–116 (orange)			
 (XI)	2,35 s	5,05 m 5,50 m 4H	7,95 m, 2H 7,45 m, 3H	2,05 s	1635 w	1970 s 1890 s	a			

 (XII)	2.25 s	5.05 m 5.35 m 4H	7.90 m, 2H 7.46 m, 3H	2.05 s	1640 w	1965 s 1890 s	88–90 (yellow)	62.46 (62.61)	4.40 (4.35)	4.25 (4.06)
 (XIII)	2.05 s or 2.12 s	5.0 m 5.40 m 4H	6.08 m, 2H 5.4 m, 3H	2.12 s or 2.05 s	1640 w	1965 s 1975 (sh) 1895 s	134–140 (orange)	52.40 (52.39)	3.16 (3.12)	3.07 (2.91)
 (XIV)	2.0 s [b]	5.22 m, 3H	7.92 m, 2H 7.42 m, 3H	2.13 s	1635 w	1965 s 1890 s	126–129 (orange)			

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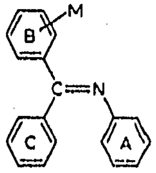
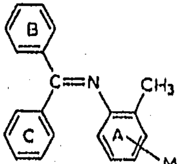
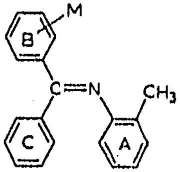
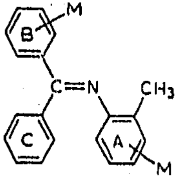
[a] XI has not been obtained pure, but as a mixture with the corresponding binuclear complex. [b] The intensities of the singlets permit the assignement.

TABLE 6

CARACTERISTICS OF COMPLEXES A, B AND AB OBTAINED FROM IMINES Ih AND Ii.

Complexes	^{1}H NMR (δ, ppm)				IR (cm^{-1}		M.p. (°C)	Elemental analysis (found (calcd.) (%))		
	ring C	ring A	ring B	CH_3 (A)	ν(C=N)	ν(C≡O)	(colour)	C	H	N
 (XV)	7.25 (br) 5H	7.1 m, 3H 6.75 m, 2H	5.90 m, 2H 5.40 m, 3H		1620 w	1980 s 1900 s	140—142 (orange)			
 (XVI)	7.4 (br), 5H	5.35 d, 1H 5.05 d, 1H 4.75 t, 2H	7.7 m, 2H 7.25 m, 3H	2.15 s	1610 w	1960 s 1885 s	164—166 (orange)	67.75 (67.81)	4.12 (4.18)	3.34 (3.44)
 (XVII)	7.1 (br), 5H	6.80 m, 3H 6.35 m, 1H	5.90 m, 2H 5.3 m, 3H	2.2 s	^{a}					
 (XVIII)	7.3 m, 5H	5.2 m 4.9 m 4H	6.0 m 5.2 m 5H	2.2 s	1610 w	1965 s 1975 (sh) 1895 s	165—166 (red)	57.41 (57.46)	3.46 (3.13)	2.75 (2.58)

[a] Detected in a mixture of XVI and XVII.

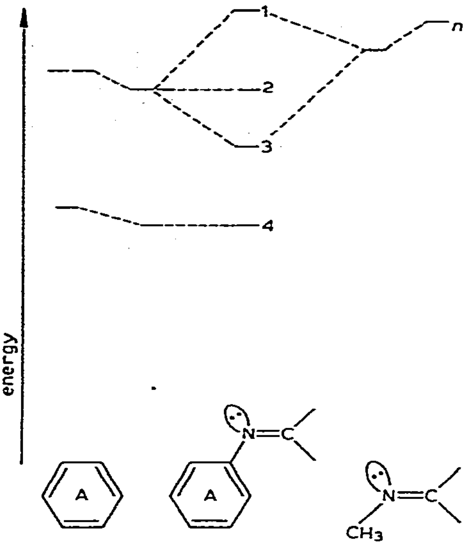


Fig. 3. Qualitative interaction diagram; case where orbitals 2,3 and 4 are representative of the ring A.

will be 1, 2, 3 or 1, 2, 4. Similarly, depending on the level of the *n*-lone pair (Scheme 5), π orbital 1 is (or is not) representative of ring A.

Photoelectron spectroscopy may throw some light onto this problem, and studies are in progress in collaboration with Dr. G. Pfister-Guilouzo.

Experimental

Identification of the various complexes was by IR and ^{1}H NMR spectroscopy. An average shielding of 1.8 to 2 ppm is observed for the chemical shift of protons belonging to a complexed ring compared with the same protons in the starting imine; this allows an unambigous assignment of the site of complexation. The two carbonyl stretching modes characteristic of $Cr(CO)_3$ groups are easily detected, and they fall in the correct region.

Very good elemental analyses were obtained for chromatographed samples which were shown to be pure on the basis of NMR spectroscopy, and so NMR can be safely used for identification. Titration was carried out subsequently.

Spectral and physical properties are shown in Tables 4, 5 and 6. For convenience the spectral properties of starting imines are also given in Table 7. The IR spectra in $CHCl_3$ were recorded on a Perkin—Elmer 257 spectrometer and ^{1}H NMR spectra on a Perkin—Elmer R-24A instrument (in $CDCl_3$ with TMS as internal reference).

Preparation of the complexes

Equimolar quantities of chromium hexacarbonyl and the ligand are refluxed at 150—160°C under argon in a 1/1 mixture of diglyme/heptane in a Strohmeier apparatus. The concentration of each reactant is about 0.1 *M*. Heating is maintained until $Cr(CO)_6$ no longer condenses in the cool part of the apparatus, and the mixture is then cooled to room temperature under argon, and the solvents

TABLE 7

^{1}H NMR AND IR DATA FOR THE STARTING IMINES Ia TO Ii

Imines	^{1}H NMR (δ, ppm)				IR (cm^{-1}) ν(C=N)
	H—C=N or CH_3C=N or ring C	ring A	ring B	CH_3 (A) [CH_3 (B)]	
Ia	8.30 s	7.17 m, 5H	7.83 m, 2H 7.35 m, 3H		1630 m
Ib	8.33 s	7.12 m, 4H	7.85 m, 2H 7.42 m, 3H	2.35 s	1625 m
Ic	8.63 s	7.15 m, 4H	8.06 m, 1H 7.30 m, 3H	2.35 s [2.60 s]	1625 m
Id	8.20 s	7.02 m, 3H	7.92 m, 2H 7.50 m, 3H	2.15 s	1640 m
Ie	2.2 s	7.25 m, 3H 6.8 m, 2H	8.1 m, 2H 7.45 m, 3H		1640 m
If	2.15 s	7.1 m, 3H 6.62 m, 2H	8.0 m, 2H 7.45 m, 3H	2.1 s	1635 m
Ig	2.05 s	6.9 m, 3H	8.0 m, 2H 7.4 m, 3H	1.98 s	1640 m
Ih	7.2 m, 5H	7.05 m, 3H 6.75 m, 2H	7.75 m, 2H 7.40 m, 3H		1615 m
Ii	7.15 m, 5H	6.95 m, 3H 6.48 m, 1H	7.78 m, 2H 7.48 m, 3H	2.18 s	1620 m

are removed in vacuum (argon, 1 mmHg, at 80° C).

Method a, for spectroscopic examination and identification. The residue is cooled to room temperature, anhydrous ether is added, the solution is rapidly filtered to remove traces of chromium oxide, and the ether is removed under vacuum. The residue is weighed and studied by NMR and IR spectroscopy.

Method b, to get pure samples for analysis and titration. The residue is cooled to room temperature under argon and chromatographed on Silicagel 60 with a mixture of ether and petroleum ether. The coloured fractions, which contain the various complexes, are evaporated to dryness, weighed and studied (IR, NMR and elemental analysis).

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