Amidino-complexes of Rhenium. Bidentate NN'- and *ortho*-Metallated Derivatives

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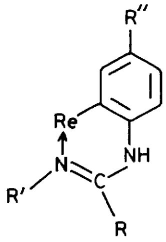
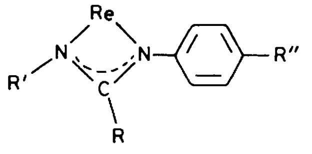
$[Re(CO)_4\{R'NC(R)NR'\}]$ complexes (I; R = Me or Ph; R' = Ph or C_6H_4Me-*p*), containing delocalised bidentate NN'-chelated amidino-groups, have been prepared by reactions of (*i*) $[\{Re(CO)_4X\}_2]$ (X = Cl or Br) with $R'N(Li)C(R)NR'$, (*ii*) $[Re(CO)_4\{R'NC(R)NHR'\}X]$ with $LiBu^n$, (*iii*) $[Re_2(CO)_{10}]$ with $R'NHC(R)NR'$, and (*iv*) by decarbonylation of $[Re(CO)_4\{CON(R')C(R)NR'\}]$ complexes. Triphenylphosphine displaces CO from (I) to form $[Re(CO)_3(PPh_3)\{R'NC(R)NR'\}]$ (II), which are more conveniently prepared by the reactions of $[Re(CO)_4L'Br]$ (L' = PPh_3 or $AsPh_3$) with amidines in refluxing toluene. This reaction stops at the intermediate compound $[Re(CO)_3(PPh_3)\{R'NC(R)N(Me)R'\}Br]$ when a NNN'-trisubstituted amidine is used. Related complexes $[Re(CO)_3(PPh_3)\{R'NC(R)NHR'\}Br]$ are formed when (II) are treated with hydrobromic acid. $[Re(CO)_5X]$ (X = Cl or Br) and $[\{Re(CO)_4Br\}_2]$ react with amidines to form *o*-metallated $[Re(CO)_3\{R'NC(R)NHC_6H_3R''\text{-}p\}\{R'NC(R)NHR'\}]$ (R = H, R' = Ph; R'' = H; R = Me or Ph, R' = C_6H_4Me-*p*, R'' = Me; R = Me or Ph, R' = Ph, R'' = H) complexes which contain a six-membered *o*-metallated ring. Benzamidines (R = Ph) produce in addition an isomeric complex in which *o*-metallation of the R substituent occurs to give complexes having five-membered *o*-metallated rings. Intermediate $[Re(CO)_3\{R'NC(R)NHR'\}_2X]$ complexes were isolated for R' = C_6H_4Me-*p*, R = Me, and X = Cl or Br. A 1,3-proton-shift mechanism for the *o*-metallation reaction is eliminated by the formation of the complex $[Re(CO)_3\{R'NC(Me)N(Me)C_6H_3Me\text{-}p\}\{R'NC(Me)N(Me)R'\}]$ (R' = C_6H_4Me-*p*) from $R'N(Me)C(Me)NR'$. Reaction schemes are suggested for the course of the reactions, and structures for the new complexes are proposed on the basis of spectroscopic data.

The amidino-group although known to act as a monodentate one-electron ligand to transition metals,[1] bonds in the majority of its complexes as a NN'-chelate [2–9] or NN'-bridging [10–17] three-electron donor. Symmetrical chelate amidino-groups (I) have been characterised in a variety of different complexes including $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{PhNC(Me)NPh\}]$ [5] and $[Pd\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}_2]$,[5] though unsymmetrical chelate groups (II), as found in $[TaMeCl_2\{Pr^iNC(Me)NPr^i\}_2]$,[11] are less well documented. Spectroscopic data lead to the assignment of symmetrical NN'-bonded amidino-groups to a range of molybdenum, tungsten,[3,4,7–9] manganese,[2,6] rhenium,[6] platinum, and palladium [18] complexes and related triazine complexes. NN'-Bridging amidino-groups (III) and (IV) occur in many complexes such as $[Mo_2\{PhNC(Ph)NPh\}_4]$,[10] $[Re_2\{PhNC(Ph)NPh\}_2Cl_4]$,[19] and $[Cu_2\{PhNC(Ph)NPh\}_4]$,[20] as well as in dinuclear complexes, *e.g.* $[\{Me_2NCH_2(C_6H_3)CH_2NMe_2\}Pt\{N(C_6H_4Me\text{-}p)CH\text{-}NC_6H_4Me\text{-}p\}AgBr]$,[21] having an amidino-group bridging between two different metals, structure (IV). Diarylamidines

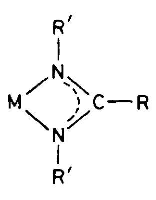


o-metallated

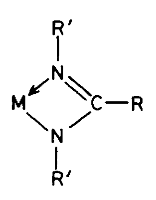


NN'-chelated

ML	R	R'	R''
L^1	Me	Ph	H
L^2	Me	C_6H_4Me-*p*	Me
L^3	Ph	Ph	H
L^4	Ph	C_6H_4Me-*p*	Me
L^5	H	Ph	H



I



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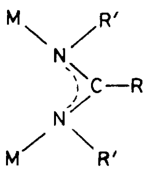

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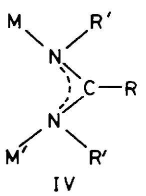
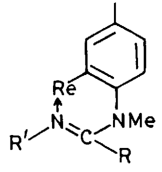


IV



ML^m	R	R'	R''
L^{2m}	Me	C_6H_4Me-*p*	Me

Table 1. Analytical data, melting points, and yields for NN′-bidentate $[Re(CO)_4L]$ and $[Re(CO)_3L'L]$ ($L' = PPh_3$ or $AsPh_3$) complexes

Complex	M.p. (°C)	Analysis (%) * C	H	N	Yield (%)
$[Re(CO)_4\{PhNC(Ph)NPh\}]$	148	48.5 (48.5)	2.55 (2.65)	4.85 (4.9)	21
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}]$	114	49.9 (50.2)	3.25 (3.2)	4.65 (4.7)	20
$[Re(CO)_4\{PhNC(Me)NPh\}]$	146	42.6 (42.6)	2.4 (2.55)	5.5 (5.5)	20
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	140	45.7 (44.8)	3.25 (3.2)	5.3 (5.25)	18
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	196 (decomp.)	57.8 (57.8)	4.2 (4.15)	3.65 (3.65)	31
$[Re(CO)_3(PPh_3)\{PhNC(Me)NPh\}]$	196 (decomp.)	56.7 (56.7)	3.8 (3.75)	3.8 (3.75)	45
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}]$	190 (decomp.)	61.6 (60.7)	4.2 (4.1)	3.35 (3.35)	38
$[Re(CO)_3(PPh_3)\{PhNC(Ph)NPh\}]$	192 (decomp.)	59.9 (59.8)	3.85 (3.75)	3.65 (3.5)	42
$[Re(CO)_3(AsPh_3)\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	185 (decomp.)	54.7 (54.6)	4.0 (3.95)	3.5 (3.45)	13

* Calculated values are in parentheses.

Table 2. I.r. carbonyl stretching frequencies for NN′-bidentate $[Re(CO)_4L]$ and $[Re(CO)_3L'L]$ ($L' = PPh_3$ or $AsPh_3$) complexes

Complex	Medium	$\tilde{\nu}(CO)/cm^{-1}$
$[Re(CO)_4\{PhNC(Ph)NPh\}]$	CH_2Cl_2	2 117w, 2 005vs, 1 981vs, 1 947vs
	Nujol	2 110w, 1 995vs, 1 973vs, 1 918vs
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}]$	CH_2Cl_2	2 103w, 2 002vs, 1 947vs, 1 930vs
	Nujol	2 106w, 2 000vs, 1 978vs, 1 911vs
$[Re(CO)_4\{PhNC(Me)NPh\}]$	CH_2Cl_2	2 114w, 1 998vs, 1 976vs, 1 933vs
	Nujol	2 110w, 1 992vs, 1 978vs, 1 940vs
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	CH_2Cl_2	2 110w, 2 000vs, 1 976vs, 1 932vs
	Nujol	2 000w, 1 992vs, 1 977vs, 1 938vs
$[Re(CO)_3(PPh_3)\{PhNC(Me)NPh\}]$	CH_2Cl_2	2 019vs, 1 912vs, 1 888vs
	Nujol	2 016vs, 1 909vs, 1 885vs
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	CH_2Cl_2	2 018vs, 1 914vs, 1 882vs
	Nujol	2 012vs, 1 907vs, 1 883vs
$[Re(CO)_3(PPh_3)\{PhNC(Ph)NPh\}]$	CH_2Cl_2	2 020vs, 1 917vs, 1 888vs
	Nujol	2 022vs, 1 911vs, 1 894vs
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}]$	CH_2Cl_2	2 021vs, 1 917vs, 1 890vs
	Nujol	2 019vs, 1 918vs, 1 907vs 1 899vs, 1 887vs

act also as three-electron donor groups as a result of *o*-metallation of an aryl substituent. Six-membered metallocycles (V) are usually formed, as illustrated by $[Pd(\eta^5\text{-}C_5H_5)\{p\text{-}MeC_6H_4NC(Me)NHC_6H_3Me\text{-}p\}]$.[5,18]

As an extension to our work on amidino-complexes of manganese,[2] we have investigated the reactions of amidines with various rhenium carbonyl complexes. Derivatives of the type $[Re(CO)_4\{CON(R')C(R)NR'\}]$ and $[Re(CO)_4\{R'NC(R)\text{-}NHR'\}X]$ (X = Cl or Br) [22] will be reported elsewhere, and the formation and characterisation of a range of NN′-chelated and *o*-metallated amidine complexes (see below) are the subjects of this paper.* The NN′-chelate complexes are analogous to the manganese derivatives,[2] and to the formamidine complexes $[Re(CO)_4\{R'NCHNR'\}]$ reported by Abel and Skittrall.[6] Distinct differences between manganese and rhenium occur with respect to *o*-metallation. Such reactions have not been reported for manganese though it is found here to be a common reaction for rhenium. The only other *o*-metallation reactions of amidines reported previously occur for palladium and platinum complexes,[18,23] and mercury.[16]

Results and Discussion

A. $[Re(CO)_4L]$ (HL = *Amidine*) *Complexes.*—Complexes of the type $[Re(CO)_4L]$ were prepared by the reaction of $[\{Re(CO)_4X\}_2]$ (X = Cl or Br) with lithiodiaryl-acetamidines and -benzamidines in monoglyme (1,2-dimethoxyethane) solution. They were bright yellow air-stable solids (m.p. *ca.* 140 °C) which formed yellow air-stable solutions in organic solvents. The complexes were identical with the decarbonylation products of $[Re(CO)_4(COL)]$ (ref. 22), and i.r. spectroscopic monitoring of the reactions indicated that although the yield of recovered material was only *ca.* 20%, the complexes were formed in solution in very good yield. Two additional products, $[Re(CO)_4(HL)X]$ and an *o*-metallated complex $[Re(CO)_4L(HL)]$ were formed, and separation proved difficult because of similar solubilities. Pure material was obtained using fractional crystallisation methods and the seeding

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* Throughout this paper a bridge bond through L indicates *ortho*-metallation.

Table 3. I.r. absorptions associated with the delocalised NN′-chelate amidino-groups

Complex	I.r. absorptions (cm^{-1})
$[Re(CO)_4\{PhNC(Me)NPh\}]$	1 590m, 1 575w, 1 495s, 1 475s 1 412s, 1 364m, 1 312w, 1 297w
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	1 606w, 1 570vw, 1 502s, 1 490s 1 475s, 1 412s, 1 368m, 1 315w, 1 293w
$[Re(CO)_4\{PhNC(Ph)NPh\}]$	1 590m, 1 570w, 1 525w, 1 490s 1 475 (sh), 1 425s, 1 365w, 1 273w
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}]$	1 606w, 1 569w, 1 502s, 1 432s 1 365w, 1 298w, 1 272w
$[Re(CO)_3(PPh_3)\{PhNC(Me)NPh\}]$	1 590w, 1 500m, 1 475m, 1 429w 1 410m, 1 218m
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$	1 600vw, 1 500m, 1 475m, 1 429wm 1 413m, 1 408w, 1 358wm, 1 288w, 1 222m
$[Re(CO)_3(PPh_3)\{PhNC(Ph)NPh\}]$	1 588w, 1 576w, 1 495m, 1 485m, 1 468m 1 430s, 1 375m, 1 312w, 1 275w, 1 212w
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}]$	1 603w, 1 565w, 1 500m, 1 465m 1 425s, 1 408w, 1 310w, 1 295w, 1 268w

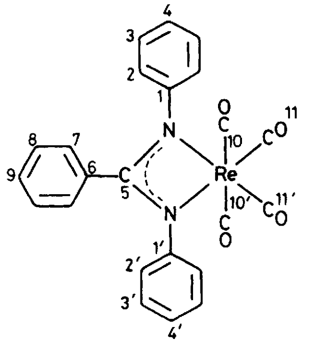
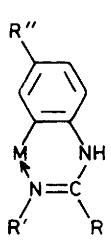


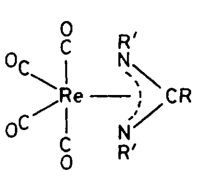
Figure 1. Carbon-13 n.m.r. data ($CDCl_3$) for $[Re(CO)_4\{PhNC(Ph)NPh\}]$: 1 = 1′ = 145.97, 2 = 2′ = 123.74, 3 = 3′ = 128.55, 4 = 4′ = 122.96, 5 = 165.00, 6 = 123.68, 7 = 128.94, 8 = 129.98, 9 = 132.71, 10 = 10′ = 189.77, 11 = 11′ = 186.78 p.p.m.

technique. Excessive loss through retention of the complexes on silica gel and alumina columns prevented their use.

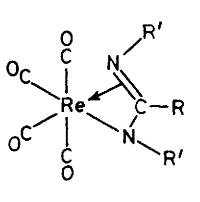
Attempts to find alternative preparative routes to avoid these difficult product separations led firstly to the use of toluene and hexane as alternative reaction solvents, then to the reactions of $[Re(CO)_4(HL)X]$ (X = Cl or Br) with n-butyl-lithium, and finally to the direct reactions of dirhenium decacarbonyl with amidines using u.v. irradiation. All reactions led to the desired complex, but in the last case the yield was very small. Using toluene or hexane, mixtures of products were again obtained and the yields were not significantly different. The similarity between the solution i.r. spectra of $[Re(CO)_4L]$ and $[Re(CO)_4(HL)X]$ (X = Cl or Br) in monoglyme or hydrocarbon solvents made monitoring of the $LiBu^n$ reaction most difficult, and because the reaction produced the *o*-metallated complex as a by-product, this preparative route provided no advantages over the route using $[\{Re(CO)_4X\}_2]$. Yields were slightly better, though this advantage was off-set by the necessary presynthesis of $[Re(CO)_4(HL)X]$ complexes.



V



VI

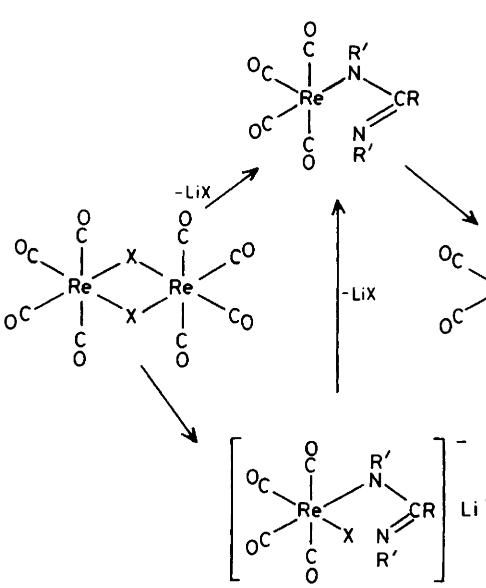


VII

Formulation of the complexes as $[Re(CO)_4L]$ is based on analytical data (Table 1), i.r. spectra (Table 2), and mass spectrometry. The pattern, position, and relative intensities of the carbonyl stretching absorptions in the i.r. spectrum are consistent with a *cis*-disubstituted octahedral structure. In the mass spectrometer all the complexes exhibited molecular ions, and fragmentation occurred by successive loss of four carbonyl groups before fragmentation of the amidino-ligand. The formulation of the complex and the known adherence of complexes of this type to the 18-electron rule imply that the amidino-group is a three-electron bidentate ligand. Of the possible types of chelate bonding, *viz.* π-type (VI), σ,π-type (VII), symmetrical σ,σ-type (I) and unsymmetrical σ,σ-type (II), previous experience favours the symmetrical σ,σ-type (I) which is found both for $[Pd\{PhNC(Ph)NPh\}_2]$[5] and $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{PhNC(Me)NPh\}]$.[5] This is confirmed for the diphenylbenzamidino-complex by the ^{13}C n.m.r. spectrum, data from which is given in Figure 1. The symmetrical nature of the amidino-group is indicated by the equivalence of the corresponding aryl carbon atoms of the N-substituents and the occurrence of only two signals due to carbonyl carbons. No appreciable change occurred in the spectrum over a range of temperatures down to −60 °C, eliminating the possibility of equivalence due to rapid interchange of the bonding mode. Though the π-type bonding mode (VI) cannot be eliminated by the n.m.r. data it is unlikely to occur in preference to bonding through donor nitrogen atoms, as shown notably for the palladium complex $[Pd\{PhNC(Ph)NPh\}_2]$.[5]

Some characteristic i.r. absorptions for the amidino-group are recorded in Table 3. Compared with the spectra of the free amidines the predominantly asymmetric NCN stretching vibration at *ca.* 1 600 cm^{-1} absorbs *ca.* 20 cm^{-1} lower in the complex. The symmetric stretch is similarly lowered with the absorption now occurring at *ca.* 1 500 cm^{-1}. These changes are similar to those observed for other rhenium–amidine complexes.

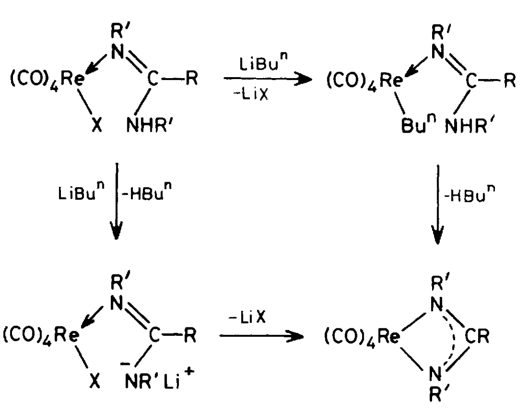
The formation of $[Re(CO)_4L]$ complexes from $[\{Re(CO)_4X\}_2]$ (X = Cl or Br) and lithioamidines is thought not to take place *via* attack at a carbonyl group as there is no evidence of carbamoyls being formed. Two routes are possible for the reaction, as shown in Scheme 1. It is not possible to predict which of the reaction routes is followed. The formation of $[Re(CO)_4L]$ from the reaction of $[Re(CO)_4(HL)X]$ with n-butyl-lithium can also take place *via* two similar routes in-



Scheme 1. Reaction schemes for the formation of [Re(CO)$_4${R′NC(R)NR′}] complexes (X = Cl or Br)

volving elimination of LiX in the first or second stages of the reaction (Scheme 2). Interestingly, the reaction of [Re(CO)$_4$L] with HBr forming *cis*-[Re(CO)$_4$(HL)Br] can be regarded as the reverse reaction. Protonation of the nitrogen leads to the formation of a monodentate amidine ligand and a vacant co-ordination site at the metal. Nucleophilic attack by a bromide ion leads to the product. Preliminary work demonstrates that this type of reaction can be achieved using other aqueous acids, *e.g.* nitric acid.

B. [Re(CO)$_3$L′L] (HL = *Amidine*, L′ = PPh$_3$ *or* AsPh$_3$) *Complexes.*—Reaction of [Re(CO)$_4$L] complexes with amidines in refluxing monoglyme or toluene is unusual in that the products, [Re(CO)$_3$L(HL)] contain an *o*-metallated amidine group (see section *C*). With PPh$_3$ in refluxing toluene, however, only a simple substitution reaction occurs to form [Re(CO)$_3$(PPh$_3$)L], with no evidence of *o*-metallation. The amidine retains its bidentate attachment to the metal, and it is a carbonyl group which is displaced. The phosphine and related arsine complexes are more easily obtained from the reactions between [Re(CO)$_4$L′Br] complexes (L′ = PPh$_3$ or AsPh$_3$) and amidines in refluxing toluene. Hydrogen bromide is eliminated and captured by the excess amidine as HL·HBr, and displacement of carbon monoxide results from the co-ordinated amidino-group becoming bidentate. The reaction proceeds in moderate yield (about 40%), the products being white, air-stable, crystalline solids with melting points around 195 °C. Only the *facial* isomer is observed, having three carbonyl stretching frequencies at *ca.* 2 020, 1 900, and 1 890 cm^{-1}. The analogous reaction using the NNN′-trisubstituted amidine *p*-MeC$_6$H$_4$N(Me)C(Me)NC$_6$H$_4$Me-*p* (HL^{2m}) is very slow and the tricarbonyl product, [Re(CO)$_3$(PPh$_3$)(HL^{2m})Br], which is isolated represents the intermediate stage in the formation of [Re(CO)$_3$(PPh$_3$)L] complexes from [Re(CO)$_4$(PPh$_3$)Br] and HL. Elimination of MeBr is not achieved in the same way as elimination of HBr, and the reaction consequently stops at the substitution stage.



Scheme 2. Reaction of [Re(CO)$_4${R′NC(R)NHR′}X] (X = Cl or Br) with LiBu^n

Table 4. Analytical data for the *o*-metallated complexes [Re(CO)$_3${R′NC(R)N(R‴)C$_6$H$_3$R″-*p*}{R′NC(R)N(R‴)R′}] (R = Ph, Me, or H; R′ = Ph or C$_6$H$_4$Me-*p*; R″ = H or Me; R‴ = H or Me) and also for [Re(CO)$_3${R′NC(Me)NHR′}$_2$X] (R′ = C$_6$H$_4$Me-*p*, X = Cl or Br)

Complex	Analysis (%) [a] C	H	N
[Re(CO)$_3$L^1(HL^1)]	54.1	4.15	8.1
	(54.0)	(3.9)	(8.15)
[Re(CO)$_3$L^2(HL^2)]	56.5	7.2	4.7
	(56.4)	(7.5)	(4.7)
[Re(CO)$_3$L^3(HL^3)]			
Isomer I	61.0	3.9	6.8
Isomer II	62.0	4.05	7.0
	(60.5)	(3.8)	(6.9)
[Re(CO)$_3$L^4(HL^4)]			
Isomer I	62.1	4.5	6.45
Isomer II	62.4	4.85	6.4
	(62.6)	(4.9)	(6.4)
[Re(CO)$_3$L^5(HL^5)]	52.6	3.5	8.5
	(52.6)	(3.5)	(8.45)
[Re(CO)$_3$(HL^2)$_2$Cl] [b]	53.8	4.6	7.2
	(53.7)	(4.7)	(7.15)
[Re(CO)$_3$(HL^2)$_2$Br] [c]	47.0	4.35	6.8
	(46.6)	(4.1)	(6.8)
[Re(CO)$_3$L^{2m}(HL^{2m})]	57.6	5.3	7.45
	(57.4)	(5.05)	(7.25)

[a] Calculated values are in parentheses. [b] Cl, 4.60 (4.55%). [c] Br, 10.0 (9.70%).

For the complexes [Re(CO)$_3$(PPh$_3$)L] where L = L^2 and L^4, ^{1}H n.m.r. spectroscopy showed the two *p*-tolyl methyl groups to be magnetically equivalent, and the skeletal C–CH$_3$ signal to consist of a doublet (J = 4 Hz). The splitting is attributed to long-range P–H coupling, since the coupling is absent from the spectra of the corresponding arsine complexes.

Substantial amounts (up to 20% yield) of *trans*-[Re(CO)$_3$(PPh$_3$)$_2$Br] form in the reactions of [Re(CO)$_4$(PPh$_3$)Br] with amidines and represents the reaction of displaced PPh$_3$ with the starting material. The fate of the rhenium complex from which the triphenylphosphine was lost was not discovered though a probable product, *o*-metallated [Re(CO)$_3$L(HL)], was not detected. Interestingly, no *o*-metallated amidino-groups were formed although they form readily when amidine solutions are refluxed with [Re(CO)$_4$(HL)Br] and other rhenium complexes. Three explanations are possible, (*i*) [Re(CO)$_3$(PPh$_3$)L] complexes are both thermally stable (m.p. *ca.* 190 °C) and stable towards reaction with other reagents; (*ii*) *o*-metallated amidines may have more steric interactions with a *cis*-PPh$_3$ than a NN′-chelated amidino-group, and (*iii*)

Table 5. I.r. carbonyl and N–H stretching frequencies for $[\mathrm{Re(CO)_3(HL)_2X}]$ (X = Cl or Br) and *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}\mathrm{(HL)}]$ complexes

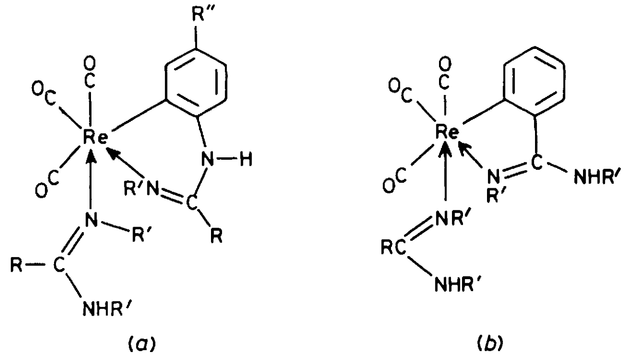
Complex	Medium	$\tilde{\nu}$(CO)/cm^{-1}	$\tilde{\nu}$(N–H)/cm^{-1}
$[\overline{\mathrm{Re(CO)_3L^1}}\mathrm{(HL^1)}]$	CH_2Cl_2	2 012vs, 1 890vs br	3 343w
	Nujol	2 002vs, 1 894vs, 1 879vs	3 342m
$[\overline{\mathrm{Re(CO)_3L^2}}\mathrm{(HL^2)}]$	CH_2Cl_2	2 015vs, 1 887vs br	3 348w
	Nujol	2 002vs, 1 887vs, 1 878vs	3 346m
$[\overline{\mathrm{Re(CO)_3L^3}}\mathrm{(HL^3)}]$			
Isomer I	CH_2Cl_2	2 018vs, 1 898vs, 1 885vs	3 341w
Isomer II	Nujol	2 010vs, 1 880vs br	3 340m
	Nujol	2 016vs, 1 912vs, 1 873vs	3 341w
$[\overline{\mathrm{Re(CO)_3L^4}}\mathrm{(HL^4)}]$			
Isomer I	CH_2Cl_2	2 012vs, 1 895vs, 1 882vs	3 340w
Isomer II	Nujol	2 010vs, 1 890vs, 1 877vs	3 340m
	CH_2Cl_2	2 016vs, 1 916vs, 1 868vs	3 332w
$[\overline{\mathrm{Re(CO)_3L^5}}\mathrm{(HL^5)}]$	CH_2Cl_2	2 020vs, 1 885vs br	3 365w
	Nujol	2 015vs, 1 900vs, 1 878vs	3 348m
$[\overline{\mathrm{Re(CO)_3L^{2m}}}\mathrm{(HL^{2m})}]$	CH_2Cl_2	2 018vs, 1 900vs, 1 875vs	—
	Nujol	2 018vs, 1 900vs br	—
$[\mathrm{Re(CO)_3(HL^2)_2Cl}]$	CH_2Cl_2	2 022vs, 1 895vs br	
	Nujol	2 022vs, 1 904vs, 1 888vs	3 210w, 3 150w
$[\mathrm{Re(CO)_3(HL^2)_2Br}]$	Nujol	2 020vs, 1 905vs, 1 890vs	3 210w

steric interactions of a chelate *o*-metallated transition state prevent this process occurring. Since molecular models show that the *o*-metallated group interacts sterically with adjacent groups to a lesser extent than the NN′-chelated group, the first explanation seems the most plausible. Further, *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}\mathrm{(HL)}]$ reacts with PPh_3 to produce the NN′-chelated complex $[\mathrm{Re(CO)_3(PPh_3)L}]$.

Preliminary work suggests that *fac*-$[\mathrm{Re(CO)_3(PPh_3)(HL)X}]$ complexes can be produced by reaction of $[\mathrm{Re(CO)_3(PPh_3)L}]$ with a range of protic acids *i.e.* HCl, HBr, HI, HF, HNO_3, HCO_2H, and PhOH.

C. o-*Metallated Amidine Complexes.*—When $[\mathrm{Re(CO)_5X}]$ (X = Cl or Br) and $[\{\mathrm{Re(CO)_4Br}\}_2]$ are refluxed in monoglyme with amidines, the complexes $[\overline{\mathrm{Re(CO)_3L}}\mathrm{(HL)}]$ (L = L^1—L^5 and L^{2m}) are formed in good yield. The complexes were identified by elemental analysis (Table 4) and mass spectrometry, and confirmed by i.r. (Table 5) and n.m.r. data. In order that the complexes fulfil the 18-electron rule, the amidino-groups must contribute a total of five electrons to the rhenium, which is most likely achieved by one amidino-group acting as a three-electron donor and the other as a two-electron donor. The occurrence of a medium-intensity sharp i.r. absorption at *ca.* 3 340 cm^{-1} for each of the complexes {except for $[\overline{\mathrm{Re(CO)_3L^{2m}}}\mathrm{(HL^{2m})}]$} indicates the presence of a N–H group. Moreover, the unusually sharp nature of this band and its relatively high frequency indicates that it arises from an *o*-metallated amidino-group, as found in the palladium complex $[\overline{\mathrm{Pd}(\eta^5\text{-}\mathrm{C_5H_5})\{p\text{-}\mathrm{MeC_6H_4NC(Me)NHC_6H_3}}\mathrm{Me}\text{-}p\}]$.[5] Related complexes are well documented for rhenium and, indeed, *o*-metallation is a common reaction of rhenium complexes with nitrogen ligands having aryl substituents.[24] The sharpness, intensity, and high frequency of ν(NH) have been found to be diagnostic of this type of attachment. The three strong ν(CO) absorptions observed in the i.r. are consistent with a *facial* isomer as shown in Figure 2.

o-Metallated six-membered-ring structures are assigned to the acetamidine (L^1) and formamidine (L^5) complexes prepared. Similarly, one of the isomeric products obtained using

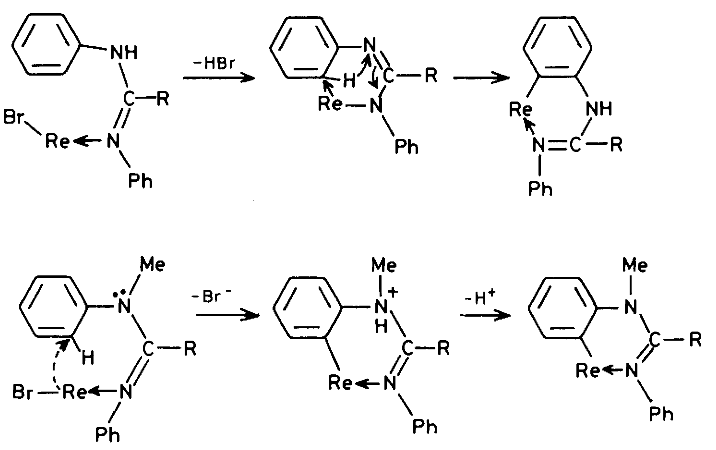


(*a*) (*b*)

Figure 2. (*a*) Structure of the *o*-metallated complex $[\overline{\mathrm{Re(CO)_3\{R'NC(R)NHC_6H_3}}\mathrm{R''}\text{-}p\}\{\mathrm{R'NC(R)NHR'}\}]$ (R″ = H or CH_3); (*b*) structure of the *o*-metallated complex $[\overline{\mathrm{Re(CO)_3\{R'NC(C_6}}\mathrm{H_4)NHR'}\}\{\mathrm{R'NC(R)NHR'}\}]$

HL^3 (isomer I) and the major product (isomer I) obtained using HL^4 are assigned related structures. However, for benzamidines (HL^3 and HL^4) a second *o*-metallated product is possible, having a five-membered ring incorporating the $C–C_6H_5$ substituent [see Figure 2(*b*)]. Because of the similarity in the carbonyl stretching frequencies for all the complexes except isomer II for the benzamidino (L^3 and L^4) complexes, they are assigned the same structure. Isomers II in common with the other complexes have the distinctive N–H absorption. However, the three carbonyl stretching frequencies are noticeably different to those of the other *o*-metallated complexes, particularly in the position of two absorption bands. Thus a slightly different structure seems probable, and the available data are consistent with the presence of a five-membered-ring system as shown in Figure 2(*b*). The diphenylbenzamidino (L^3) derivative was not detected in the reaction between $[\mathrm{Re(CO)_5Br}]$ and HL^3, although such a complex was isolated as a minor product of the reaction of $[\mathrm{Re(CO)_4L^3}]$ with HL^3 (ref. 22).

Hydrogen-1 n.m.r. spectra of all the *p*-tolyl *o*-metallated complexes, both five- and six-membered rings, consist of two methyl resonances attributable to the *p*-tolyl methyl groups in

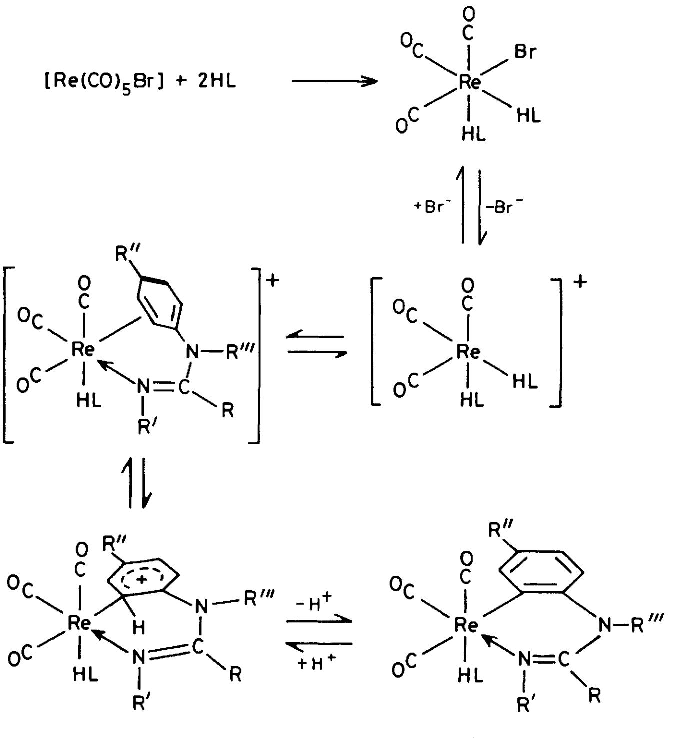


Scheme 3. Possible reaction schemes leading to *o*-metallation of amidines

the ratio 3 : 1. It is concluded that the two *p*-tolyl methyl groups of the monodentate amidine and the *p*-tolyl methyl of the *o*-metallated amidino-group remote from the metal have coincidental overlap of resonances. The unique methyl resonance is assigned to the methyl group on the *o*-metallated aromatic ring. The acetamidine derivatives show two more methyl resonances arising from the different environments of the skeletal C–CH_3 groups.

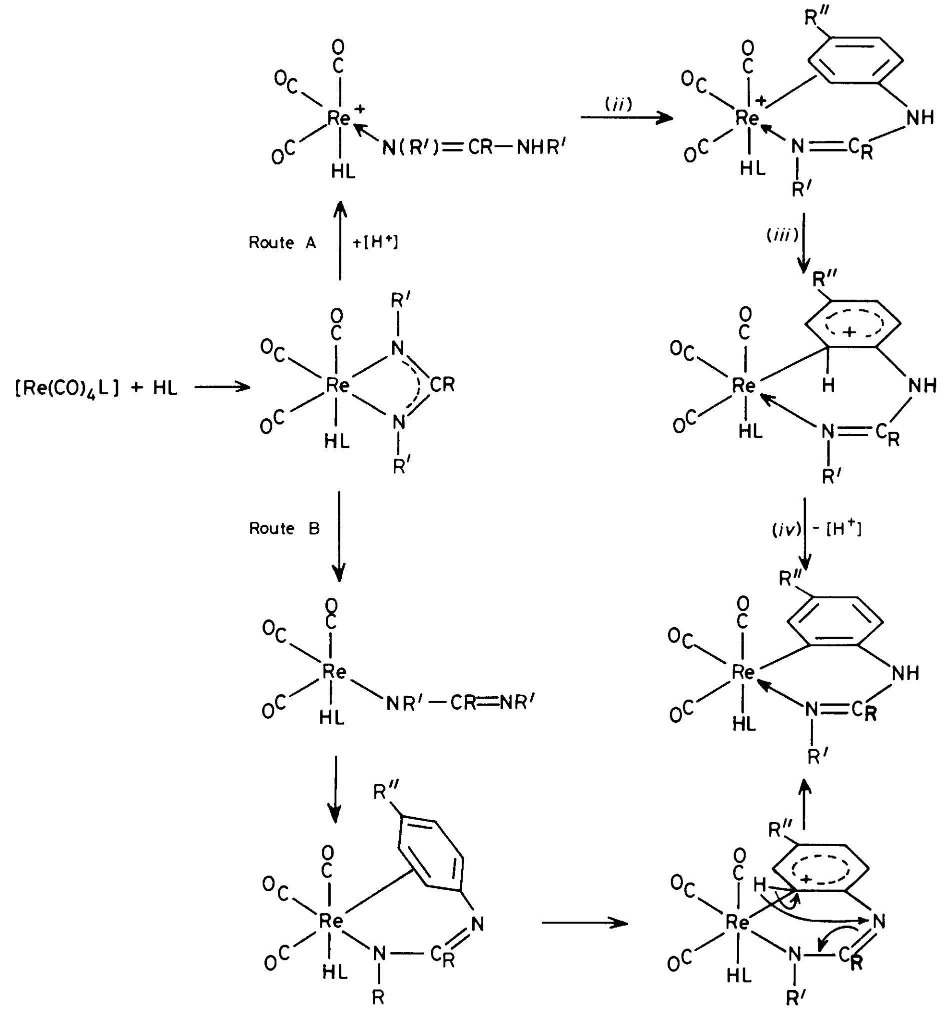
In reactions involving HL^2 intermediate complexes of the type $[Re(CO)_3(HL^2)_2X]$ (X = Cl or Br) were obtained in small yield. Related complexes for other amidines were not detected. The complexes showed three strong carbonyl stretching frequencies in the i.r. spectrum consistent with a facial tricarcarbonyl complex, and showed (for X = Cl) the expected two methyl resonances (ratio 2 : 1) in the ^1H n.m.r. spectrum. The parent ion $[Re(CO)_3(HL^2)_2Cl]^+$ in the mass spectrum gave a weak peak, the predominant peaks arising from *o*-metallated $[Re(CO)_3L^2(HL^2)]$, the thermolysis product formed in the ion source. Interestingly, in attempting to separate the last two complexes in the preparative work to obtain a pure sample of the latter, heating the mixture to 190 °C was effective in removing the chloro-complex as a contaminant. Elimination of HCl (or HBr) appears important in the reaction scheme leading to *o*-metallated complexes.

With regard to the mechanism of the *o*-metallation reactions, another important reaction is that of the NNN′-trisubstituted amidine p-$MeC_6H_4N(Me)C(Me)NC_6H_4Me$-$p$ with $[Re(CO)_5Br]$ which leads to the *o*-metallated compound $[Re(CO)_3L^{2m}(HL^{2m})]$. Following the failure of this amidine to produce an *o*-metallated complex with $[PdCl_4]^{2-}$, in contrast with the NN′-disubstituted amidine, it was suggested [18] that the N–H group was an important feature which would allow a 1,3-shift of an *o*-hydrogen to an adjacent nitrogen (see Scheme 3). Though this type of mechanism is not entirely eliminated by the *o*-metallation of the trisubstituted amidine, such a process will produce a quaternary nitrogen prior to proton loss [Scheme 3, reaction (*b*)]. For these amidines proton loss may be assisted by the nitrogen lone pair in a 1,3-proton-transfer reaction. Such base promoted reactions are well documented.[25] Current thinking favours an intramolecular aromatic substitution mimicking classical electrophilic aromatic substitutions, as illustrated in Schemes 3 and 4, and we suggest that the process involves the presynthesis of $[Re(CO)_3(HL)_2Br]$, isolated or detected as an intermediate in some of the reactions. The following steps, the elimination of Br^-, the formation of a metal–arene complex, and the formation of a carbonium ion prior to final elimination of H^+, are similar to those proposed for the formation of other *o*-metallated products,[25] for example a five-membered *o*-metallated product from $[PdCl_4]^{2-}$ and diarylhydrazines.[26] The reversible nature of the *o*-metallated amidine reaction was demonstrated by the action of hydrobromic acid on *o*-metallated $[Re(CO)_3L^2(HL^2)]$ in methanol. This caused the formation of $[Re(CO)_3(HL^2)_2Br]$, and indicates the route by which the other rhenium complexes of this type may be synthesised.



Scheme 4. Formation of *o*-metallated $[Re(CO)_3L(HL)]$

There are other recorded examples of reverse *o*-metallation reactions. For example the loss of hydrogen and the formation of an *o*-metallated product from $[RuHCl\{P(OPh)_3\}_4]$ can be reversed using hydrogen gas, and this type of reaction can be used to exchange *ortho* aromatic protons with D_2.[25] Also, the reaction of $[PdX_2\{P(OR)_3\}_2]$ to form the palladated complex $[Pd\{o$-$C_6H_4OP(OR)_2\}\{P(OR)_3\}X]$ (X = Cl, Br, or I; R = Ph or C_6H_4Cl-p) can be reversed by treating the latter complexes with hydrogen chloride in dichloromethane.[27]



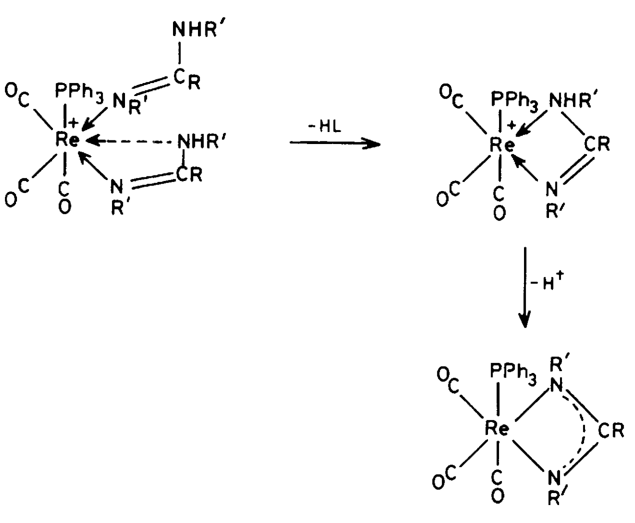
Scheme 5. Possible mechanism for the interchange of amidino-group bonding from NN′-chelate to *o*-metallate type

The formation of some five-membered *o*-metallated ring complexes when benzamidines were used represents an alternative reaction route available to these materials. A similar mechanism for the formation is envisaged. Interestingly, although five-membered-ring systems are generally favoured over six-membered rings (minimal ring strain being the determining factor), six-membered rings are favoured over five-membered rings for the benzamidine complexes in terms of the yields of product formed. Though it is conceivable that the six-membered rings may be stabilised by a substantial degree of delocalisation of π electrons (pseudo-aromatic 6π-electron system), this is not realised in practice for other complexes. The *X*-ray crystal structure of the complex $[\mathrm{Pd}(\eta^5\text{-}C_5H_5)\{p\text{-}\mathrm{MeC_6H_4NC(Me)NHC_6H_3Me}\text{-}p\}]$,[5] for example, showed a puckered, non-delocalised ring system having a variety of C–N bond distances.

o-Metallated complexes are the ultimate products of most reactions of rhenium carbonyl halides or amidine complexes with excess amidines. $[\mathrm{Re(CO)_5X}]$, $[\{\mathrm{Re(CO)_4Br}\}_2]$, and $[\mathrm{Re(CO)_4(HL)X}]$ (X = Cl or Br) in the presence of excess amidine and at a suitably high temperature all form *o*-metallated $[\mathrm{Re(CO)_3L(HL)}]$ complexes. Similarly, $[\mathrm{Re(CO)_4L}]$ and $[\mathrm{Re(CO)_4(COL)}]$ react with amidines in refluxing toluene to form the same complexes. A similar reaction route to Scheme 4 is envisaged, the initial step being the ligand substitution of carbonyl by amidine and protonation (from the solvent or other amidine species) of one nitrogen of the chelated amidine (Scheme 5, route A). π-Arene co-ordination, followed by electrophilic substitution of the ring by the metal would regenerate the proton. Alternatively, a 1,3-proton-switch reaction (Scheme 5, route B) could occur.

The extent to which steric crowding influences the *o*-metallation reactions is of interest. It is found that such reactions occur only when two amidines are attached to the metal, and not when a combination of amidine and PPh_3 or $AsPh_3$ groups are present. Molecular models suggest that for both types of complexes, $[\mathrm{Re(CO)_4L(HL)}]$ and $[\mathrm{Re(CO)_4L(PPh_3)}]$, strong interactions between ligands occur but only in certain configurations. However, it is likely that steric interactions in the intermediates, *viz.* $[\mathrm{Re(CO)_3(HL)_2X}]$ and $[\mathrm{Re(CO)_3(PPh_3)(HL)X}]$ are more important. The bis(amidine) complex shows a much greater degree of steric interaction than the amidine–phosphine complex, causing one of the aryl groups to approach closely to the metal. It is most likely that the different steric interactions are responsible for the presence of an *o*-metallated group in $[\mathrm{Re(CO)_3L(HL)}]$ but a NN′-chelate group in the corresponding phosphine complex $[\mathrm{Re(CO)_3(PPh_3)L}]$.

An additional factor to be taken into consideration for the $[\mathrm{Re(CO)_4L}]$ reaction with amidines is the relative stability of the NN′-chelate *versus* *o*-metallated chelate complexes. Indeed the NN′-chelate group would be the straightforward



Scheme 6. Possible later stages in the reaction of *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$ with PPh_3

derivative envisaged, and it seems likely that the strong electron donation, which would result in a complex $[\mathrm{Re(CO)_3L(HL)}]$ from σ donation by three nitrogen atoms, would produce an unacceptably high electron density on the metal. This could be relieved by detachment of one nitrogen from the metal, followed by the subsequent *o*-metallation reaction. Thus in such circumstances formation of a metal–carbon bond would not be unexpected. Such an interpretation is supported by the numerous $[\mathrm{Re(CO)_3L'_2X}]$ complexes which form with L′ = amine, phosphine, and arsine, *etc.*, and which fail to undergo further displacement of carbon monoxide (see below).[24]

$$[\mathrm{Re(CO)_5Br}] + \mathrm{RNH_2} \xrightarrow{-2\mathrm{CO}} [\mathrm{Re(CO)_3(NH_2R)_2Br}]$$

The change in bonding of the amidine which results when *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$ reacts with PPh_3 is more difficult to explain. Since reaction of the complex with hydrobromic acid reverses the *o*-metallation reaction, we envisage an acid-catalysed reversal of stages (*iii*) and (*iv*) of route A (Scheme 5) in the reaction with PPh_3. The reversal of stage (*ii*) will be favoured by the presence of PPh_3. Steric crowding of the facially substituted $[\mathrm{Re(CO)_3(PPh_3)(HL)_2}]^+$ intermediate (Scheme 6) would cause the displacement of a monodentate amidine group by the unco-ordinated nitrogen of the second amidine group, and loss of a proton would generate the NN′-amidinochelate complex $[\mathrm{Re(CO)_3(PPh_3)L}]$.

Experimental

The amidines, $[\mathrm{Re(CO)_5X}]$, $[\{\mathrm{Re(CO)_4X}\}_2]$, and $[\mathrm{Re(CO)_4L'X}]$ (X = Cl or Br; L′ = PPh_3 or $AsPh_3$) were prepared by published methods.[28,29] All solvents were dried and rigorously degassed before use. Alumina used was by Woelm (neutral, activity III). n-Butyl-lithium in hexane solution (3.5 mol dm^{-3}) was supplied by Alfa. All reactions were carried out under an atmosphere of nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 456 spectrometer, proton n.m.r. spectra at 60 MHz on a Varian E.M. 360L spectrometer, and ^{13}C n.m.r. spectra on a Bruker HX90E spectrometer modified for Fourier-transform operation using a Nicolet B.N.C.12 computer. N.m.r. samples were dissolved in deuteriochloroform and $SiMe_4$ was employed as an internal reference. Raman spectra of solid samples were recorded on a Cary 82 spectrometer utilising a Spectrophysics 164 argon-ion laser source.

Carbon, hydrogen, and nitrogen contents were determined using a Perkin-Elmer 240 Elemental Analyser. Chlorine and bromine analyses were obtained by combustion of the complexes in oxygen followed by potentiometric titration of the halide ions.

Reaction of $[\{\mathrm{Re(CO)_4Br}\}_2]$ *with* PhN(Li)C(Ph)NPh.—n-Butyl-lithium (3.46 mol dm^{-3} in hexane) was added to a frozen (−196 °C) solution of *NN′*-diphenylbenzamidine (0.941 g, 3.46 mmol) in monoglyme (40 cm^3). The mixture was allowed to warm to room temperature, and then stirred for 15 min. The lithio-reagent was then transferred by syringe onto solid $[\{\mathrm{Re(CO)_4Br}\}_2]$ (1.31 g, 1.73 mmol) and the mixture stirred. After 30 min the white suspension had dissolved, and a clear yellow solution formed. The solution was evaporated *in vacuo* to dryness, small additions of diethyl ether being used to prevent gum formation. After extraction with toluene (25 cm^3), the solution was filtered through alumina (1 in-thick) before reduction in volume and cooling to −10 °C. White crystals of $[\mathrm{Re(CO)_4(HL^3)Br}]$ separated. Addition of hexane to the mother-liquor and cooling gave yellow crystals of $[\mathrm{Re(CO)_4L^3}]$ which were recrystallised from toluene solution.

The peak at highest *m*/*e* value in the mass spectrum of the yellow crystals was due to the parent ion at *m*/*e* 570. Daughter ions corresponded to the stepwise loss of the four carbonyl groups. Metastable peaks were not observed.

Reaction of $[\{\mathrm{Re(CO)_4Br}\}_2]$ *with* *p*-MeC$_6$H$_4$N(Li)C(Ph)NC$_6$H$_4$Me-*p*.—The reaction conditions and procedure were identical to those described above. The crude product contained $[\mathrm{Re(CO)_4L^4}]$, $[\mathrm{Re(CO)_4(HL^4)Br}]$, and *o*-metallated $[\overline{\mathrm{Re(CO)_3L^4}}(\mathrm{HL^4})]$ which were identified by i.r. spectroscopy. This crude product was recrystallised from toluene–hexane giving yellow crystals of $[\mathrm{Re(CO)_4L^4}]$. ^1H N.m.r. ($CDCl_3$): δ (number of protons in parentheses) 6.95 (2), 6.74 (2), 6.61 (4), 6.45 (5), 2.18 p.p.m. (6).

Reaction of $[\{\mathrm{Re(CO)_4Cl}\}_2]$ *with* PhN(Li)C(Ph)NPh *and* *p*-MeC$_6$H$_4$N(Li)C(Ph)=NC$_6$H$_4$Me-*p*.—The reaction conditions and procedure were identical to those described above for LiL^3. The products, $[\mathrm{Re(CO)_4L^3}]$ and $[\mathrm{Re(CO)_4L^4}]$ respectively, were identified by i.r. spectroscopy.

Reaction of $[\{\mathrm{Re(CO)_4Cl}\}_2]$ *with* PhN(Li)C(Me)NPh.—The reaction conditions and procedures were identical to those described above for LiL^3. The initial crude product contained $[\mathrm{Re(CO)_4L^1}]$, $[\mathrm{Re(CO)_4(HL^1)Cl}]$, and *o*-metallated $[\overline{\mathrm{Re(CO)_3L^1}}(\mathrm{HL^1})]$, identified by i.r. spectroscopy. Later samples were yellow crystals of $[\mathrm{Re(CO)_4L^1}]$ which were recrystallised twice from hexane solution. ^1H N.m.r. ($CDCl_3$): δ 7.25, 7.13, 6.93, 6.80 (10), 2.07 p.p.m. (3).

Reaction of $[\{\mathrm{Re(CO)_4Cl}\}_2]$ *with* *p*-MeC$_6$H$_4$N(Li)C(Me)NC$_6$H$_4$Me-*p*.—The reaction conditions and procedure were identical to those described above for LiL^3. The product was recrystallised twice from hexane giving yellow crystals. ^1H N.m.r. ($CDCl_3$): δ 6.87, 6.73 (8), 2.30 (6), 2.03 p.p.m. (3).

Reaction of $[\mathrm{Re_2(CO)_{10}}]$ *with* *p*-MeC$_6$H$_4$NHC(Ph)NC$_6$H$_4$Me-*p*.—$[\mathrm{Re_2(CO)_{10}}]$ (0.788 g, 1.21 mmol) and HL^4 (0.725 g, 2.42 mmol) were dissolved in toluene (20 cm^3), and the solution refluxed for 12 h. Although the solution became dark brown no changes occurred in the ν(CO) stretching frequency region of the i.r. spectrum. U.v. irradiation over 8 h caused a further darkening of the colour, and eventual loss of ν(CO) absorptions. Evaporation of the reaction mixture to small bulk (5 cm^3), addition of diethyl ether (2 cm^3), and cooling to −10 °C gave a mustard coloured precipitate. Recrystallisation from dichloromethane–hexane solution gave a very small quantity of [Re(CO)$_4$L^4].

Decarbonylation of [Re(CO)$_4$(COL)] *Complexes.*—This preparative route will be described in a following paper.[22]

Reaction of [Re(CO)$_4$(HL^3)Br] *with n-Butyl-lithium.*—n-Butyl-lithium (1.14 mmol) in hexane solution was added to a frozen solution of [Re(CO)$_4$(HL^3)Br] (0.743 g, 1.14 mmol) in monoglyme (40 cm^3) at −196 °C. The mixture was warmed to ambient temperature, stirred for 30 min, then the solvent was removed from the yellow solution *in vacuo*. The residue was extracted with toluene (40 cm^3), the solution filtered, reduced in volume (to 5 cm^3), then cooled to −10 °C. Yellow crystals of [Re(CO)$_4$L^3] were produced (yield 0.402 g, 62%). Further crystals produced from the solution were identified as *o*-metallated [$\overline{\text{Re(CO)}_3\text{L}}^3$(HL^3)].

Reaction of [Re(CO)$_4$(HL^4)Br] *with n-Butyl-lithium.*—Reaction procedure and conditions were identical to those described above. [Re(CO)$_4$L^4] was obtained in 60% yield, but two other crystalline products were produced, and were identified as the two isomers of *o*-metallated [$\overline{\text{Re(CO)}_3\text{L}}^4$(HL^4)].

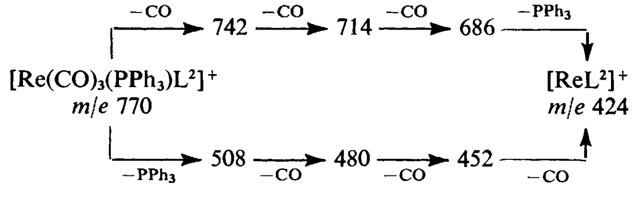
Reactions of [Re(CO)$_4$(HL)Br] (HL = HL^1 *or* HL^2) *with n-Butyl-lithium.*—Reaction conditions and procedure were identical to those described previously. The products were [Re(CO)$_4$L] and *o*-metallated [$\overline{\text{Re(CO)}_3\text{L}}$(HL)] (L = L^1 or L^2), the [Re(CO)$_4$L] complexes being obtained in 30 and 24% yield respectively.

Reactions of [Re(CO)$_4$(HL)Cl] *with n-Butyl-lithium.*—The complexes formed were identical to those described for reactions involving the bromo-complex, and in similar yields.

Reaction of [Re(CO)$_4$L^3] *with Hydrobromic Acid.*—[Re(CO)$_4$L^3] (0.100 g, 1.75 mmol) was suspended in methanol (10 cm^3) and hydrobromic acid (0.3 cm^3, 47%, 1.75 mmol) added slowly dropwise. The solid which changed colour from yellow to white was separated by filtration, washed with methanol, and dried under vacuum. The product was identified by i.r. spectroscopy as [Re(CO)$_4$(HL^3)Br].

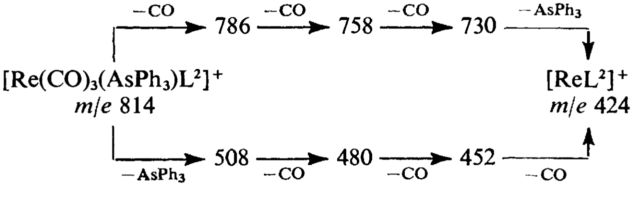
Mass Spectra of [Re(CO)$_4$L] *Complexes.*—Parent ions were the highest *m/e* fragments detected for all [Re(CO)$_4$L] complexes. Daughter ions corresponded to stepwise loss of the four carbonyl groups, and preceded the fragmentation of the amidino-groups. No metastable peaks were observed.

Reaction of [Re(CO)$_4$(PPh$_3$)Br] *with* HL^2.—The complex (0.500 g, 0.78 mmol) and HL^2 (0.371 g, 1.56 mmol) were dissolved in toluene (40 cm^3) and the mixture refluxed for 4 h. The solvent was evaporated *in vacuo* to 10 cm^3, diethyl ether (10 cm^3) added, and the mixture cooled to −10 °C. A white precipitate of the amidine hydrobromide separated and was identified by ^{1}H n.m.r. and i.r. spectroscopy. Pentane (10 cm^3) was added to the mother-liquor, and further cooling produced hard, white crystals of [Re(CO)$_3$(PPh$_3$)$_2$Br] (0.151 g). Removal of the solvent from the mother-liquor *in vacuo*, followed by extraction of the residue with carbon tetrachloride (10 cm^3), and cooling the solution, produced white [Re(CO)$_3$(PPh$_3$)L^2]. Yield 0.19 g, 31%. ^{1}H N.m.r. (CDCl$_3$): δ 7.20 (7), 7.10 (2), 6.92 (1), 6.60 (1), 6.47 (1), 2.31 (s, 6), 1.45 p.p.m. (d, 3, J = 4 Hz). Mass spectrum: peak at highest *m/e* value due to parent ion [^{187}Re(CO)$_3$(PPh$_3$)L^2]$^+$ at *m/e* 770; the fragmentations shown below were observed; no metastable ions were observed.



Reactions of [Re(CO)$_4$(PPh$_3$)Br] *with* HL^1, HL^4, *and* HL^3.—The reaction conditions and procedure were identical to those described above for HL^2. The products were off-white solids, [Re(CO)$_3$(PPh$_3$)L], formed in the following yields: L = L^1 (45%), L^4 (38%), L^3 (42%). ^{1}H N.m.r. (CDCl$_3$): δ [Re(CO)$_3$(PPh$_3$)L^1], 7.13 (17), 6.75 (4), 6.61 (4), 1.62 p.p.m. (d, 3, J = 4 Hz); [Re(CO)$_3$(PPh$_3$)L^4], 7.40 (1), 7.25 (4), 7.17 (3), 6.87 (4), 6.63 (1), 6.30 (1), 2.19 p.p.m. (3). Mass spectrum: the parent ions were observed for L = L^4 and L^3 at *m/e* 832 and 804 respectively. As described above for [Re(CO)$_3$(PPh$_3$)L^2], two fragmentation routes are observed, involving either three successive losses of carbonyl groups followed by triphenylphosphine to form [ReL]$^+$, or initial loss of triphenylphosphine followed by the successive loss of three carbonyl groups. Most of the ion current arose from the former process. For [Re(CO)$_3$(PPh$_3$)L^4], metastable peaks at m^* 721 and 696 were assigned to [Re(CO)$_2$(PPh$_3$)L^4]$^+$ $\longrightarrow$ [Re(CO)(PPh$_3$)L^4]$^+$ and [Re(CO)(PPh$_3$)L^4]$^+$ $\longrightarrow$ [Re(PPh$_3$)L^4]$^+$ fragmentations respectively. For [Re(CO)$_3$(PPh$_3$)L^3] two metastable peaks at m^* 721 and 693 are assigned to these same processes, and m^* 749 to [Re(CO)$_3$(PPh$_3$)L^3]$^+$ $\longrightarrow$ [Re(CO)$_2$(PPh$_3$)L^3]$^+$. Similar mass spectrum fragmentation patterns were observed for [Re(CO)$_3$(PPh$_3$)L^1], all daughter ions being detected although the parent ion at *m/e* 742 was not observed. Again the initial loss of a carbonyl group was the favoured route.

Reaction of [Re(CO)$_4$(AsPh$_3$)Br] *with* *p*-MeC$_6$H$_4$NHC(Me)NC$_6$H$_4$Me-*p*.—[{Re(CO)$_4$Br}$_2$] (0.500 g, 0.66 mmol) and triphenylarsine (0.405 g, 1.32 mmol) suspended in carbon tetrachloride (40 cm^3) were heated at 50 °C for 2.5 h. An i.r. spectrum showed that [Re(CO)$_4$(AsPh$_3$)Br] had formed in good yield. The amidine (0.62 g, 2.64 mmol) was added and the mixture refluxed for 3 h. Removal of the solvent *in vacuo*, followed by solvent extraction of the residue with toluene (4 cm^3), filtering the solution, and cooling to −10 °C yielded a white precipitate of the amidine hydrobromide, which was identified by i.r. and ^{1}H n.m.r. spectroscopy. Further cooling and reduction in volume of the mother-liquor yielded a white solid, which after recrystallisation from dichloromethane–hexane, was identified as [Re(CO)$_3$(AsPh$_3$)L^2]. ^{1}H N.m.r. (CDCl$_3$): δ 7.07 (m), 2.31 (s, 2), 1.63 p.p.m. (s, 1). Mass spectrum: parent ion [^{187}Re(CO)$_3$(AsPh$_3$)L^2]$^+$ at *m/e* 814 was the highest mass peak, and fragmentation patterns were identical to those of the phosphine derivatives (see below).



Reaction of [Re(CO)$_4$(PPh$_3$)Br] *with* *p*-MeC$_6$H$_4$N(Me)C(Me)NC$_6$H$_4$Me-*p*.—[Re(CO)$_4$(PPh$_3$)Br] (0.200 g, 0.31 mmol) and HL^{2}m (0.079 g, 0.31 mmol) were dissolved in toluene

(10 cm^3), and the mixture refluxed for 21 h. The solution was filtered from a white precipitate, which contained neither amidine nor carbonyl groups, and after reducing to small bulk (2 cm^3) and cooling, *trans*-[Re(CO)$_3$(PPh$_3$)$_2$Br] separated. Attempts to obtain the main product from the solution using a variety of solvents and conditions failed, though the i.r. solution spectrum [in CH$_2$Cl$_2$: ν(CO) 2 020s and 1 904s, br cm^{-1}] suggests strongly that the complex is [Re(CO)$_3$(PPh$_3$)(HL^{2m})Br].

Reactions of [Re(CO)$_4$L] (L = L^3 *or* L^2) *with* PPh$_3$.—[Re(CO)$_4$L] (0.21 mmol) and PPh$_3$ (0.055 g, 0.21 mmol) were dissolved in toluene (20 cm^3) and the mixture refluxed for 2 h. After evaporation to small bulk (10 cm^3), cooling and addition of pentane (5 cm^3), white crystals of [Re(CO)$_3$(PPh$_3$)L] complexes were obtained. Yield for L = L^3, 0.12 g (67%).

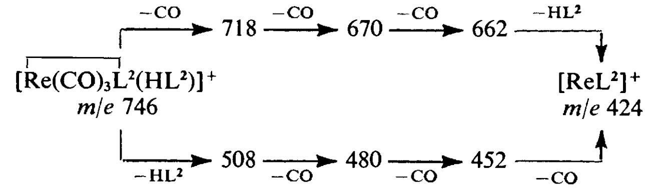
Reaction of [Re(CO)$_4$L^3] *with* PhNHC(Ph)NPh.—The complex (0.205 g, 0.36 mmol) and HL^3 (0.098 g, 0.36 mmol) were dissolved in toluene (12 cm^3), and the solution refluxed for 4 h. After evaporation to small bulk (3 cm^3) *in vacuo*, a few drops of hexane were added and the mixture cooled to −10 °C. Yellow crystals of *o*-metallated [Re(CO)$_3$L^3(HL^3)] were produced (yield 0.20 g, 66%). This product is described fully later in the Experimental section. Addition of more pentane produced a second yellow crystalline product, identified as an isomer of *o*-metallated [Re(CO)$_3$L^3(HL^3)]. It was recrystallised from pentane (Found: C, 62.0; H, 4.05; N, 7.0. C$_{41}$H$_{31}$N$_4$Re requires C, 60.5; H, 3.8; N, 6.9%). The mass spectrum of the second isomer was identical to that of the first isomer which is discussed further below. I.r. (Nujol): ν(N–H) 3 341m; ν(CO) 2 016vs, 1 912vs, and 1 873vs cm^{-1}.

Reactions of [Re(CO)$_4$L] (L = L^4, L^1, *or* L^2) *with Amidines* (HL^4, HL^1, *and* HL^2 *respectively*).—The reaction conditions and procedures were identical to those described above. The products were the *o*-metallated complexes [Re(CO)$_3$L(HL)], which are described in detail later.

Reaction of [Re(CO)$_5$Br] *with* *p*-MeC$_6$H$_4$NHC(Me)NC$_6$H$_4$Me-*p*.—(*i*) HL^2 (1.72 g, 4.92 mmol) and [Re(CO)$_5$Br] (1.00 g, 2.46 mmol) were suspended in monoglyme (40 cm^3) and the mixture refluxed for 3 h. After removal of the solvent *in vacuo*, the residue was extracted with toluene (10 cm^3) and the filtered solution cooled to −10 °C. The crystalline product (1.26 g) consisted of two components, one yellow and the other white. Evaporation of the mother-liquor, then extraction of the gummy residue with carbon tetrachloride gave a pale yellow solution which on adding pentane and cooling yielded small quantities of [Re(CO)$_4$(HL^2)Br] and HL^2·HBr.

The mixture of yellow and white precipitates were heated *in vacuo*; a faint sublimate of HL^2 appeared on the cold-finger at 145 °C. Further heating caused the mixture to melt at 190 °C, followed by the formation of a yellow deposit on the cold-finger. Recrystallisation of this material from toluene–pentane mixtures gave yellow crystals of *o*-metallated [Re(CO)$_3$L^2(HL^2)]. An i.r. spectrum of the residue from the attempted sublimation showed only the yellow product to be present. By comparison with the white product formed from an identical reaction using [Re(CO)$_5$Cl] as the reactant, the white product isolated in this reaction is believed to be [Re(CO)$_3$(HL^2)$_2$Br].

Data for o-*metallated* [Re(CO)$_3$L^2(HL^2)]. In the mass spectrum the parent ion [^{187}Re(CO)$_3$L^2(HL^2)]$^+$ was detected at *m*/*e* 746. Subsequent fragmentation was by either loss of HL^2 or carbonyl groups (see below); [Re$_2$(CO)$_6$(L^2)$_2$]$^+$ was observed to higher *m*/*e* values than the product complex.

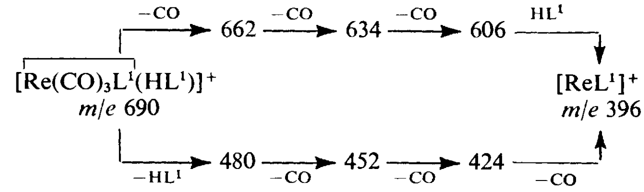


The mass spectrum of the white product was identical to that of *o*-metallated [Re(CO)$_3$L^2(HL^2)]. ^{1}H N.m.r. (CDCl$_3$): δ 6.78 (m), 2.28 (3), 2.17 (1), 2.08 (1), 1.68 p.p.m. (1).

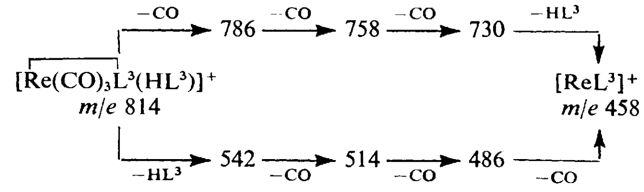
(*ii*) Using a large excess of HL^2 over [Re(CO)$_5$Br] (8 : 1 molar ratio), but an identical procedure to that described above, the yellow product, *o*-metallated [Re(CO)$_3$L^2(HL^2)], was isolated in 60% yield by fractional recrystallisation from a mixture containing excess amidine and its hydrobromide salt.

Reaction of [Re(CO)$_5$Br] *with* PhNHC(Me)NPh.—The amidine HL^1 (1.372 g, 6.54 mmol) and [Re(CO)$_5$Br] (0.885 g, 2.18 mmol) were suspended in monoglyme (50 cm^3) and the mixture heated at the reflux temperature for 5.5 h. The pale green solution was allowed to cool, the solvent removed *in vacuo*, and the residue extracted with toluene (10 cm^3). Pentane (2 cm^3) was added to the filtered extract solution which was then cooled to −10 °C. A pale yellow solid separated, which after filtration from the mother-liquor, was recrystallised from toluene–pentane mixtures to yield pale yellow crystals of *o*-metallated [Re(CO)$_3$L^1(HL^1)] (yield 0.85 g, 56%).

Addition of more pentane to the mother-liquor and further cooling produced more product, [Re(CO)$_4$(HL^1)Br] and HL^1·HBr, which were separated by fractional crystallisation procedures. In the mass spectrum of [Re(CO)$_3$L^1(HL^1)] the parent ion was detected at *m*/*e* 690 with daughter ions corresponding to two fragmentation pathways (see below); [Re$_2$(CO)$_6$(L^1)$_2$]$^+$ was detected to high mass values of the parent product ion. Metastable peaks were not observed. ^{1}H N.m.r. (CDCl$_3$): δ 7.26 (m), 2.10 (1), 1.68 p.p.m. (1).



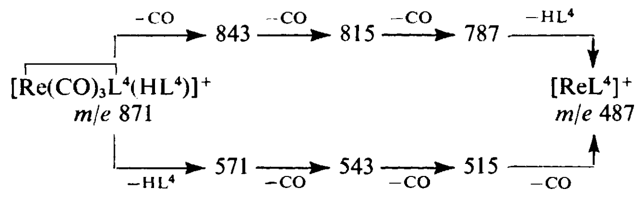
Reaction of [Re(CO)$_5$Br] *with* PhNHC(Ph)NPh.—Using an identical procedure to that described above with the reactants [Re(CO)$_5$Br] and HL^3 in a 1 : 3 molar ratio, yellow crystals of *o*-metallated [Re(CO)$_3$L^3(HL^3)] were obtained in 60% yield. In the mass spectrum the parent ion was observed at *m*/*e* 814 with daughter ions corresponding to two fragmentation pathways (see below); [Re$_2$(CO)$_6$(L^3)$_2$]$^+$ was detected to high mass values of the parent ion.



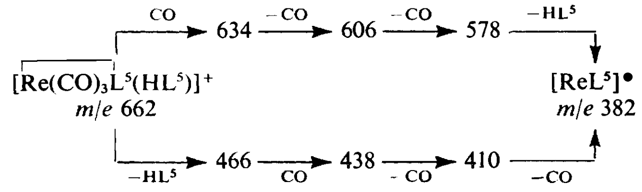
Reaction of $[Re(CO)_5Br]$ *with* p-$MeC_6H_4NHC(Ph)NC_6H_4$-Me-p.—Using the reagents in a 1 : 3 molar ratio, the procedure described above was adopted for the reaction though the product separation method used was different. At the end of the reaction after evaporation of the solvent, extraction of the residue with toluene (10 cm^3) and addition of pentane to the filtered solution produced a gummy precipitate at −10 °C. The gum and the pale yellow solution above were then treated separately.

The solution was filtered through alumina (2-cm column), then evaporated *in vacuo* to small bulk before the addition of pentane. The yellow product formed on cooling to −10 °C was shown by i.r. spectroscopy to be a predominantly *o*-metallated $[Re(CO)_3L^4(HL^4)]$ with impurities of $[Re(CO)_4(HL^4)Br]$ and a second tricarbonyl complex, identified later as $[Re(CO)_3(HL^4)_2Br]$. The mixture was heated *in vacuo* in an attempt to remove impurities by sublimation, but the mixture melted at 180 °C and pure *o*-metallated $[Re(CO)_3L^4(HL^4)]$ was collected on the cold-finger, although at a slow rate at 190 °C. Recrystallisation of the residue from toluene–pentane mixtures was preferred, and yellow crystals of *o*-metallated $[Re(CO)_3L^4(HL^4)]$ were obtained (yield 0.515 g, 28%).

The yellow gum was heated to 70 °C *in vacuo* for 2 h and crisp yellow flakes of a new tricarbonyl complex were produced with $HL^4{\cdot}HBr$. Recrystallisation twice from diethyl ether–pentane mixtures gave yellow crystals of a second isomer of *o*-metallated $[Re(CO)_3L^4(HL^4)]$ (yield 0.13 g, 7%). ^1H N.m.r. ($CDCl_3$): δ (isomer I) 6.89 (m), 2.20 (3), 2.09 p.p.m. (1); δ (isomer II) 6.83 (m), 2.17 (3), 2.07 p.p.m. (1). The mass spectra of the two isomers were identical, the parent ion being observed at *m/e* 871. Daughter ions correspond to two fragmentation pathways (see below); $[Re_2(CO)_6(L^4)_2]^+$ was detected to high mass values of the parent ion. Metastable peaks were not observed.



Reaction of $[\{Re(CO)_4Br\}_2]$ *with* PhNHCHNPh.—A mixture of the carbonyl (0.500 g, 0.661 mmol) and HL^5 (0.777 g, 3.97 mmol) in monoglyme (30 cm^3) was heated at reflux for 1.5 h. The solvent was then removed *in vacuo* from the pale yellow solution, and the residue extracted with toluene (10 cm^3). Addition of pentane (4 cm^3) and cooling to −10 °C produced yellow crystals of *o*-metallated $[Re(CO)_3L^5(HL^5)]$ which were recrystallised from toluene–pentane (yield 0.421 g, 48%). In the mass spectrum the parent ion was observed at *m/e* 662 with daughter ions corresponding to two fragmentation pathways (see below); $[Re_2(CO)_6(L^5)_2]^+$ was detected to high mass values of the parent ion.

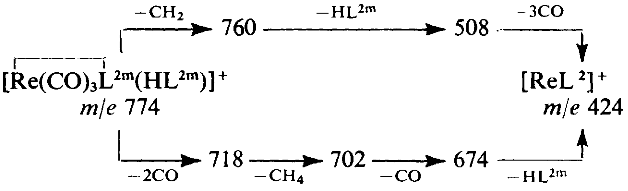


Reaction of $[Re(CO)_5Cl]$ *with* p-$MeC_6H_4NHC(Me)N$-C_6H_4Me-p.—(*i*) 1 : 3 *Molar ratio*. The procedure adopted was identical to that described above for the bromide complex. Hexane extraction of the original residue of the reaction gave yellow crystals of *o*-metallated $[Re(CO)_3L^2(HL^2)]$ (yield 0.259 g, 25%). The remaining residue consisted of a mixture of complexes, which were separated by fractional crystallisation from chloroform–hexane mixtures followed by solvent extraction with light petroleum (b.p. 100—120 °C) at 80 °C. The hot extract yielded white $[Re(CO)_3(HL^2)_2Cl]$ (yield 0.416 g, 38%). ^1H N.m.r. ($CDCl_3$): δ 7.09, 7.03 (8), 6.02, 5.90 (1), 2.33 (6), 1.63 p.p.m. (3).

The parent ion in the mass spectrum was observed as a weak peak at *m/e* 782. Thermal decomposition in the source caused loss of HCl and the formation of the *o*-metallated $[Re(CO)_3L^2(HL^2)]$, and the remaining spectrum was identical to that obtained for an authentic sample of the latter complex.

(*ii*) 1 : 2 *Molar ratio*. The reaction procedure was identical to that described immediately above. The products, $[Re(CO)_3(HL^2)_2Cl]$, *o*-metallated $[Re(CO)_3L^2(HL^2)]$, and $[Re(CO)_4(HL^2)Cl]$, were separated by fractional crystallisation methods.

Reaction of $[Re(CO)_5Br]$ *with* p-$MeC_6H_4N(Me)C(Me)N$-C_6H_4Me-p.—A mixture of $[Re(CO)_5Br]$ (0.500 g, 1.23 mmol) and HL^{2m} (0.931 g, 3.69 mmol) in monoglyme (40 cm^3) was heated to the reflux temperature for 2.5 h, forming an orange solution. On cooling a white precipitate of $HL^{2m}{\cdot}HBr$ (0.212 g) separated. Evaporation of the filtered solution *in vacuo* gave a gummy residue which was extracted with toluene (10 cm^3). Chromatography on an alumina column using toluene as eluant removed HL^{2m} but left the product complex absorbed on the alumina. Soxhlet extraction of the alumina with monoglyme, followed by reduction in volume of the pale yellow solution and cooling to −10 °C yielded pale yellow crystals of *o*-metallated $[Re(CO)_3L^{2m}(HL^{2m})]$ (yield 0.113 g, 12%). The parent ion in the mass spectrum was observed at *m/e* 774. Fragmentation was complex with initial loss of CH_2 or CO; principal daughter ions are indicated below. No metastable peaks were observed.



Reaction of o-*Metallated* $[Re(CO_3)L^{2m}(HL^{2m})]$ *with* PPh_3.—A mixture of PPh_3 (0.035 g, 0.13 mmol) and the complex (0.100 g, 0.13 mmol) dissolved in toluene (10 cm^3) was stirred at room temperature for 24 h. Reduction of the volume of the solution *in vacuo* and cooling to −10 °C produced a white solid identified as $[Re(CO)_3(PPh_3)L^2]$ which has been described earlier in this paper (yield 0.08 g, 80%).

Reactions of Other o-*Metallated* $[Re(CO)_3L(HL)]$ *Complexes with* PPh_3.—The complexes $[Re(CO)_3(PPh_3)L]$, where $L = L^1$, L^4, and L^3, were similarly prepared by the procedure described above.

Reaction of o-*Metallated* $[Re(CO)_3L^2(HL^2)$ *with* HBr.—A small sample of the complex was suspended in methanol

(10 cm^3) and hydrobromic acid (47% aqueous solution) was added dropwise. The solid changed colour from yellow to white. The liquid was removed by syringe and the white residue washed with methanol before drying *in vacuo*. I.r. spectroscopy provided identification of the product as [Re(CO)$_3$(HL^2)$_2$Br] by comparison with an authentic sample.

Reactions of [Re(CO)$_4$(COL)] *and* [Re(CO)$_4$L] *Complexes with Amidines*.—The formation of *o*-metallated products by these routes is described earlier and elsewhere.[22]

Acknowledgements

We thank the S.E.R.C. for a studentship (to J. A. C.).

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Received 28*th March* 1983; *Paper* 3/495