Rhenium Carbonyl Complexes. Synthesis and Characterisation of *NN'*-Diarylamidines, R'NHC(R)NR' (R = H, Me, or Ph, R' = Ph or C_6H_4Me-*p*), and Related Carbamoyl Derivatives

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NN'-Diarylacetamidines R'NHC(Me)NR', *NN'*-diarylbenzamidines R'NHC(Ph)NR', and *NN'*-diarylformamidines R'NHC(H)NR' (R' = Ph or C_6H_4Me-*p*) react thermally or photolytically with $[Re(CO)_5X]$ and/or $[\{Re(CO)_4X\}_2]$ (X = Cl or Br) to afford air-stable, white complexes, $[Re(CO)_4\{R'NC(R)NHR'\}X]$, containing monodentate amidine ligands. The corresponding lithioamidines (R = Me or Ph) gave white carbamoyl complexes $[Re(CO)_4\{CON(R')C(R)NR'\}]$, which are converted thermally to *NN'*-bidentate $[Re(CO)_4\{R'NC(R)NR'\}]$ and *ortho*-metallated $[\overline{\mathrm{Re(CO)_4\{R'NC(R)NHC}}\mathrm{{}_6H_3R''\}\{R'NC(R)NHR'\}}]$ (R'' = H or Me). The latter complexes are also formed by further reaction of the carbamoyl complexes with the corresponding amidine. The carbamoyl complexes react with PPh_3 to form $[Re(CO)_3(PPh_3)\{R'NC(R)NR'\}]$. Lithioamidines in excess react with $[Re(CO)_5X]$ (X = Cl or Br) complexes to give adducts formulated as $Li^+[Re(CO)_3\{CON(R')C(R)NR'\}_2]^-$. The new complexes are characterised, and structural data obtained by i.r. and n.m.r. spectroscopy.

The various bonding modes of amidines and triazines to metals have attracted much interest. In addition to bridging homo-[1-4] and hetero-nuclear[5-7] metal units, and co-ordination to metals as monodentate[8] and bidentate[9-11] groups, amidines act also as nucleophilic reagents towards co-ordinated carbonyl[9,10] and nitrile[12] groups to form five- and six-membered delocalised rings respectively. In a previous report it was shown that carbamoyl derivatives of manganese result from reactions with lithioamidines [equation (1)], but but with the parent amidines the lower nucleophilicity of the reagent leads to derivatives having symmetrical NN'-bidentate amidino-groups and displacement of carbon monoxide [equation (2)]. Related formamidino-complexes of rhenium[13]

$$[Mn(CO)_5X] + R'N(Li)C(R)NR' \longrightarrow$$
$$(X = Cl \text{ or } Br)$$
$$[Mn(CO)_4\{CON(R')C(R)NR'\}] + LiX \quad (1)$$

$$[Mn(CO)_5X] + 2R'NHC(R)NR' \longrightarrow$$
$$(X = Cl \text{ or } Br)$$
$$[Mn(CO)_4\{R'NC(R)NR'\}] + [R'NHC(R)NHR']^+X^- \quad (2)$$

and some substitution products[14] have recently been reported and shown to have properties closely similar to the properties of manganese complexes.

In this paper we report reactions of rhenium carbonyl halides with acetamidines and benzamidines which represent an extension of the previously reported manganese reactions.[10] Many differences are noted between the manganese and rhenium systems. For example, amidines (HL) react with $[Mn(CO)_5X]$ (X = Br or Cl) in a 2 : 1 mol ratio to form NN'-bidentate $[Mn(CO)_4L]$ complexes and HL·HX with no evidence for the intermediate formation of $[M(CO)_4(HL)X]$ which are found for rhenium. For both manganese and rhenium, $[M(CO)_4L]$ complexes can be synthesised, although in the case of manganese substitution of carbon monoxide by triphenylphosphine could not be achieved as occurs for rhenium. Furthermore, *ortho*-metallated complexes were found for rhenium but not for manganese.

Results and Discussion

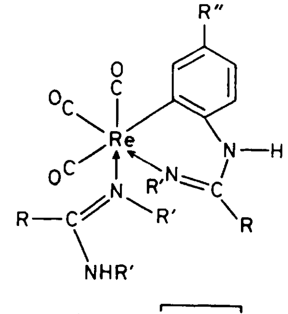
A. Carbamoyl Complexes.—Lithiodiaryl-benzamidines and -acetamidines in monoglyme (1,2-dimethoxyethane) or diethyl ether solutions react with $[Re(CO)_5X]$ (X = Cl or Br) to form air-stable white complexes of the type $[Re(CO)_4(COL)]$ (see Table 1). In solution the complexes decompose only over a period of months when exposed to air. Overall yields of pure materials were low, 20—30%, although the reactions themselves were more efficient, estimated as 60%

Table 1. Analytical data, melting points, and yields for $[Re(CO)_4(COL)]$ and $[Re(CO)_3(PPh_3)L]$ complexes

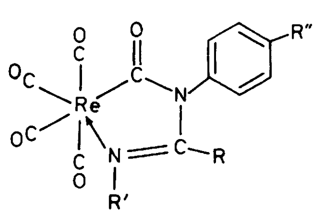
		Analysis * (%)			
Complex	M.p./°C	C	H	N	Yield (%)
$[Re(CO)_4\{CON(Ph)C(Me)NPh\}]$	123.5	42.6 (42.6)	2.45 (2.45)	5.35 (5.25)	32
$[Re(CO)_4\{CON(C_6H_4Me\text{-}p)C(Me)NC_6H_4Me\text{-}p\}]$	158 (decomp.)	44.7 (44.7)	3.15 (3.05)	5.15 (4.95)	31
$[Re(CO)_4\{CON(Ph)C(Ph)NPh\}]$	123 (decomp.)	48.0 (48.2)	2.55 (2.50)	4.70 (4.70)	18
$[Re(CO)_4\{CON(C_6H_4Me\text{-}p)C(Ph)NC_6H_4Me\text{-}p\}]$		49.9 (49.9)	3.10 (3.05)	4.50 (4.50)	22
$[Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}]$		57.8 (57.5)	3.65 (3.75)	4.15 (4.65)	80

* Calculated values in parentheses.

from solution i.r. measurements of the reaction mixture. Some difficulty was encountered in increasing the recovered yield of product due to the presence of starting materials and secondary products such as *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$ (see below). A good separation could not be achieved by chromatography on silica gel and alumina using a wide variety and combination of solvents, and sublimation was successful only for $[\mathrm{Re(CO)_4(COL^2)}]$ where the impurities sublimed. The other complexes melted at approximately the same temperature as that of sublimation of the parent amidine (*ca.* 125 °C) and the resulting melt decomposed with the formation of NN′-bidentate $[\mathrm{Re(CO)_4L}]$ and *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$. Fractional crystallisation from dichloromethane solutions proved the most reliable purification method, although attempts to increase the recovery by forcing precipitation resulted in samples contaminated with $[\mathrm{Re(CO)_5X}]$ and *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$.



o-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$



$[\mathrm{Re(CO)_4(COL)}]$

	R	R′	R″
L^1	Me	Ph	H
L^2	Me	$\mathrm{C_6H_4Me}$-*p*	Me
L^3	Ph	Ph	H
L^4	Ph	$\mathrm{C_6H_4Me}$-*p*	Me
L^5	H	Ph	H

The complexes are assigned the carbamoyl structure, *e.g.* see Figure 1, on the basis of i.r. and ^{13}C n.m.r. data. The complexes display the typical pattern of terminal carbonyl absorptions in the ν(CO) stretching region (Table 2) for *cis*-substituted octahedral tetracarbonyl complexes together with a carbamoyl carbonyl absorption at 1 650—1 675 cm^{-1} in the i.r. (1 661—1 673 cm^{-1} in Raman). The general formulation is confirmed by mass spectrometry for the acetamidino-complexes, for which the parent-ion peaks were detected. However, for the benzamidino-complexes, the ion of highest *m/e* value corresponded to $[\mathrm{Re(CO)_4L}]^+$, possibly due to thermal decomposition of the sample in the source and selective volatility of the product molecules. Fragmentation corresponding to loss of −COL was not detected, indicating that the carbamoyl CO−N bond is broken and carbonyl groups lost before fragmentation of the nitrogen ligand. There was no evidence of $[\mathrm{Re(CO)}_x]^+$ (x = 1—5) species (indicating that the amidine is not easily cleaved from rhenium) nor evidence for any metastable peaks.

In addition to the carbamoyl carbonyl absorptions at 1 650—1 675 cm^{-1}, the i.r. spectra are characterised by absorptions in the ranges 1 569—1 583s and 1 268—1 282ms cm^{-1}. The former absorption, assigned to a predominantly N−C−N asymmetrical stretching vibration, is approximately 40—50 cm^{-1} lower than the related vibration of the parent amidine, and is observed in a position similar to other related delocalised chelate systems.[14] The latter absorption (1 268—1 282 cm^{-1}) (Raman absorption at 1 274—1 286 cm^{-1}) is also characteristic of related chelate systems.[14] ^{1}H N.m.r. studies were found to be of limited value. No differences were observed in the *p*-tolyl methyl signals of N-substituents even though the tolyl groups are bound to nitrogens in different environments. The possibility of a rapid exchange process involving interchange of the two nitrogens was investigated by cooling a solution of $[\mathrm{Re(CO)_4(COL^2)}]$ to −60 °C, and recording its ^{1}H n.m.r. spectrum over a range of temperatures, but no change was observed. It is concluded that the molecule is non-fluxional and that the *p*-tolyl methyl groups are too far removed from the unsymmetrical bonding of the amidino-nitrogens to be sensitive to the differing bonding situations. This conclusion was reached for the analogous manganese complexes [10] and the formamidino-complexes of rhenium.[13] The different environments of the aryl groups in $[\mathrm{Re(CO)_4(COL^1)}]$ were readily detected by ^{13}C n.m.r. spectroscopy. The data, given in Figure 1, are consistent only with the presence of a carbamoyl ligand and eliminate a $[\mathrm{Re(CO)_5\{R'NC(R){=}NR'\}}]$ structure, having a monodentate amidino-group, since the latter would show only three types of carbonyl carbon nuclei in the ratio 2 : 2 : 1, rather than the ratio observed.

The two reaction schemes which may lead to the formation of carbamoyl complexes have been outlined previously,[10] and for the reactions described here which use lithioamidines, the nucleophilic attack by the amidino-group at the carbon of a carbonyl group seems the most likely route. In common with the $[\mathrm{Mn(CO)_4(COL)}]$ [10] and formamidino-rhenium [13] complexes, the $[\mathrm{Re(CO)_4\{CON(R')C(R)NR'\}}]$ complexes also undergo decarbonylation to form NN′-bidentate tetracarbonyl complexes, $[\mathrm{Re(CO)_4\{R'NC(R)NR'\}}]$, on heating. Unlike the manganese complexes, however, this occurred only in the solid state, and not in solution except under prolonged u.v. irradiation. A mixture of products was formed including $[\mathrm{Re(CO)_4L}]$ and *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$.

The reaction of $[\mathrm{Re(CO)_4(COL)}]$ with triphenylphosphine in monoglyme results in carbonyl displacement and the amidino-group becomes bidentate [*e.g.* equation (3)]. The process may occur by route A (Figure 2), initial decarbonylation to form NN′-bidentate $[\mathrm{Re(CO)_4\{R'NC(R)NR'\}}]$ followed by a substitution reaction, *or* route B, initial dis-

Table 2. I.r. and Raman carbonyl stretching frequencies for $[Re(CO)_4\{CON(R')C(R)NR'\}]$ complexes

Complex		I.r./Raman	$\nu(CO)/cm^{-1}$	Carbamoyl $\nu(CO)/cm^{-1}$
$[Re(CO)_4(COL^2)]$	CH_2Cl_2	I.r.	2 090m, 1 990 (sh), 1 983vs, 1 948vs	
	Nujol	I.r.	2 081m, 1 988vs, 1 980vs, 1 970vs, 1 924vs	1 665s
	Solid	Raman	2 080s, 1 980vs, 1 927s	1 670w
$[Re(CO)_4(COL^1)]$	CH_2Cl_2	I.r.	2 096w, 1 990 (sh), 1 987vs, 1 942m	
	Nujol	I.r.	2 090m, 1 994vs, 1 967vs, 1 932vs	1 671s
	Solid	Raman	2 095w, 2 076s, 1 979vs, 1 947m, 1 918w	1 673w
$[Re(CO)_4(COL^3)]$	CH_2Cl_2	I.r.	2 098m, 1 997 (sh), 1 987vs, 1 947s	
	Nujol	I.r.	2 096m, 2 022vs, 1 988vs, 1 969vs, 1 937vs, 1 913vs	
	Solid	Raman	2 095vs, 1 999vs, 1 990vs, 1 946vs, 1 912vs	1 663w
$[Re(CO)_4(COL^4)]$	CH_2Cl_2	I.r.	2 093w, 2 000 (sh), 1 988vs, 1 948s	
	Nujol	I.r.	2 093m, 2 008 (sh), 1 989vs, 1 973vs, 1 938vs, 1 921vs	1 650s
	Solid	Raman	*	
$[Re(CO)_4(COL^5)]$	CH_2Cl_2	I.r.	2 098m, 1 996 (sh), 1 990vs, 1 948s	
	Nujol	I.r.	2 108w, 2 000 (sh), 1 977vs, 1 940vs	1 675s

* Sample fluoresced.

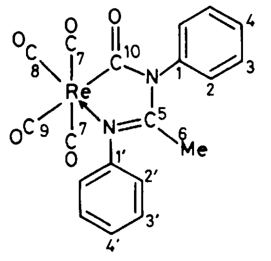


Figure 1. Structure and ^{13}C n.m.r. data for $[Re(CO)_4\{CON(Ph)C(Me)NPh\}]$: 1,1′ = 152.6, 138.8; 2,2′ = 123.38, 122.8; 3,3′ = 129.5, 129.8; 4,4′ = 126.5, 124.2; 5 = 167.6; 6 = 16.84; 7 = 193.3; 8,9 = 188, 186.3; 10 = 176.7

$$[Re(CO)_4\{CON(C_6H_4Me\text{-}p)C(Me)NC_6H_4Me\text{-}p\}] + PPh_3 \longrightarrow [Re(CO)_3(PPh_3)\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}] + 2CO \quad (3)$$

placement of a terminal carbonyl group by the phosphine followed by further loss of carbon monoxide to enable the amidino-group to become bidentate. The reaction was slow, requiring more than 24 h for completion. No intermediate complexes were detected by i.r. spectroscopy, although $[Re(CO)_4\{R'NC(R)NR'\}]$, if formed in sufficient concentration, would be detectable. This complex is known (see later) to react with triphenylphosphine to form $[Re(CO)_3(PPh_3)\{R'NC(R)NR'\}]$. The individual stages of route A have been separately established, and this route is the most probable considering the reaction time involved. Although stages (*i*) and (*ii*) were not achieved over a 2 h period in the absence of phosphine (see Experimental section), it is quite possible that over 27 h, reactions (*i*) and (*ii*) could be achieved for the small sample used. Route B involves the intermediate formation of a substituted carbamoyl complex which might be expected to be detectable, although its i.r. spectrum would be very similar to the final product except in the carbamoyl carbonyl stretching region. No evidence for this intermediate was obtained.

A further slow substitution reaction occurred between the carbamoyl complexes and amidines. The product results from carbonyl substitution but also involves a change in the bonding mode of one of the amidines to the *ortho*-metallated type to form *o*-metallated $[Re(CO)_3L(HL)]$ complexes.

Reaction of excess $p\text{-}MeC_6H_4N(Li)C(Me)NC_6H_4Me\text{-}p$ with $[Re(CO)_5Br]$ gave a red solution containing a new carbonyl complex having $\nu(CO)$ stretching frequencies at low frequencies [tetrahydrofuran (thf) solution: 1 990s, 1 893s, 1 862s, cm^{-1}]. The low frequencies suggest the formation of an anionic species, which partially reverted to $[Re(CO)_4(COL^2)]$ overnight, and suggests that the complex retains five carbonyl groups. The evidence is consistent with the formation of a complex of the type $Li^+[Re(CO)_3(COL^2)_2]^-$ having one amidino-group in a carbamoyl ring, with the other forming a unidentate carbamoyl group (Figure 3). The lithium would probably be co-ordinated to the carbamoyl carbonyl group of the chelate ring, and either a nitrogen or carbonyl of the unidentate carbamoyl group. The slow reverse reaction to form $[Re(CO)_4(COL^2)]$ was probably caused by consumption of the lithioamidine through air, or moisture diffusing into the apparatus, or through reaction with the solvent [equation (4)].

$$[Re(CO)_4(COL^2)] + LiL^2 \rightleftharpoons Li^+[Re(CO)_3(COL^2)_2]^- \quad (4)$$

In the mass spectra of the L^2 and L^4 carbamoyl complexes, ions corresponding to $[Re_2(CO)_6(L)_2]^+$ were detected, arising possibly from small fractions of impurities in the samples, or to thermal decomposition products in the heated source. Complexes of the type $[Re_2(CO)_6(L)_2]$ have not however been isolated, and if the mass spectral data relate to a molecular species $[Re_2(CO)_6(L)_2]$, the most probable structure is one having two amidino-groups bridging $Re(CO)_3$ units linked with a Re=Re double bond. Interestingly the same ion is not observed in the mass spectra of $[Re(CO)_4L]$ complexes, the thermolysis products of the carbamoyl complexes, nor could the dimeric complex be synthesised from these materials.

B. Complexes containing Amidines as Two-electron Donors.—The complexes $[Re(CO)_4(HL)X]$ (X = Cl or Br) were formed readily in good yield by the reaction of $[\{Re(CO)_4X\}_2]$ with *NN′*-diaryl-benzamidines, -acetamidines, and -formamidines in monoglyme solution. At room temperature reaction proceeded slowly, and gentle heating was necessary for convenient reaction times (16 h). The reaction temperature was

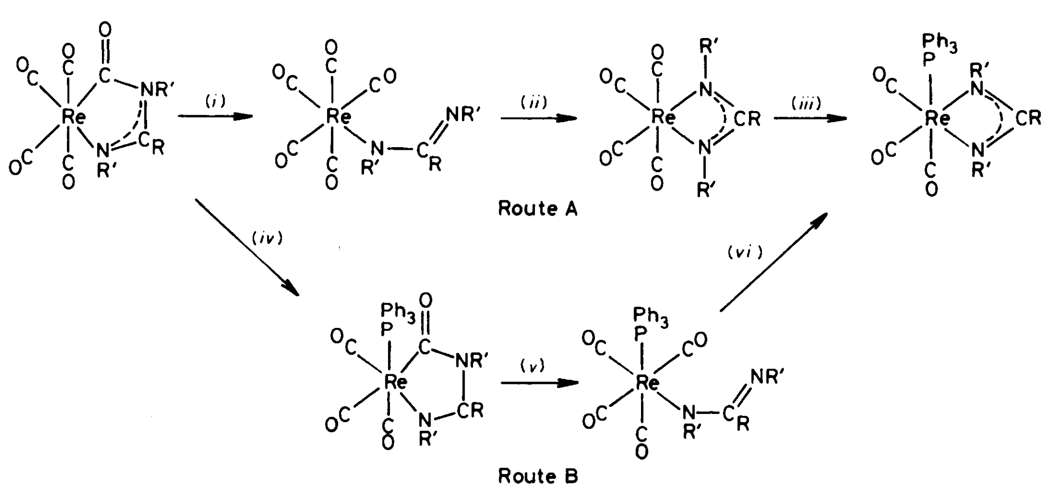


Figure 2. Alternative schemes for the reaction of $[Re(CO)_4(COL)]$ carbamoyl complexes with PPh_3

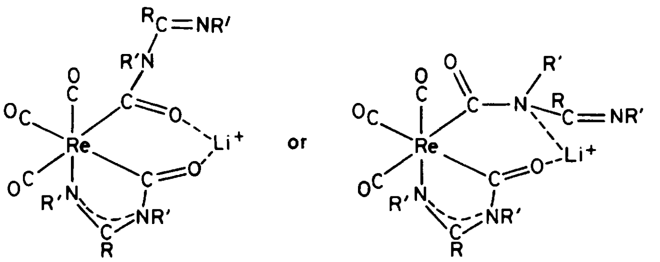


Figure 3. Suggested alternative structures for $Li[Re(CO)_3(COL)_2]$ complexes

critical because above a threshold (*ca.* 40 °C for the bromide and 55 °C for the chloride) a second product, *o*-metallated $[\overline{Re(CO)_3L}(HL)]$, began to form. U.v. irradiation of 1 : 1 mol ratios of $[Re(CO)_5Br]$ and HL^2 in toluene also produced $[Re(CO)_4(HL^2)Br]$ as well as small amounts of $[Re(CO)_4L]$, but a 1 : 2 reaction did not produce $[Re(CO)_4L]$ and $HL{\cdot}HBr$ nor $[Re(CO)_3(HL)_2Br]$ as desired, the only product being the monosubstituted derivative.

The complexes are all pure white crystalline solids of moderately good solubility in organic solvents. They are stable indefinitely in air, both as a solid and in solution. They sublime *in vacuo* at 100 °C but decompose above this temperature. The formulation of the complexes as $[Re(CO)_4(HL)X]$ from analytical data (Table 3) is strongly supported by spectroscopic results. The i.r. spectra show four terminal carbonyl stretching frequencies (Table 4) consistent with a *cis*-substituted octahedral species. The broad weak ν(N–H) stretching frequencies at *ca.* 3 220 cm^{-1} [*cf.* free amidine ν(N–H) *ca.* 3 280 cm^{-1}] are consistent with the amidine acting as a two-electron donor and retaining the N–H unit.

In mass spectrometry, the parent ion is not observed for any of the complexes; a peak corresponding to the daughter ion $[Re(CO)_4(HL)]^+$ was always observed followed by further peaks corresponding to the stepwise loss of four carbonyl groups. The spectrum of $[Re(CO)_4(HL^2)Br]$ showed that a second fragmentation pattern was possible; here an ion corresponding to $[^{187/185}Re^{79/81}Br(CO)_4]^+$ was observed at *m/e* 378, followed by daughter ions corresponding to the loss of four carbonyl groups. Metastable peaks were only observed for one of the series, and arose from the $[Re(CO)_4L^1]^+ \longrightarrow [Re(CO)_3L^1]^+$ and $[Re(CO)_3L^1]^+ \longrightarrow [Re(CO)_2L^1]^+$ fragmentations.

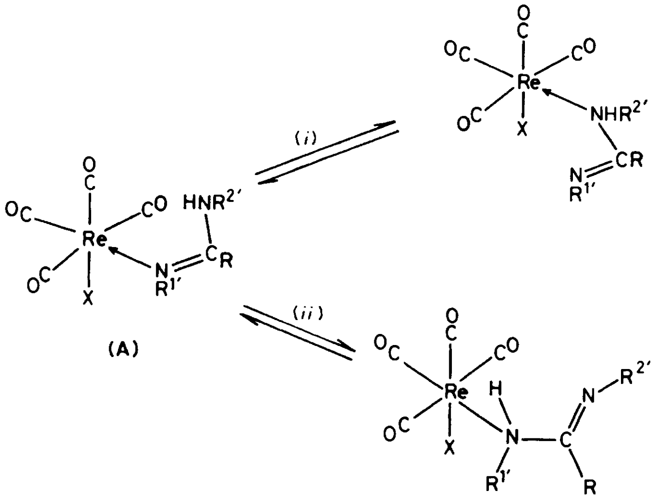


Figure 4. Fluxional processes possible for $[Re(CO)_4(HL)X]$ (X = Cl or Br)

Although an amidine has the potential to bond to a metal as a two-electron donor through either of two nitrogen atoms or the C=N π system, bonding through the imino-nitrogen is most likely. The imino-nitrogen is more basic than the amino-nitrogen and would be expected to form a stronger bond to the rhenium. Such a structure [Figure 4, structure (A)] is most likely to occur in the solid state, but in solution there remains the possibility of (*i*) interchange between imino- and amino-bonding by movement of the amidine or (*ii*) the N-proton undergoing 1,3-shifts with a corresponding change in the position of the C=N double bond, and consequent changes between Re–imino and Re–amino bonding. However, for process (*i*) the $R^{1'}$ substituent will experience changes from a co-ordinated imino-substituent to an unco-ordinated imino-substituent and $R^{2'}$ from an unco-ordinated amino- to a co-ordinated amino-substituent. For process (*ii*), $R^{1'}$ is transformed from a co-ordinated imino- to a co-ordinated amino-subsubstituent, and $R^{2'}$ from an unco-ordinated amino- to an unco-ordinated imino-substituent. The effects of this type of fluxionality would not lead necessarily to the equivalence of the signals for the two nitrogen substituents in the ^{13}C n.m.r. spectra, but would lead more to a broadening of the two distinct sets of signals. No evidence

Table 3. Analytical data, melting points, and yields for $[Re(CO)_4(HL)X]$ (X = Cl or Br) and $[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)N(Me)C_6H_4Me\text{-}p\}Br]$

Compound	M.p.[a]/°C	Analysis [b] (%)				Reaction yield (%)
		C	H	N	Br or Cl	
$[Re(CO)_4(HL^2)Br]$	113	39.20	3.00	4.50	12.80	83
		(38.95)	(3.90)	(4.55)	(12.95)	
$[Re(CO)_4(HL^1)Br]$	115	36.45	2.40	4.70	13.45	80
		(36.70)	(2.30)	(4.75)	(13.50)	
$[Re(CO)_4(HL^4)Br]$	112	43.95	3.00	4.00	12.95	70
		(44.25)	(2.95)	(4.15)	(11.80)	
$[Re(CO)_4(HL^3)Br]$	124	42.30	2.55	4.15	12.40	70
		(42.50)	(2.45)	(4.30)	(12.30)	
$[Re(CO)_4(HL^5)Br]$	125	34.50	1.95	4.50	14.15	60
		(35.55)	(2.10)	(4.90)	(13.90)	
$[Re(CO)_4(HL^2)Cl]$	112	41.70	2.75	4.75	6.25	55
		(42.00)	(2.95)	(4.90)	(6.20)	
$[Re(CO)_4(HL^1)Cl]$	110	40.10	2.60	5.20	6.60	53
		(39.70)	(2.55)	(5.15)	(6.55)	
$[Re(CO)_4(HL^4)Cl]$	125	47.60	3.80	4.50	5.65	50
		(47.35)	(3.45)	(4.40)	(5.60)	
$[Re(CO)_4(HL^5)Cl]$	124	45.80	2.75	4.65	5.90	54
		(45.55)	(2.65)	(4.60)	(5.85)	
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)N(Me)C_6H_4Me\text{-}p\}Br]$	90	39.60	3.35	4.40	12.75	24
		(40.00)	(3.15)	(4.45)	(12.70)	

[a] With decomposition. [b] Calculated values are given in parentheses.

Table 4. Infrared spectral data for $[Re(CO)_4(HL)X]$ (X = Cl or Br) and $[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)N(Me)C_6H_4Me\text{-}p\}Br]$

Compound	ν(CO) */cm⁻¹				ν(NH)/cm⁻¹ (Nujol)
	1m	2vs	3vs	4vs	
$[Re(CO)_4(HL^2)Br]$	2 102	2 002	1 981	1 918	3 228w, br
	(2 122)	(2 022)	(1 991)	(1 949)	
$[Re(CO)_4(HL^1)Br]$	2 104	1 993	1 984	1 924	3 210w, br
	(2 108)	(2 012)	(1 986)	(1 936)	
$[Re(CO)_4(HL^4)Br]$	2 110	2 020	1 991	1 911	3 210w, br
	(2 108)	(2 013)	(1 985)	(1 913)	
$[Re(CO)_4(HL^3)Br]$	2 100	2 010	1 982	1 912	3 230w, br
	(2 121)	(2 020)	(1 992)	(1 939)	
$[Re(CO)_4(HL^5)Br]$	2 102	2 018	1 982	1 910	3 228w, br
	(2 120)	(2 018)	(1 994)	(1 941)	
$[Re(CO)_4(HL^2)Cl]$	2 104	2 002	1 980	1 913	3 222w, br
	(2 115)	(2 018)	(1 985)	(1 931)	
$[Re(CO)_4(HL^1)Cl]$	2 104	1 996	1 982	1 922	3 220br
	(2 108)	(2 012)	(1 986)	(1 932)	
$[Re(CO)_4(HL^4)Cl]$	2 104	2 016	1 990	1 922	3 210w, br
	(2 108)	(2 015)	(1 986)	(1 931)	
$[Re(CO)_4(HL^5)Cl]$	2 104	2 020	1 986	1 918	3 224w, br
	(2 110)	(2 017)	(1 986)	(1 913)	
$[Re(CO)_4\{p\text{-}MeC_6H_4NC(Me)N(Me)C_6H_4Me\text{-}p\}Br]$	2 102	2 002	1 969	1 910	—
	(2 100)	(2 006)	(1 972)	(1 911)	

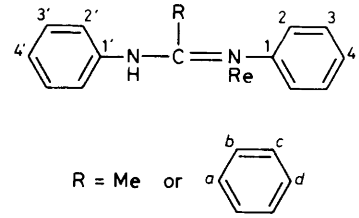
* In Nujol mull; values in parentheses denote frequencies obtained in CH_2Cl_2 solution.

for fluxionality was obtained from ^1H and ^{13}C n.m.r. spectra over a range of temperatures, and separate ^{13}C signals were observed for the nitrogen substituents. This is in contrast to platinum and palladium complexes where exchange process (*i*) occurs involving interchange of nitrogen atoms bonded to the metal.

For the *NN'*-di-*p*-tolylbenzamidine complex, ^1H n.m.r. failed to distinguish clearly between the two *p*-tolyl methyl environments; only for $[Re(CO)_4(HL^2)X]$ (X = Cl or Br) was a small difference observed [$\Delta\delta = 0.03$ (Br), 0.02 (Cl) p.p.m.]. The ^{13}C n.m.r. spectra (Table 5), however, showed clearly that the aryl groups were in different chemical environments. Three types of carbonyl carbon were also observed, consistent with a *cis*-substituted tetracarbonyl species. Interestingly the central carbon atom of the N–C–N skeleton has a chemical shift about 16 p.p.m. downfield from that of the the free amidine, at approximately the same value as for the carbamoyls, $[Re(CO)_4(COL)]$, and NN'-chelate $[Re(CO)_4L]$ complexes. This indicates a similar environment in each case, and which is probably due to a similar degree of delocalisation in each complex.

The very slow reaction of the NNN'-trisubstituted amidine, PhN(Me)C(Me)NPh, with $[\{Re(CO)_4Br\}_2]$ may be partially attributable to steric effects. NN'-Disubstituted amidines can attack the metal using either of the nitrogen atoms and lead to the same product because of facile 1,3-proton transfer once the amidine is co-ordinated, *e.g.* equation (5). Such a mechanism is not possible for a NNN'-trisubstituted amidine

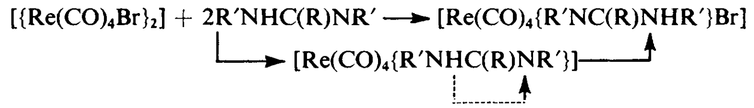
Table 5. ^{13}C N.m.r. Spectra (δ/p.p.m.) of $[Re(CO)_4(HL)X]$ (X = Cl or Br)



Complex	Aromatic carbons				Carbonyls	
	C^1, $C^{1'}$	C^2, $C^{2'}$	C^3, $C^{3'}$	C^4, $C^{4'}$	2CO	CO
$[Re(CO)_4(HL^1)Cl]$	153.71	124.33	130.05	126.93	187.14	185.29
	138.24	124.98	130.83	130.83		187.94
$[Re(CO)_4(HL^2)Cl]$	157.48	123.68	130.05	125.38	186.59	184.82
	141.76	123.81	130.05	129.38		187.47
$[Re(CO)_4(HL^2)Br]$	157.41	123.66	130.02	125.82	186.55	184.82
	141.95	124.57	130.02	130.68		187.47
$[Re(CO)_4(HL^3)Cl]$	151.73	124.59	130.53	126.93	186.20	185.69
	140.02	125.37	130.18	129.66		187.37
$[Re(CO)_4(HL^3)Br]$	153.00	124.81	130.33	125.72	185.70	185.03
	136.76	125.46	129.03	130.72		186.68
$[Re(CO)_4(HL^4)Cl]$	150.98	125.11	129.40	135.57	186.20	185.68
	135.88	122.14	129.01	134.82		187.50
$[Re(CO)_4(HL^4)Br]$	150.90	125.17	130.76	134.53	186.78	185.34
	135.57	122.18	130.11	135.18		185.74
$[Re(CO)_4(HL^5)Br]$	154.57	123.61	129.98	125.30	185.61	183.62
	137.78	123.09	129.59	127.12		186.26

Complex	*p*-Tolyl Me	R = Me	N-C=N	R = phenyl			
				a	*b*	*c*	*d*
$[Re(CO)_4(HL^1)Cl]$	—	17.88	169.31	—	—	—	—
$[Re(CO)_4(HL^2)Cl]$	21.00 21.00	17.36	168.93	—	—	—	—
$[Re(CO)_4(HL^2)Br]$	20.87 20.87	17.10	168.88	—	—	—	—
$[Re(CO)_4(HL^3)Cl]$	—	—	167.64	122.14	128.03	128.62	123.68
$[Re(CO)_4(HL^3)Br]$	—	—	168.24	122.14	128.25	128.70	123.83
$[Re(CO)_4(HL^4)Cl]$	20.61 20.61	—	168.66	123.45	129.92	130.44	129.68
$[Re(CO)_4(HL^4)Br]$	20.80 20.80	—	168.06	123.61	128.16	129.20	129.59
$[Re(CO)_4(HL^5)Br]$	—	—	159.10	—	—	—	—

for which the amino-nitrogen is sterically shielded, and the reaction proceeds only by attack by the imino-nitrogen. Consequently the rate is much slower.



$$[\{Re(CO)_4Br\}_2] + 2R'NHC(R)NR' \longrightarrow [Re(CO)_4\{R'NC(R)NHR'\}Br] \qquad (5)$$
$$[Re(CO)_4\{R'NHC(R)NR'\}]$$

The complex $[\{Re(CO)_3Br\}_4]$, detected in the mass spectra of $[Re(CO)_4\{PhNC(Me)N(Me)Ph\}Br]$, is thought to arise from loss of the amidine ligand through decomposition of the complex when injected into the mass spectrometer. This is a feature common to many rhenium complexes, and indeed Abel and Bhatti[15] noted that it is difficult to obtain mass spectra for many complexes without the tetramer appearing as an ion along with all of its fragmentation products. The absence of the tetramer in the mass spectra of the $[Re(CO)_4(HL)X]$ complexes arises from an alternative facile reaction, the loss of HX to form $[Re(CO)_4L]$ on mild thermolysis, a process which is excluded for $[Re(CO)_4\{PhNC(Me)N(Me)Ph\}Br]$.

The complexes $[Re(CO)_4(HL)X]$ (X = Cl or Br) may be used as precursors for other rhenium amidine complexes. It was found that in hydrocarbon or ether solutions the complexes could be converted to the NN'-chelated amidino-complex $[Re(CO)_4L]$ by the addition of an equimolar amount of n-butyl-lithium, and to the *ortho*-metallated complexes $[Re(CO)_3L(HL)]$ in monoglyme solution containing additional amidine either thermally or photolytically. These reactions [equations (6) and (7)] have been previously discussed.[16]

$$[Re(CO)_4(HL)X] + LiBu^n \longrightarrow [Re(CO)_4L] + LiX + Bu^nH \qquad (6)$$

$$[Re(CO)_4(HL)X] + 2HL \longrightarrow [Re(CO)_3L(HL)] + HL{\cdot}HX \qquad (7)$$

Experimental

The amidines, [$Re(CO)_5X$], [{$Re(CO)_4X$}$_2$], and [$Re(CO)_4(EPh_3)X$] (X = Cl or Br; E = P or As) were prepared by standard methods.[17,18] All solvents were dried and rigorously degassed before use. Reactions were undertaken under an atmosphere of nitrogen. Alumina used was by Woelm (neutral activity III); $LiBu^n$ in hexane solution (3.5 mol dm^{-3}) was supplied by Alfa.

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 [$Re(CO)_5Br$] *with* p-$MeC_6H_4N(Li)C(Me)NC_6H_4Me$-$p$.—n-Butyl-lithium (1.23 mmol in hexane solution) was added to a frozen solution of HL^2 (0.293 g, 1.23 mmol) in diethyl ether (35 cm^3) at −196 °C, and the mixture allowed to warm to room temperature. After stirring at this temperature for 15 min the suspension formed was refrozen to −196 °C and a suspension of [$Re(CO)_5Br$] (0.500 g, 1.23 mmol) in diethyl ether (5 cm^3) added. The pale yellow solution, formed on warming to room temperature, was stirred for an additional 2 h, before cooling to −16 °C for 24 h to encourage precipitation of the product. I.r. spectroscopy showed [$Re(CO)_5Br$] remaining in solution, but additional time did not result in further changes taking place. After filtration of the reaction mixture, the solid was dissolved in dichloromethane (20 cm^3), and the solution filtered through a column (2.5 cm) of alumina to remove lithium bromide. Crystallisation of the product was induced by reducing the volume of solvent, addition of ether, and cooling. The product, [$Re(CO)_4(COL^2)$], was obtained as a white crystalline solid (yield 0.216 g, 31%). ^1H N.m.r. ($CDCl_3$): δ (number of protons in parentheses) 7.1 (m) (8), 2.40 (s) (6), and 1.87 (3) p.p.m.

In an attempt to increase the yield of the pure product, thf was used as the solvent but a mixture of products was obtained at room temperature. Heating this solution to the reflux temperature led to the formation of an *ortho*-metallated complex, [$\overline{Re(CO)_3L^2}(HL^2)$].

Using an excess of LiL^2 in thf in a room temperature reaction, new absorptions appeared in the i.r. spectra at 1 990vs, 1 893vs, and 1 862vs cm^{-1} but on prolonged stirring of the solution (12 h), absorptions due to the original product, [$Re(CO)_4(COL^2)$], reappeared at 2 095w, 1 975vs, and 1 945vs cm^{-1}. Addition of a further quantity of the lithioreagent again produced the new product, and the process was found to be reversible. The new complex could not be isolated, the original carbamoyl complex being the only product.

Reaction of [$Re(CO)_5Br$] *with* $PhN(Li)C(Me)NPh$.—To a solution of HL^1 (0.517 g, 2.46 mmol) in monoglyme (50 cm^3) frozen to −196 °C was added n-butyl-lithium (2.46 mmol in hexane solution), and the mixture allowed to warm to room temperature and stirred for 15 min. The pale yellow solution was refrozen to −190 °C and finely powdered [$Re(CO)_5Br$] (1.00 g, 2.46 mmol) added. On warming the solution to room temperature and stirring for 2.5 h, an i.r. spectrum showed the presence of more than one product. The solution was reduced in volume to 4 cm^3, hexane (1 cm^3) added, and the mixture cooled to −10 °C. Unreacted [$Re(CO)_5Br$] and some lithium bromide separated. The mother-liquor was evaporated (*in vacuo*) to dryness and the residue extracted with dichloromethane (10 cm^3). The resulting solution was filtered through alumina (2.5 cm) and reduced in volume before the addition of ether. The main product, [$Re(CO)_4(COL^1)$], crystallised first on cooling as white needles (0.423 g, 32%), followed, on addition of hexane, by *ortho*-metallated [$\overline{Re(CO)_3L^1}(HL^1)$]. ^1H N.m.r. spectrum of [$Re(CO)_4(COL^1)$] ($CDCl_3$): δ 7.38 (m) (10) and 1.86 (s) (3) p.p.m.

Reaction of [$Re(CO)_5Br$] *with* $PhN(Li)C(Ph)NPh$.—The procedure described above for HL^1 was adopted. The main product, [$Re(CO)_4(COL^3)$], was obtained as a white solid (yield 0.268 g, 18.3%). Attempts to obtain further quantities of product from the mother-liquor produced a mixture of [$Re(CO)_5Br$], [$Re(CO)_4(COL^3)$], [$\overline{Re(CO)_3L^3}(HL^3)$], and HL^3.

Reaction of [$Re(CO)_5Br$] *with* p-$MeC_6H_4N(Li)C(Ph)NC_6H_4Me$-$p$.—The procedure described above for HL^1 was followed, giving the product, [$Re(CO)_4(COL^4)$], as a white powder (yield 0.167 g, 21.7%).

Reaction of [$Re(CO)_5Cl$] *with Lithioamidines*.—[$Re(CO)_5Cl$] was used in place of the bromide in analogous reactions with LiL (L = L^1—L^4). The products [$Re(CO)_4(COL)$] were formed similarly but yields were not improved.

Decarbonylation of [$Re(CO)_4(COL^2)$].—(*i*) The complex (0.042 g) was heated to 155 °C under vacuum (10^{-2} Torr, ≈ 13 Pa) for 1 h. The sample remained unchanged, as confirmed by i.r. spectroscopy. On gradually increasing the temperature to 180 °C, causing the sample to turn yellow, a yellow sublimate appeared on a cold-finger (6 °C). The sublimate was identified as the decarbonylated complex [$Re(CO)_4L^2$] [ν(CO) absorptions at 2 101w, 1 991vs, 1 975vs, 1 938s, and 1 915wm (sh) cm^{-1}, Nujol]. Extraneous ν(CO) absorptions at 2 084s and 1 928s cm^{-1} were also observed.

(*ii*) Attempts to decarbonylate the complex in refluxing thf for 4 h and refluxing monoglyme for 2 h were unsuccessful. U.v. irradiation of the thf solution for 2.5 h resulted in the formation of a brown solution, and although new ν(CO) absorptions were detected at 2 008m, 1 994m, 1 912m, and 1 890m cm^{-1}, no product could be isolated.

Reaction of [$Re(CO)_4(COL^2)$] *with* HL^2.—A mixture of [$Re(CO)_4(COL^2)$] (0.016 g, 0.11 mmol) and HL^2 (0.026 g, 0.11 mmol) was dissolved in monoglyme (10 cm^3), and the colourless solution refluxed. Over a total of 33 h, i.r. showed *o*-metallated [$\overline{Re(CO)_3L^2}(HL^2)$] to be formed (slowly) [ν(CO) at 2 008vs, 1 892vs, and 1 885vs cm^{-1}].

Reaction of [$Re(CO)_4(COL^2)$] *with Triphenylphosphine*.—Triphenylphosphine (0.030 g, 0.115 mmol) and [$Re(CO)_4(COL^2)$] (0.065 g, 0.115 mmol) were dissolved in monoglyme (10 cm^3) and the solution refluxed. The reaction was complete after 27 h. Evaporation of the solution to smaller bulk *in vacuo* caused precipitation of the product, [$Re(CO)_3(PPh_3)L^2$].

Reactions of [$Re(CO)_4(COL^1)$], [$Re(CO)_4(COL^3)$], *and* [$Re(CO)_4(COL^4)$].—(*i*) These complexes were decarbonylated when heated strongly under vacuum to form NN′-bidentate

$[\mathrm{Re(CO)_4L}]$, but not in solution even after prolonged refluxing in monoglyme.

(*ii*) Complexes of $[\mathrm{Re(CO)_3(PPh_3)L}]$ were formed when $[\mathrm{Re(CO)_4(COL)}]$ was refluxed in monoglyme with a stoicheiometric amount of $\mathrm{PPh_3}$ as described above for $[\mathrm{Re(CO)_4(COL^2)}]$.

(*iii*) When refluxed in monoglyme solutions with the parent amidine for 24 h or more, all the carbamoyl complexes reacted to form the *ortho*-metallated complexes $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$.

Reaction of $[\{\mathrm{Re(CO)_4Br}\}_2]$ *with* NN'-*Di*-p-*tolylacetamidine*.—The amidine (0.315 g, 1.322 mmol) and $[\{\mathrm{Re(CO)_4Br}\}_2]$ (0.500 g, 0.661 mmol) were suspended in toluene (40 cm^3) and stirred at 38—40 °C for 16 h. All traces of the dimeric complex had disappeared by this time. The resulting pale yellow solution was reduced in volume (to 10 cm^3) *in vacuo*, and precipitation induced by the addition of hexane (5 cm^3) and by cooling. The product, recrystallised from a toluene–hexane mixture, was obtained as air-stable white crystals and identified as $[\mathrm{Re(CO)_4(HL^2)Br}]$ (yield 0.67 g, 83%). ^{1}H N.m.r. spectrum ($\mathrm{CDCl_3}$): δ 7.10 (m) (8), 2.38 (s), 2.35 (s) (6), 1.77 (s) (3) p.p.m. Mass spectrum: the parent ion was not observed; peaks were recorded at *m*/*e* 537, 509, 481, and 425 corresponding to $[^{187}\mathrm{Re(CO)_4(HL^2)}]^+$ and the subsequent stepwise loss of four carbonyl groups. The peaks of higher intensity correspond to the isotopic distribution pattern for $[^{187}\mathrm{Re(CO)_4Br}]^+$ at *m*/*e* 378, and peaks corresponding to the loss of 1, 2, and 4 carbonyls were observed at *m*/*e* 350, 322, and 266.

Reaction of $[\{\mathrm{Re(CO)_4Br}\}_2]$ *with* $\mathrm{HL^1}$, $\mathrm{HL^4}$, $\mathrm{HL^3}$, *and* $\mathrm{HL^5}$.—The reaction procedure and conditions used were identical to those described above. $[\mathrm{Re(CO)_4(HL^1)Br}]$: ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.27 (m) (10) and 1.83 (s) (3) p.p.m.; mass spectrum: the parent ion was not observed; peaks were recorded at *m*/*e* 509, 481, 453, 425, and 397 corresponding to $[^{187}\mathrm{Re(CO)_4(HL^1)}]^+$ and the stepwise loss of four carbonyl groups. $[\mathrm{Re(CO)_4(HL^4)Br}]$: ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.03 (s), 6.83 (s), 2.19 (s) p.p.m.; mass spectrum: the parent ion was not observed; peaks were recorded at *m*/*e* 599, 571, 543, 515, and 487 corresponding to $[^{187}\mathrm{Re(CO)_4(HL^4)}]^+$ and the stepwise loss of four carbonyl groups. $[\mathrm{Re(CO)_4(HL^3)Br}]$: mass spectrum: the parent ion was not observed; peaks were recorded at *m*/*e* 571, 543, 515, 487, and 459 corresponding to $[^{187}\mathrm{Re(CO)_4(HL^3)}]^+$ and the subsequent stepwise loss of four carbonyl groups. $[\mathrm{Re(CO)_4(HL^5)Br}]$: mass spectrum: the parent ion was not observed; peaks were recorded at *m*/*e* 495, 467, 439, 411, and 383 corresponding to $[^{187}\mathrm{Re(CO)_4(HL^5)}]^+$ and the subsequent loss of four carbonyl groups.

Reaction of $[\{\mathrm{Re(CO)_4Br}\}_2]$ *with* *p*-$\mathrm{MeC_6H_4N(Me)C(Me)NC_6H_4Me}$-*p*.—$[\{\mathrm{Re(CO)_4Br}\}_2]$ (0.500 g, 0.661 mmol) and *p*-$\mathrm{MeC_6H_4N(Me)C(Me)NC_6H_4Me}$-*p* (0.333 g, 1.322 mmol) were suspended in monoglyme (40 cm^3) and the mixture stirred at 38 °C for 120 h. A pale yellow solution containing a trace of white precipitate (unreacted $[\{\mathrm{Re(CO)_4Br}\}_2]$) was formed. After filtration, the solution was reduced in volume (*in vacuo*) and cooled to -10 °C. The mother-liquor produced a white crystalline precipitate and a yellow gum shown to be predominantly unreacted amidine. The white crystals of $[\mathrm{Re(CO)_4}\{p\text{-}\mathrm{MeC_6H_4NC(Me)N(Me)C_6H_4Me}\text{-}p\}\mathrm{Br}]$ were separated and crystallised from a toluene–hexane mixture. ^{1}H N.m.r. ($\mathrm{CDCl_3}$): δ 7.47 (s) (6), 7.37 (2), 3.90 (s) (3), 2.47 (s) (3), 2.41 (s) (3), 2.07 (s) (3) p.p.m. Mass spectrum: the peak of highest *m*/*e* value assigned to the complex occurred at *m*/*e* 495, corresponding to $[^{187}\mathrm{Re(CO)_2}\{p\text{-}\mathrm{MeC_6H_4NC(Me)N(Me)C_6H_4Me}\text{-}p\}]^+$. Stepwise loss of two carbonyl groups gave peaks at *m*/*e* 467 and 439. Peaks arising from $[\{\mathrm{Re(CO)_3Br}\}_4]$, a thermolysis product or a very minor contaminant of the sample, were strong and very distinct.

Reaction of $[\{\mathrm{Re(CO)_4Cl}\}_2]$ *with* $\mathrm{HL^2}$.—$[\{\mathrm{Re(CO)_4Cl}\}_2]$ (0.500 g, 0.749 mmol) and $\mathrm{HL^2}$ (0.356 g, 1.498 mmol) were suspended in toluene (40 cm^3) and the mixture stirred at 55 °C for 23 h. The pale yellow solution was filtered to remove traces of the dimeric starting material, reduced in volume (*in vacuo*), and cooled to -10 °C. The white crystals formed were identified as $[\mathrm{Re(CO)_4(HL^2)Cl}]$. ^{1}H N.m.r. ($\mathrm{CDCl_3}$): δ 7.12 (m) (8), 2.38, 2.36 (6), 1.76 (s) (3) p.p.m. Mass spectrum: the parent ion was not observed: peaks were recorded at *m*/*e* 537, 509, 481, 453, and 425 corresponding to $[^{187}\mathrm{Re(CO)_4(HL^2)}]^+$ and the subsequent loss of four carbonyl groups.

Reactions of $[\{\mathrm{Re(CO)_4Cl}\}_2]$ *with* $\mathrm{HL^1}$, $\mathrm{HL^4}$, *and* $\mathrm{HL^3}$.—The reaction procedure and conditions used were identical to those described above. Details of the complexes formed are as follows. $[\mathrm{Re(CO)_4(HL^1)Cl}]$: ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.23 (m) (10) and 1.80 (s) (3) p.p.m.; mass spectrum: the parent ion was not observed; peaks at *m*/*e* 509, 481, 453, 425, and 397 are assigned to $[^{187}\mathrm{Re(CO)_4(HL^1)}]^+$ and the subsequent loss of four carbonyl groups. Metastable peaks were recorded at 455 and 427 arising from $[^{187}\mathrm{Re(CO)_4(HL^1)}]^+ \longrightarrow [^{187}\mathrm{Re(CO)_3(HL^1)}]^+$ and $[^{187}\mathrm{Re(CO)_3(HL^1)}]^+ \longrightarrow [^{187}\mathrm{Re(CO)_2(HL^1)}]^+$ fragmentations. $[\mathrm{Re(CO)_4(HL^4)Cl}]$: ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.12 (s) (4), 6.93 (s) (4), 2.27 (s) (6) p.p.m.; mass spectrum: the parent ion was not observed; the spectrum was identical to that described previously for the bromo-complex. $[\mathrm{Re(CO)_4(HL^3)Cl}]$: mass spectrum: the parent ion was not observed; the spectrum was identical to that described previously for the bromo-complex.

Photochemical Reaction of $[\mathrm{Re(CO)_5Br}]$ *with* $\mathrm{HL^2}$.—$[\mathrm{Re(CO)_5Br}]$ (0.500 g, 1.23 mmol) and $\mathrm{HL^2}$ (0.293 g, 1.23 mmol), suspended in toluene (40 cm^3) in a silica flask were irradiated for 35 min. Infrared spectroscopy showed that the main product was $[\mathrm{Re(CO)_4(HL^2)Br}]$, together with some unreacted $[\mathrm{Re(CO)_5Br}]$ which was removed by reducing the volume of solution *in vacuo* to 25 cm^3, by cooling to -10 °C, and filtering the solution from the white precipitate. Filtration of the solution through an alumina column (1″ thick) and elution with toluene removed all traces of $[\mathrm{Re(CO)_5Br}]$. After reduction in volume *in vacuo* and addition of hexane white crystals of $[\mathrm{Re(CO)_4(HL^2)Br}]$ formed, which were recrystallised from toluene–hexane mixtures (yield 0.191 g, 25%).

Sublimation of $[\mathrm{Re(CO)_4(HL)X}]$ (X = Cl *or* Br) *Complexes*.—All the complexes of this type listed in Table 4 could be sublimed *in vacuo* at 100 °C onto a water-cooled cold-finger. White crystalline solids were obtained. Above 100 °C, decomposition to *o*-metallated $[\overline{\mathrm{Re(CO)_3L}}(\mathrm{HL})]$ occurred.

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