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FORMAMIDINO BRIDGED COMPLEXES OF RHODIUM AND IRIDIUM CARBONYLS

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Summary

Lithio-1,3-diarylformamidines undergo reaction with the carbonyl chlorides of rhodium and iridium, $[\{Rh(CO)_2Cl\}_2]$ and $[Ir(CO)_3Cl]$, to yield the deep red formamidino bridges dimeric species $[\{M(CO)_2(CH\{NR\}_2)\}_2]$ (M = Rh, Ir).

Introduction

As a continuation to our work on the pseudo-allyl complexes of the metal carbonyls [1—3], we have investigated the reactions of lithioformamidines with the carbonyl chlorides of rhodium and iridium. This has resulted in the formation and characterisation of a range of binuclear formamidino-bridged metal carbonyl complexes.

It has been previously shown that the formamidino ligand attatches to metals in several modes, both as η^1 monodentate [4—8] and as a formally three electron donor ligand, where it may act as a chelate [9,10] a bridge [11,12], or an orthometallate [4]. Carbamoyl type complexes, where the carbon atom of a carbonyl group is incorporated as a fourth atom in the chelate chain have also been reported [3,13]. Other amidine groupings such as acetamidines and benzamidines have shown similar bonding modes [14—16].

Results and discussion

Interaction of bis(chlorocarbonylrhodium) or chlorotricarbonyliridium with lithio-formamidines (prepared in situ from the formamidine and n-butyllithium) proceeds in good yields according to equations 1 and 2.

$$[\{Rh(CO)_2Cl\}_2] + 2\ Li\{CH(NC_6H_4X)_2\} \rightarrow [\{Rh(CO)_2(CH\{NC_6H_4X\}_2)\}_2] + 2\ LiCl \quad (1)$$

$$2[Ir(CO)_3Cl] + 2\ Li\{CH(NC_6H_4X)_2\} \rightarrow [\{Ir(CO)_2(CH\{NC_6H_4X\}_2)\}_2] + 2\ LiCl + 2\ CO \quad (2)$$

(X = MeO, Me, H, Cl, F)

These bridged species were the only products isolated from the reactions, with no evidence for the formation of any type of chelate species.

Essentially two mechanisms are available for each reaction where the first step is either elimination of lithium chloride or coordination of the formamidino anion via nitrogen, as illustrated by equations 3—6 (Scheme 1). Of these equations 3 and 5, where lithium chloride elimination is the first step, are preferred, as in the iridium reactions an intermediate could be isolated which exhibited three ν(CO) stretching frequencies in the infra-red (Table 1). These intermediates could not be fully characterised as they were very unstable, and converted to the dimeric species in the mass spectrometer. Analyses proved

SCHEME 1

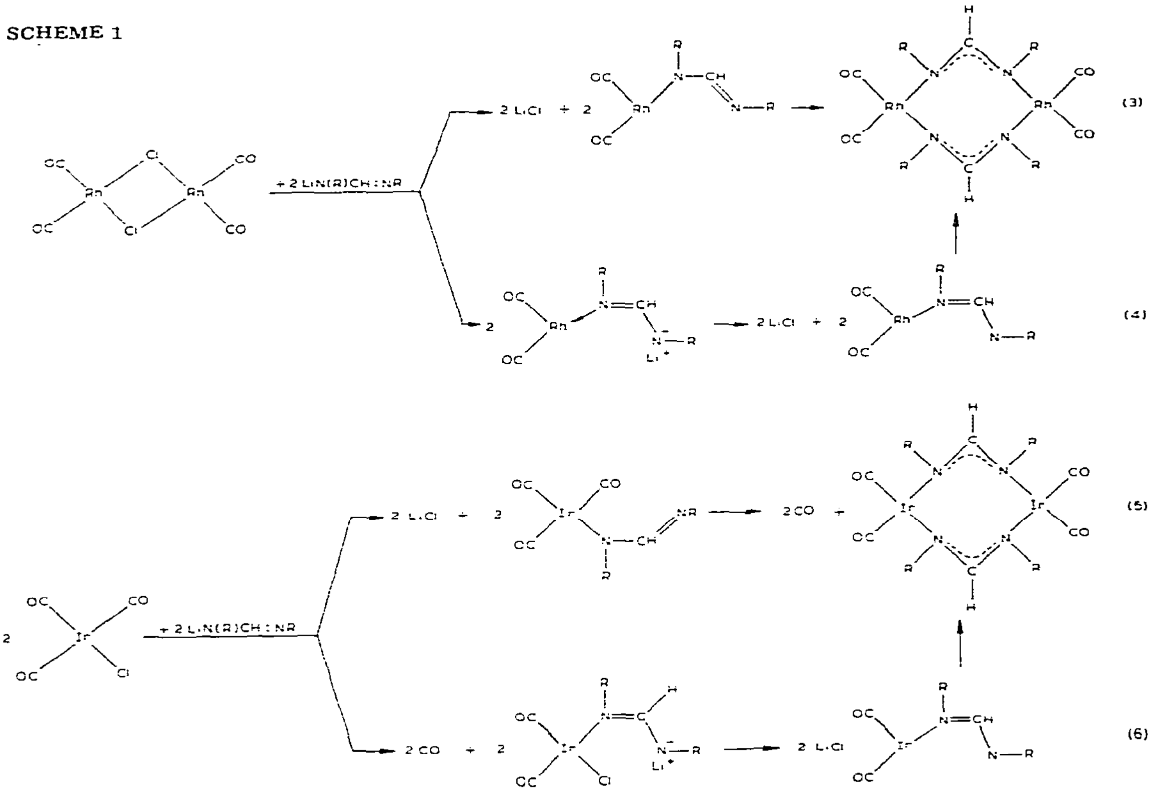


TABLE 1

INFRARED SPECTRA OF THE PROPOSED INTERMEDIARY η^1-COMPLEXES $[Ir(CO)_3N(R)CH{=}NR]$

Complex from	ν(CO) stretching frequencies (cm^{-1}) [a]
N,N'-di-*p*-anisylformamidine	2066s, 2024m, 1992m
N,N'-di-*p*-tolylformamidine	2066s, 2024m, 1993m
N,N'-diphenylformamidine	2066s, 2026m, 1995m
N,N'-di-*p*-chlorophenylformamidine	2068s, 2028s, 1997m
N,N'-di-*p*-fluorophenylformamidine	2070s, 2030s, 1997m

[a] In diethylether/THF (1 : 1).

TABLE 2

INFRARED SPECTRAL DATA FOR THE FORMAMIDINO-BRIDGED RHODIUM AND IRIDIUM CARBONYL COMPLEXES

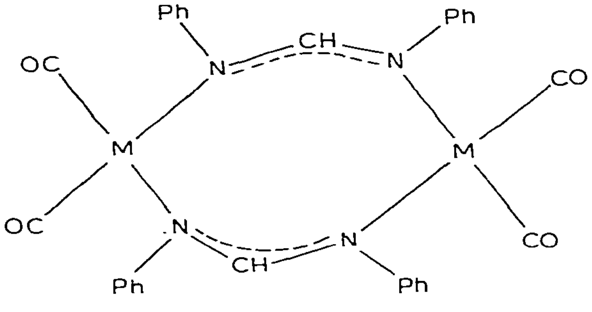
Complex	ν(CO) stretching frequencies (cm^{-1})
$[(Rh(CO)_2\{CH(NC_6H_4\textit{p}\text{-}OCH_3)_2\})_2]$	2084vs, 2059s, 2017vs
$[(Rh(CO)_2\{CH(NC_6H_4\textit{p}\text{-}CH_3)_2\})_2]$	2085vs, 2060s, 2018vs
$[(Rh(CO)_2\{CH(NC_6H_5)_2\})_2]$	2088vs, 2062m, 2021vs
$[(Rh(CO)_2\{CH(NC_6H_4\textit{p}\text{-}Cl)_2\})_2]$	2088vs, 2064m, 2022vs
$[(Rh(CO)_2\{CH(NC_6H_4\textit{p}\text{-}F)_2\})_2]$	2090vs, 2065m, 2024vs
$[(Ir(CO)_2\{CH(NC_6H_4\textit{p}\text{-}OCH_3)_2\})_2]$	2075vs, 2043m, 2001vs
$[(Ir(CO)_2\{CH(NC_6H_4\textit{p}\text{-}CH_3)_2\})_2]$	2077vs, 2045m, 2004vs
$[(Ir(CO)_2\{CH(NC_6H_5)_2\})_2]$	2078vs, 2047s, 2006vs
$[(Ir(CO)_2\{CH(NC_6H_4\textit{p}\text{-}Cl)_2\})_2]$	2082vs, 2050s, 2008vs
$[(Ir(CO)_2\{CH(NC_6H_4\textit{p}\text{-}F)_2\})_2]$	2081vs, 2049m, 2010vs

unreliable as samples were impossible to obtain absolutely pure. On the evidence available, however, we feel that these complexes are the η^1 complexes $[Ir(CO)_3N(C_6H_4X)CH : NC_6H_4X]$, which easily lose carbon monoxide to form the corresponding dimers.

All of the binuclear complexes exhibit three terminal carbonyl stretching frequencies in the infra-red (Table 2). The variation of the *para* substituent on the aromatic rings causes the predictable changes in the frequencies of the ν(CO).

The mass spectra of all these dimeric complexes exhibit molecular ions, and the successive loss of four carbonyl groups. In most cases ions were also observed which correspond to half the molecular ion, followed by the successive loss of two carbonyl groups. The relative intensities of these latter ions were usually very low. The identity of all ions was confirmed by computer simulation of isotope patterna for the proposed formulation.

^{1}H NMR data indicates (Table 3) the symmetrical nature of the bridge, with only a single methyl resonance being observed in the anisyl and tolyl derivatives. The bridging nature of the ligand is emphasised in the rhodium series, where ^3J(Rh—H) coupling is observed for the formamidino proton from two identical ^{103}Rh atoms, giving a triplet. The single ^{19}F resonances, at 42.45 ppm from C_6F_6 in the case of rhodium, and at 41.46 ppm in the case of iridium, also suggest a symmetrical structure, as illustrated in I.



(I)

M = Rh and Ir

TABLE 3

^{1}H NMR DATA FOR THE FORMAMIDINO RHODIUM AND IRIDIUM CARBONYL COMPLEXES

Complex	aryl protons	CH	CH_3	^3J(Rh—H) (Hz)
$[(Rh(CO)_2\{CH(NC_6H_4p\text{-}OCH_3)_2\})_2]$	6.80—7.24(q)	7.62(t)	3.80(s)	2.50
$[(Rh(CO)_2\{CH(NC_6H_4p\text{-}CH_3)_2\})_2]$	6.80—7.00(q)	7.52(t)	2.21(s)	2.55
$[(Rh(CO)_2\{CH(NC_6H_5)_2\})_2]$	6.90—7.45(m)	7.75(t)	—	2.44
$[(Ph(CO)_2\{CH(NC_6H_4p\text{-}Cl)_2\})_2]$	7.05—7.35(m)	7.74(t)	—	2.45
$[(Rh(CO)_2\{CH(NC_6H_4p\text{-}F)_2\})_2]$	6.80—7.20(m)	7.71(t)	—	2.60
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}OCH_3)_2\})_2]$	6.65—7.15(q)	7.65	3.76(s)	—
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}CH_3)_2\})_2]$	6.75—7.05(q)	7.75	2.19(s)	—
$[(Ir(CO)_2\{CH(NC_6H_5)_2\})_2]$	6.70—7.25(m)	7.68	—	—
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}Cl)_2\})_2]$	7.00—7.15(m)	7.87	—	—
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}F)_2\})_2]$	6.80—7.25(m)	7.88	—	—

^{13}C NMR spectra (Table 4) also indicate the symmetrical nature of the structure, with only four aromatic carbon resonances, showing the equivalence of the two aromatic rings. No ^2J(Rh—C) coupling was observed to the formamidino carbon, though ^2J(Rh—C) coupling to the metal carbonyl groups was noted.

Experimental

Infrared spectra were recorded in hexane on a Perkin-Elmer 257 spectrophotometer, and a Jeol JNM-MH-100 was used to record ^{1}H NMR spectra at 100 MHz. A Jeol PS/PFT-100 spectrometer was used to record ^{1}H (100 MHz), ^{19}F (94.09 MHz), and ^{13}C (25.15 MHz) spectra, ^{13}C and ^{19}F spectra were proton noise decoupled. Mass spectra were recorded on a VG-Micromass MM-30 mass spectrometer (20 eV) with samples directly inserted into the ion source at 220°C. Elemental analyses were determined with a Carlo-Erba 1102 analyser.

Reactions were routinely carried out under nitrogen, hydrocarbon solvents were freshly distilled from potassium-benzophenone and diethyl ether dried over sodium wire.

1,3-Diarylformamidines were prepared by the literature methods [17,18], n-butyllithium (ca. 1.5 *M* in hexane) and $[Ir(CO)_3Cl]$ were used as supplied, and $[Rh_2(CO)_4Cl_2]$ was prepared as previously reported [19].

Preparation of $[\{Rh(CO)_2(CH\{NC_6H_4\text{-}p\text{-}OCH_3\}_2)\}_2]$

A suspension of lithio-*N*,*N'*-di(-*p*-anisyl)formamidine was formed from the formamidine (0.58 g, 2.5 mmol) and n-butyllithium (1.53 cm^3 of 1.63 *M* soln.) in ether (30 cm^3) by stirring the mixture for two minutes at room temperature. Addition to this product of solid $[Rh_2(CO)_4Cl_2]$ (0.49 g, 1.25 mmol), and stirring for twenty minutes gave a deep red solution and a fine white precipitate of lithium chloride. The solvent was removed under reduced pressure and the residue extracted with boiling hexane (2 × 20 cm^3) and filtered. The solution

TABLE 4

^{13}C NMR SPECTRAL DATA FOR THE FORMAMIDINO RHODIUM AND IRIDIUM CARBONYL COMPLEXES

(δ, ppm relative to TMS) [a]

Complex	Aryl carbons				CH	CH_3	CO	^1J(Rh—C) (Hz)
	C_1	C_2	C_3	C_4				
$[(Rh(CO)_2\{CH(NC_6H_4p\text{-}OCH_3)_2\})_2]$	144.82	124.56	113.94	156.47	163.02	55.51	185.23, 187.84	65.6
$[(Rh(CO)_2\{CH(NC_6H_4p\text{-}CH_3)_2\})_2]$	148.77	123.53	129.23	133.36	163.38	20.69	185.17, 187.77	65.6
$[(Rh(CO)_2\{CH(NC_6H_5)_2\})_2]$	151.07	123.77	128.74	124.01	163.81	—	184.86, 187.53	67.1
$[(Rh(CO)_2\{CH(CN_6H_4p\text{-}Cl)_2\})_2]$	149.20	124.56	128.92	129.89	163.44	—	184.20, 186.87	67.1
$[(Rh(CO)_2\{CH(NC_6H_4p\text{-}F)_2\})_2]$	147.07	124.62	115.09	155.13	163.57	—	184.61, 187.23	65.7
	147.19	124.92	116.00	164.84	*b*			
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}OCH_3)_2\})_2]$	143.55	125.83	114.18	157.38		55.51	*c*	
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}CH_3)_2\})_2]$	147.92	124.68	129.29	134.51	162.71	20.69	—	
$[(Ir(CO)_2\{CH(NC_6H_5)_2\})_2]$	*b*	123.40	129.35	128.38	*b*	—	—	
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}Cl)_2\})_2]$	148.40	125.77	128.99	131.17	*b*	—	—	
$[(Ir(CO)_2\{CH(NC_6H_4p\text{-}F)_2\})_2]$	146.22	120.07	115.52	*b*	*b*	—	—	
	148.40	120.49	116.43	—	—	—	—	

[a] Spectra taken in chloroform solution. [b] Peaks not resolved. [c] No iridium CO bands were observed.

was concentrated and chromatographed on grade II alumina, eluting with hexane. The first band from the column was evaporated to dryness and recrystallised from hexane to yield the product (0.49 g, 47%) as dark red microcrystals. (Table 5). The other formamidino-rhodium carbonyls were prepared in a similar manner. (Table 5).

Interaction of lithium N,N'-di(p-anisyl)formamide and chlorotricarbonyliridium

The lithioformamidine suspension formed from *N,N'*-di(*p*-anisyl)formamidine (0.3 g, 1.5 mmol) and n-butyllithium (1.0 cm^3 of 1.5 *M* soln.) in diethylether/THF (1 : 1) (20 cm^3) was mixed with $[Ir(CO)_3Cl]$ (0.47 g, 1.5 mmol), and the reaction stirred. After 0.5 h all CO peaks due to $[Ir(CO)_3Cl]$ had disappeared from the infrared spectrum, and the royal blue solution showed three CO peaks (see Table 1). Over a period of 6 h the solution turned to a deep purple colour and the infrared absorptions of the blue solution were replaced by three new metal carbonyl bands (see Table 2). Solvent was removed (25°C/0.1 mm), and the residue extracted with benzene (3 × 10 cm^3) and filtered. This was chromatographed on grade II alumina, eluting with benzene. The purple band was evaporated to dryness to yield $[\{Ir(CO)_2(CH\{NC_6H_4\text{-}p\text{-}O\text{-}CH_3\}_2)\}_2]$ (0.37 g, 25%) as a dark purple, very air-sensitive microcrystalline mass.

We were unable to isolate the pale blue intermediary η^1 complex, and the final product, whilst fully characterised by infrared (Table 2), ^{1}H NMR (Table 3), ^{13}C NMR (Table 4), and mass spectrometry, did not yield quotable elemental analyses. This was probably due to (a) the remarkably high solubility of these particular complexes in all suitable organic solvents made true crystallisation almost impossible, and (b) the extreme air sensitivity of the very fine crystals obtained.

The other dimeric formamidino bridged iridium carbonyls (Tables 2, 3 and 4) were prepared in an analogous manner in 25—30% yields.

TABLE 5

CHARACTERISATION OF THE FORMAMIDINO-BRIDGED RHODIUM COMPLEXES

	Yield (%)	M.p. (°C)	Analysis: Found (calc.) (%)		
			C	H	N
$[\{Rh(CO)_2(CH\{NC_6H_4p\text{-}OCH_3\}_2)\}_2]$	47	102—103	49.6 (49.3)	4.05 (3.65)	6.30 (6.76)
$[\{Rh(CO)_2(CH\{NC_6H_4p\text{-}CH_3\}_2)\}_2]$	42	220—233	52.9 (53.4)	3.96 (3.96)	7.13 (7.33)
$[\{Rh(CO)_2(CH\{NC_6H_5\}_2)\}_2]$	47	97—99	51.3 (50.9)	3.49 (3.13)	7.58 (7.91)
$[\{Rh(CO)_2(CH\{NC_6H_4p\text{-}Cl\}_2)\}_2]$	57	216—218 (dec.)	42.2 (42.5)	2.28 (2.14)	6.36 (6.62)
$[\{Rh(CO)_2(CH\{NC_6H_4p\text{-}F\}_2)\}_2]$	24	200—201	46.0 (46.2)	2.37 (2.33)	6.98 (7.18)

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