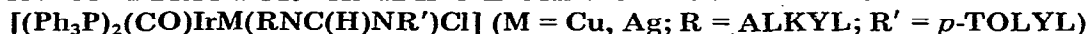


METAL–METAL BONDED COMPOUNDS

IV *. STABILIZATION OF METAL–METAL BONDING BY BRIDGING ASYMMETRIC FORMAMIDINO LIGANDS IN COMPLEXES



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Summary

Reactions of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}]$ with $[\text{M}(\text{RNC}(\text{H})\text{NR}')_n]$ ($\text{M} = \text{Cu}, \text{Ag}; \text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{cyclohexyl}; \text{R}' = p\text{-tolyl}; n = 2, 4$) afforded the complexes $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrM}(\text{RNC}(\text{H})\text{NR}')]_n$ in which the formal Ir- to -M donor bond is stabilized by a bridging formamidino group. The corresponding Rh–M compounds could not be isolated. The ease of formation and the stability of the complexes fall in the sequences $\text{Ir}^{\text{I}} > \text{Rh}^{\text{I}}; \text{Ag}^{\text{I}} > \text{Cu}^{\text{I}}$ and small R groups $>$ bulky R groups. For small R groups two isomers may be formed, the NR group being bonded either to Ir or to Ag. In the case of bulky R groups the NR group is always bonded to Ag because of steric interaction of the NR group with the two phosphine ligands on Ir. Reaction with CO gives unstable products which probably contain an acylformamidino group and two terminal CO groups.

Introduction

In previous reports it has been shown that triazenido groups $\text{RN}_3\text{R}'$ are capable of bridging pairs of metal atoms [1–9]. Of particular interest is that the otherwise unstable $\text{Rh}^{\text{I}}(\text{Ir}^{\text{I}})\text{-to-Cu}^{\text{I}}(\text{Ag}^{\text{I}})$ metal donor bonds could be stabilized in a series of complexes $[\text{L}_2(\text{CO})\text{M}'\text{M}(\text{RN}_3\text{R}')\text{X}]$ ($\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{PhMe}_2\text{P}; \text{M}' = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}; \text{M} = \text{Ag}^{\text{I}}, \text{Cu}^{\text{I}}; \text{X} = \text{Cl}, \text{Br}, \text{I}; \text{R} = \text{R}' = \text{CH}_3, p\text{-tolyl}; \text{R} = \text{CH}_3, \text{R}' = p\text{-tolyl}$). The triazenido group could be replaced by amidino, carboxylato, perchlorato and nitrate groups [8]. The triazenido complexes were formed in

* For part III see ref. 16.

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high yields by the reaction of $[L_2(CO)M'X]$ with $[MRN_3R']_n$. In view of the great similarity between the formamidino and triazenido ligands it was thus of interest to investigate the reactions leading to the analogous formamidino complexes. Although some diaryl-amidino derivatives had been previously prepared [6,8] the synthesis of complexes containing an asymmetric *N*-alkyl, *N'*-aryl formamidino ligand required initial preparation of the compounds $[M(RNC(H)NR')]_n$ ($M = Cu, Ag$; $R = \text{alkyl}$; $R' = p\text{-tolyl}$; $n = 2, 4$), which were reported recently [10]. NMR studies of these compounds indicated the presence of dimer-tetramer equilibria, and gave information about the mechanism of the dimer-tetramer exchange reactions [10].

We describe below the preparation and properties of the Ir-to-M bonded formamidino complexes and compare these complexes with those of the analogous triazenido and carboxylato complexes. We also consider the mechanism of these reactions in the light of our present knowledge of the system $[M(RNC(H)NR')]_n$ [10].

Experimental

All preparations were carried out under nitrogen in dried solvents.

Preparations of $[(Ph_3P)_2(CO)IrAg(RNC(H)NR')Cl]$ ($R = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3, C_6H_{11}$; $R' = p\text{-tolyl}$)

Silver formamidine (1 mmol) was added to a suspension of $[(Ph_3P)_2(CO)IrCl]$ (1 mmol) in CH_2Cl_2 (10 ml) and the mixture was stirred at room temperature. After 20 min in the case of $R = CH_3$, and in all other cases after 20 h a clear orange solution was obtained. Hexane was added and after cooling to $-30^\circ C$ orange crystals were obtained in 95% yield. In the case of $R = C_2H_5, CH(CH_3)_2, C(CH_3)_3, C_6H_{11}$ the crystals also contained one equivalent of CH_2Cl_2 .

Reactions of the described compounds with Ph_3P , pyridine, triazenes and formamidines were monitored by NMR spectroscopy. The reaction with HCl was monitored by IR and NMR spectroscopy.

Preparation of $[(Ph_3P)_2(CO)IrAg(RN_3R')Cl]$ ($R = CH_3, C_2H_5, C(CH_3)_3$; $R' = p\text{-tolyl}$)

The preparations of these complexes were analogous to those for the compounds described above. The compound $[(Ph_3P)_2(CO)IrAg(CH_3N_3-p\text{-tolyl})Cl]$ has been prepared before [7].

In the case of $R = CH_3$ the crystals contained no CH_2Cl_2 , and in the case of $R = C_2H_5, C(CH_3)_3$ the crystals contained 0.57 equivalent and one equivalent of CH_2Cl_2 , respectively.

Preparation of $[(Ph_3P)_2(CO)IrCu(RNC(H)NR')Cl]$ ($R = C_2H_5$; $R' = p\text{-tolyl}$)

Copper formamidine (1 mmol) was added to a suspension of $[(Ph_3P)_2(CO)IrCl]$ (1 mmol) in CH_2Cl_2 (10 ml) and stirred one week at room temperature. After filtration, concentration, addition of hexane, and cooling to $-30^\circ C$ red crystals were obtained in 20% yield. For $R = CH(CH_3)_2, C(CH_3)_3$ and C_6H_{11} only low yields of impure products were obtained.

Reactions of $[MRNC(H)NR']_n$ with $[(Ph_3P)_2(CO)M'X]$ ($M = Cu, Ag; R = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3, C_6H_{11}; R' = p\text{-tolyl}; M' = Ir$ and $X = O_2CCH_3, O_2CCH(CH_3)_2; M' = Rh$ and $X = Cl, O_2CCH_3$)

In the case of $M' = Ir$ a yellow solution and in the case of $M' = Rh$ a greenish white suspension was obtained which contained a mixture of products. In no case could products be isolated.

Reactions of $[AgRNC(H)NR]_n$ with $[(Ph_3P)_2(CO)M'X]$ ($R = CH_3, CH(CH_3)_2, p\text{-tolyl}; M' = Rh, Ir; X = Cl, O_2CCH_3$)

Mixtures of these compounds in CH_2Cl_2 , THF or C_7H_8 gave a precipitate of $AgCl$ and a mixture of products which could not be separated.

Preparation of $[(Ph_3P)_2(OCN(R)C(H)NR')(CO)IrAg(CO)Cl]$ ($R = CH(CH_3)_2, C(CH_3)_3, C_6H_{11}; R' = p\text{-tolyl}$)

A solution of $[(Ph_3P)_2(CO)IrAg(RNC(H)NR)Cl]$ (1 mmol) in CH_2Cl_2 (5 ml) was stirred at $0^\circ C$ under a CO atmosphere. After 20 min the orange solution had turned yellow and it was then filtered. Cold hexane was added with rapid stirring and a yellow precipitate was obtained (yield 70%). In solution the compound rapidly decomposed to $AgCl$, Ph_3PAgCl and a mixture of products which could not be separated. The solid compound slowly decomposed even under nitrogen.

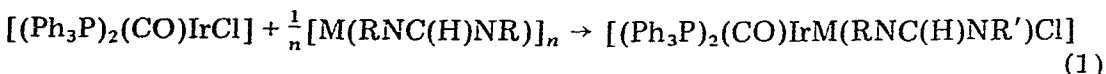
Unsuccessful attempts were made to obtain Hg-Ir, (Rh) compounds containing a formamidino group analogous to the Hg-Ir, (Rh) triazenido compounds described previously [9].

1H NMR and ^{31}P NMR spectra were recorded on a T-60 A and XL-100 Varian spectrometer, respectively. Infrared spectra were recorded on a Beckman 4250 spectrometer. Molecular weights were determined with a Hewlett Packard vapour pressure osmometer Model 320 B. C, H, N, O and Cl analyses (Table 1) were carried out at the organic laboratory of TNO in Utrecht.

Results

A. Structural characterization of the formamidino complexes

In analogy to the copper and silver triazenido compounds [6,7] the complexes $[(Ph_3P)_2(CO)IrM(RNC(H)NR')Cl]$ were prepared according to eq. 1:



($M = Ag; R' = p\text{-tolyl}; R = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3, C_6H_{11}$. $M = Cu; R' = p\text{-tolyl}; R = C_2H_5$)

From the ^{31}P NMR and IR data (Table 2) it is clear that the formamidino compounds are iso-structural with the triazenido complexes described earlier [6,7]. The 1H NMR data (Table 3) are similar to those of the copper and silver triazenido compounds, but show the presence of two modes of bonding for the bridging ligand. For $R = CH_3$ the aryl protons show a doublet of doublets at 6.77 and 6.32 ppm and a resonance at 2.20 ppm for the CH_3 group. A different resonance pattern is found for $R = C_2H_5, CH(CH_3)_2, C(CH_3)_3, C_6H_{11}$. The aryl protons appear as a sharp singlet at about 6.30 ppm while only one resonance is observed at 2.03 ppm for the CH_3 groups. In order to investigate these

TABLE 1
ANALYTICAL DATA

Compound ^a	Analysis (Found (calcd.)) ^b						Colour
	M.W. (found (calcd.)) ^b	C	H	N	O	Cl	
(Ph ₃ P) ₂ (CO)IrAg(MpTF)Cl	980 (1035)	52.63 (53.37)	3.97 (3.99)	2.57 (2.71)		3.90 (3.42)	orange
(Ph ₃ P) ₂ (CO)IrAg(EpTF)Cl · CH ₂ Cl ₂	1064 (1049)	50.87 (50.83)	4.07 (4.00)	2.55 (2.47)		9.64 (9.38)	orange
(Ph ₃ P) ₂ (CO)IrCu(EpTF)Cl · CH ₂ Cl ₂	1045 (1006)	53.02 (52.89)	4.15 (4.16)	2.59 (2.57)		9.55 (9.76)	red
(Ph ₃ P) ₂ (CO)IrAg(IPpTF)Cl · CH ₂ Cl ₂	1064 (1063)	51.61 (51.25)	4.17 (4.13)	2.45 (2.44)		8.20 (9.26)	orange
(Ph ₃ P) ₂ (CO)IrAg(GHTF)Cl · CH ₂ Cl ₂	1172 (1077)	51.61 (51.67)	4.33 (4.25)	2.45 (2.41)		9.03 (9.15)	orange
(Ph ₃ P) ₂ (CO)IrAg(GHTF)Cl · CH ₂ Cl ₂	1061 (1103)	52.33 (52.56)	4.35 (4.33)	2.43 (2.36)		9.07 (8.95)	orange
(Ph ₃ P) ₂ (CO)IrAg(EpTT)Cl · 0.57 CH ₂ Cl ₂ ^c	1071 (1050)	50.19 (50.90)	3.96 (3.95)	3.49 (3.82)		6.23 (6.90)	orange
(Ph ₃ P) ₂ (CO)IrAg(OBpTT)Cl · CH ₂ Cl ₂	1055 (1078)	50.55 (50.59)	4.16 (4.25)	3.42 (3.61)		8.86 (9.14)	orange
(Ph ₃ P) ₂ (CO)(OCiPpTF)IrAg(CO)Cl	981 (1119) ^d	53.32 (53.65)	4.14 (4.05)		4.54 (4.29)		yellow
(Ph ₃ P) ₂ (CO)(OCtBpTF)IrAg(CO)Cl	1002 (1183) ^d	53.65 (54.05)	3.98 (4.18)		4.02 (4.02)		yellow
(Ph ₃ P) ₂ (CO)(OCcHpTF)IrAg(CO)Cl	1022 (1159) ^d	54.52 (54.90)	4.38 (4.26)		4.06 (4.14)		yellow

^a MpTF = CH₃NC(H)N-*p*-tolyl; EpTF = C₂H₅NC(H)N-*p*-tolyl; IPpTF = (CH₃)₃CNC(H)N-*p*-tolyl; t-BpTF = C₆H₁₁NC(H)N-*p*-tolyl; EpTT = C₂H₅N₃-*p*-tolyl; tBpTT = C(CH₃)₃N₃-*p*-tolyl; ^b M.W. in CH₂Cl₂, the experimental error is ±10%. M.W. calculated is without CH₂Cl₂. ^c Mixture of the isomers a (43%) and b (57%). The ratio of the isomers is based upon the intensity of the ¹H NMR resonances. ^d Decomposition occurred.

TABLE 2
 ^{31}P NMR ^a AND IR DATA ^b

Compounds	^{31}P NMR data	IR data ($\nu(\text{CO})$ (cm^{-1}))
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{MpRF})\text{Cl}$	-22.75	1975
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTF})\text{Cl}$	-23.73	1969
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCu}(\text{EpTF})\text{Cl}$	-23.27	1972
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{iPpTF})\text{Cl}$	-22.89	1970
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{tBpTF})\text{Cl}$	-22.29	1971
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{cHpTF})\text{Cl}$	-23.21	1973
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{MpTT})\text{Cl}$	-22.24	1985
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCu}(\text{MpTT})\text{Cl}$	-24.31	1978
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTT})\text{Cl}$ ^c	-22.66	1963
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTT})\text{Cl}$ ^d	-23.08	1978
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{tBpTT})\text{Cl}$	-21.95	1980
$(\text{Ph}_3\text{P})_2(\text{CO})(\text{OCiPpTF})\text{IrAg}(\text{CO})\text{Cl}$	+9.07	2029; 1963; 1620
$(\text{Ph}_3\text{P})_2(\text{CO})(\text{OCtBpTF})\text{IrAg}(\text{CO})\text{Cl}$	+11.07	2035; 1981; 1625
$(\text{Ph}_3\text{P})_2(\text{CO})(\text{OCcHpTF})\text{IrAg}(\text{CO})\text{Cl}$	+8.74	2033; 1989; 1627

^a In CDCl_3 relative to 85% H_3PO_4 (δ (ppm)). ^b In CH_2Cl_2 . ^c Isomer a (Fig. 2a). ^d Isomer b (Fig. 2b).

features it was of interest to prepare the analogous triazenido compounds and to compare these with the formamidino complexes. For the compounds $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{MpTT})\text{Cl}]$ and $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{tBpTT})\text{Cl}]$ the same shift difference (Δ 0.18 ppm) for the methyl H atoms of the *p*-tolyl group is observed, as was observed for the previous mentioned formamidino compounds. However, in the case of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTT})\text{Cl}]$ both resonances patterns are present (Table 3). The ^1H NMR spectrum of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTT})\text{Cl}]$ (Fig. 1) clearly shows the presence of two isomers, which is confirmed by the IR and ^{31}P NMR data (Table 2).

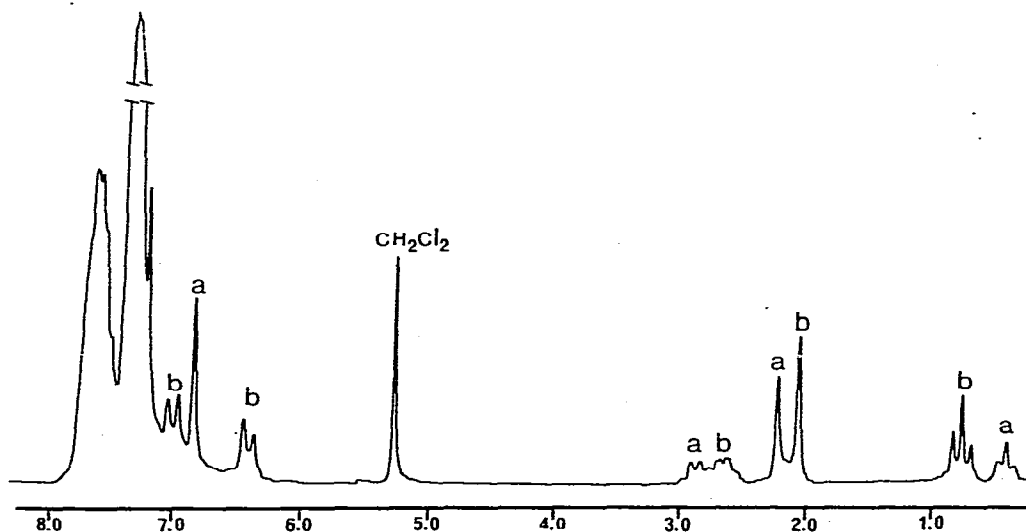


Fig. 1. ^1H NMR spectrum of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTT})\text{Cl}]$. a. Resonances of isomer a; b. Resonances of isomer b.

TABLE 3
¹H NMR DATA ^a

Compound	p-tolyl group		CH ^f	alkyl group		Ph ₃ P
	CH ₃	aryl		CH or CH ₂	CH ₃ ^b	
(Ph ₃ P) ₂ (CO)IrAg(MpTF)Cl	2.20	6.77; 6.32	b		2.20	7.39 m; 7.81 m
(Ph ₃ P) ₂ (CO)IrAg(EpTF)Cl	2.03	6.33	b	2.23 (q) ^e	0.83 (t) ^e	7.36 m; 7.59 m
(Ph ₃ P) ₂ (CO)IrCu(EpTF)Cl	2.03	6.27	b	2.19 (q) ^e	0.97 (t) ^e	7.34 m; 7.56 m
(Ph ₃ P) ₂ (CO)IrAg(EpTF)Cl	2.03	6.33	7.93	2.36 (s) ^e	0.72 (d) ^e	7.33 m; 7.56 m
(Ph ₃ P) ₂ (CO)IrAg(tBpTF)Cl	2.03	6.28	8.12		0.82	7.33 m; 7.56 m
(Ph ₃ P) ₂ (CO)IrAg(cHpTF)Cl	2.03	6.33	7.91	1.13 (vbr); 1.51 (vbr)		7.36 m; 7.56 m
(Ph ₃ P) ₂ (CO)IrAg(MpTF)Cl	2.21	6.79			2.60	7.34 m; 7.67 m
(Ph ₃ P) ₂ (CO)IrCu(MpTF)Cl	2.22	6.93; 6.85			2.60	7.36 m; 7.75 m
(Ph ₃ P) ₂ (CO)IrAg(EpTT)Cl ^c	2.20	6.89		2.95 (q) ^e	0.36 (t) ^e	7.36 m; 7.65 m
(Ph ₃ P) ₂ (CO)IrAg(EpTT)Cl ^d	2.04	7.03; 6.38		2.83 (q) ^e	0.72 (t) ^e	7.36 m; 7.65 m
(Ph ₃ P) ₂ (CO)IrAg(tBpTT)Cl	2.04	7.03; 6.38			0.68	7.36 m; 7.58 m
(Ph ₃ P) ₂ (CO)(OC)IrAg(CO)Cl	2.27	6.96	b	4.28 (s) ^e	1.05 (d) ^e	7.35 m
(Ph ₃ P) ₂ (CO)(OC)IrAg(CO)Cl	2.27	6.88	b		1.30	7.35 m
(Ph ₃ P) ₂ (CO)(OC)IrAg(CO)Cl	2.27	6.98	b	1.23 (vbr); 1.63 (vbr)		7.35 m

^a In CDCl₃ relative to TMS. ^b This resonance coincides with the resonances of Ph₃P. ^c Isomer a (Fig. 2a). ^d Isomer b (Fig. 2a). ^e $J(\text{CH}_2-\text{CH}_3)$ or $J(\text{CH}-\text{CH}_3)$ is 7 Hz. ^f C-H resonance of the formamidino ligand.

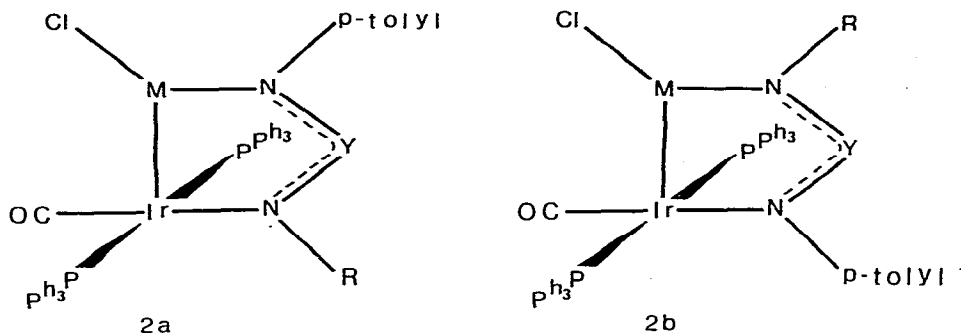
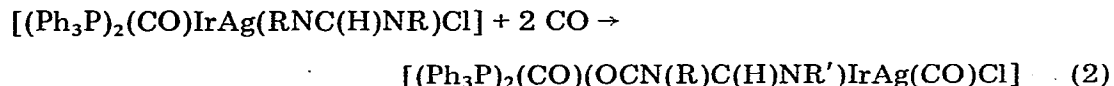


Fig. 2. (a) Structure of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrM}(\text{RNYN-}p\text{-tolyl})\text{Cl}]$ ($\text{Y} = \text{N}$ with $\text{M} = \text{Cu}, \text{Ag}$ and $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ (isomer a); $\text{Y} = \text{CH}$ with $\text{M} = \text{Ag}, \text{R} = \text{CH}_3$. (b) Structure of $[(\text{Ph}_3\text{P})(\text{CO})\text{IrM}(\text{RNYN-}p\text{-tolyl})\text{Cl}]$ ($\text{Y} = \text{N}$ with $\text{M} = \text{Ag}$ and $\text{R} = \text{C}(\text{CH}_3)_3, \text{C}_2\text{H}_5$ (isomer b); $\text{Y} = \text{CH}$ with $\text{M} = \text{Cu}; \text{R} = \text{C}_2\text{H}_5$ and $\text{M} = \text{Ag}; \text{R} = \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3, \text{C}_6\text{H}_{11}$).

Furthermore, knowledge of the crystal structure of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{MpTT})(\text{O}_2\text{CCH}(\text{CH}_3)_2)\text{H}]$ [11] and comparison of the proton resonances of this complex with those of the compound $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCu}(\text{DpTF})\text{Cl}]$ [6], allows the assignment of the observed methyl resonances of the *p*-tolyl group. A resonance at about 2.04 ppm for this type of compound can be assigned to the methyl protons of a *p*-tolyl group at the side of the Ir atom and the resonance at about 2.21 ppm is characteristic for the methyl protons of a *p*-tolyl group at the side of the Ag or Cu atom. In view of these observations we suggest for the compounds $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{MpTF})\text{Cl}]$ and $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrM}(\text{MpTT})\text{Cl}]$ ($\text{M} = \text{Cu}, \text{Ir}$) the structure shown in Fig. 2a, and for the compounds $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrM}(\text{RNC}(\text{H})\text{NR}')\text{Cl}]$ ($\text{R}' = p\text{-tolyl}; \text{M} = \text{Cu}$ and $\text{R} = \text{C}_2\text{H}_5$; $\text{M} = \text{Ag}$ and $\text{R} = \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3, \text{C}_6\text{H}_{11}$) and $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{tBpTT})\text{Cl}]$ the structure shown in Fig. 2b. In the case of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{EpTT})]$ both isomers are present.

B. Reaction of the silver formamidino compounds with CO

The compounds $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{RNC}(\text{H})\text{NR}')\text{Cl}]$ react with CO initially according to eq. 2:



($\text{R}' = p\text{-tolyl}; \text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3, \text{C}_6\text{H}_{11}$)

Complexes with a small alkyl group rapidly decompose to AgCl , Ph_3PAgCl and a mixture of products which could not be identified. The compounds with $\text{R} = \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3$, or C_6H_{11} could be isolated and were investigated by microanalyses, molecular weight determination, and IR and ^{31}P , ^1H NMR spectroscopy. The CO vibrations at around $1976 \pm 10 \text{ cm}^{-1}$ are assigned to a terminal CO group bonded to Ir [6,7,8] and the IR frequencies at about $2032 \pm 3 \text{ cm}^{-1}$ are tentatively assigned to a terminal CO group bonded to Ag [12]. The vibration around $1624 \pm 4 \text{ cm}^{-1}$ is assigned to a CO group which is inserted into a metal-nitrogen bond at the side of the alkyl group, as is observed for this type

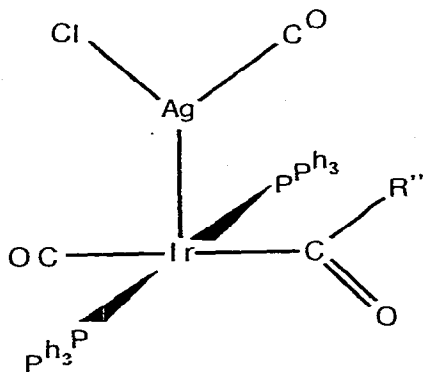


Fig. 3. Proposed structure of $[(\text{Ph}_3\text{P})_2(\text{CO})(\text{OCR}'')\text{IrAg}(\text{CO})\text{Cl}]$ ($\text{R}'' = i\text{-PpTF}, \text{tBpTF}, \text{cHpTF}$).

of ligand [13,14]. The single ^{31}P resonance at about 10 ppm and the absence of $^{107,109}\text{Ag}-^{31}\text{P}$ coupling indicates the presence of a plane of symmetry in the molecule with the PPh_3 ligands *trans* bonded to Ir.

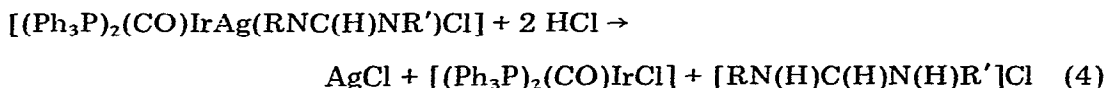
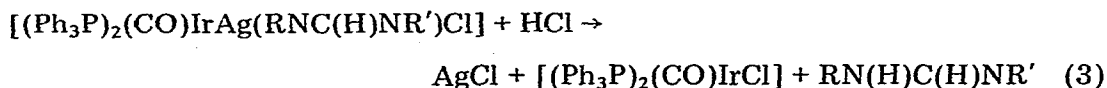
The ^1H NMR data show a drastic downfield shift for the protons on the formamido group, indicating a total change in the coordination of this ligand. Furthermore, where $\text{R} = \text{CH}(\text{CH}_3)_2$ a doublet is observed for the methyl groups and this in accordance with the ^{31}P NMR data, indicates the presence of a plane of symmetry. In the light of these observations and the fact that this type of compound, with an Ir^{I} -to- Ag^{I} metal-metal bond, contains a five coordinated Ir atom and a three coordinated Ag atom [6,7,8], we tentatively propose the structure shown in Fig. 3.

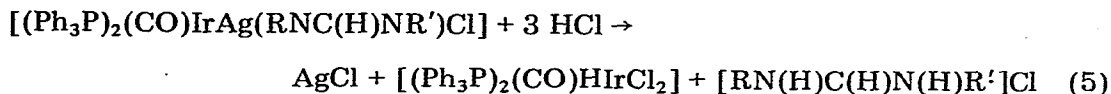
C. Reactions of the Ir-Ag formamidino compounds with isonitriles Ph_3P , pyridine, triazenes, formamidines and HCl

The formamidino complexes $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{RNC}(\text{H})\text{NR}')\text{Cl}]$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3, \text{C}_6\text{H}_{11}$; $\text{R}' = p\text{-tolyl}$) also react with isonitriles such as CH_3NC and $\text{C}_6\text{H}_{11}\text{NC}$, but rapid decomposition into AgCl , Ph_3PAgCl and a mixture of products then occur. The Ir-to-Ag bonded compounds do not react with donor ligands such as Ph_3P and pyridine.

^1H NMR experiments show that the formamidino group can be rapidly replaced by methyl-*p*-tolyltriazenido or by a formamidino group with a smaller alkyl group. It should also be noted that a considerable amount of decomposition of the complexes occurred. The order of ligand exchange is $\text{tBpTF} = \text{cHpTF} \leq \text{iPpTF} \leq \text{EpTF} \leq \text{MpTF} \leq \text{MpTT}$.

Reactions of the complexes with a strong acid (HCl), followed by IR ($\nu(\text{CO})$) and ^1H NMR (the resonances of the formamidine group), indicate that depending on the amount of acid present, reactions 3, 4 and 5 occur:





Discussion

It has been demonstrated that the isostructural formamidino derivatives may be prepared, in a procedure analogous to that used for triazenido compounds $[\text{L}_2(\text{CO})\text{M}'\text{M}(\text{RN}_3\text{R}')\text{X}]$ [6,7], by reaction of $[\text{L}_2(\text{CO})\text{MX}]$ with the complexes $[\text{M}(\text{RNC}(\text{H})\text{NR}')]\text{X}$ ($n = 2, 4$). As in the case of the triazenido and carboxylato compounds, the main feature stabilizing the metal-to-metal donor bond is the bridging formamidino group, which together with the $\text{M}'\text{--M}$ pair forms a five-membered ring in which electron delocalization occurs, as shown by the crystal structures [11,15].

Nonetheless, there are also clear differences, since the formamidino compounds appear to be less easily formed than the triazenido compounds. The relative order is $\text{Ir}^I > \text{Rh}^I(\text{M}')$; $\text{Ag}^I > \text{Cu}^I(\text{M})$ and small alkyl(R) > larger R groups. The sequence $\text{Ir}^I > \text{Rh}^I$ has also been observed for the analogous triazenido complexes [6,7] and carboxylato complexes [8], and is no doubt due to the greater basicity of the Ir^I atom which thereby stabilizes the $\text{M}'\text{--to-M}$ donor bond. This sequence has also been observed in the reaction of $\text{L}_2(\text{CO})\text{IrX}$ with $\text{Tl}(\text{O}_2\text{CR})_3$ which afforded $[\text{L}_2(\text{CO})\text{X}(\text{O}_2\text{CR})\text{IrTl}(\text{O}_2\text{CR})_2]$ with a very strong Ir--Tl bond, whilst the analogous Rh--Tl bonded compounds could not be prepared [16]. The sequence $\text{Ag}^I > \text{Cu}^I$ is interesting since it is the reverse of the order observed for the related triazenido and carboxylato complexes. Since the factors contributing to this order are not very clear, we will not attempt to explain this reversal of stability.

The influence of the bulkiness of the R substituents is obvious. However, some interesting comments can be made, since calculations based on the crystal structures of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{RhCu}(\text{DMT})\text{Cl}]$ [15] and of $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{MpTT})(\text{O}_2\text{CCH}(\text{CH}_3)_2)_2\text{H}]$ [11] show that NR (or NR') groups of (RNYNR') ($\text{Y} = \text{CH}, \text{N}$) can only be coordinated to Ir if R is small (e.g. Me, Et) or if R is an aryl group which can fit between the two phosphines. Indeed, it was found that in the case of MpTF the NMe group is coordinated to Ir [11]. In the case of EpTF the NEt group is coordinated to Ag, but the NEt group of the triazenido group $\text{EtN}_3\text{-}p\text{-tol}$ may bond either to Ag or to Ir thereby giving rise of two isomers. For the larger alkyl (R) groups the $\text{N-}p\text{-tolyl}$ group is bonded to Ir. In view of these considerations it is no surprise that no compounds could be prepared from symmetric formamidino ligands with large alkyl substituents.

Of special interest is the mechanism of the reactions leading to the $\text{M}'\text{--M}$ bonded complexes, since they involve an interaction of a large planar complex with large dimeric and/or tetrameric units. Very recently it was shown from NMR studies on the asymmetric substituted compounds $[\text{M}(\text{RNC}(\text{H})\text{NR}')]\text{X}$ that in many cases an equilibrium between the tetrameric and dimeric species exists, which is a function of temperature and concentration, and that the equilibrium occurs via M--N bond breaking and bond formation [10].

It was also apparent that monomeric species do not occur. This implies that the reaction leading to the $\text{M}'\text{--M}$ bonded complexes probably proceeds first

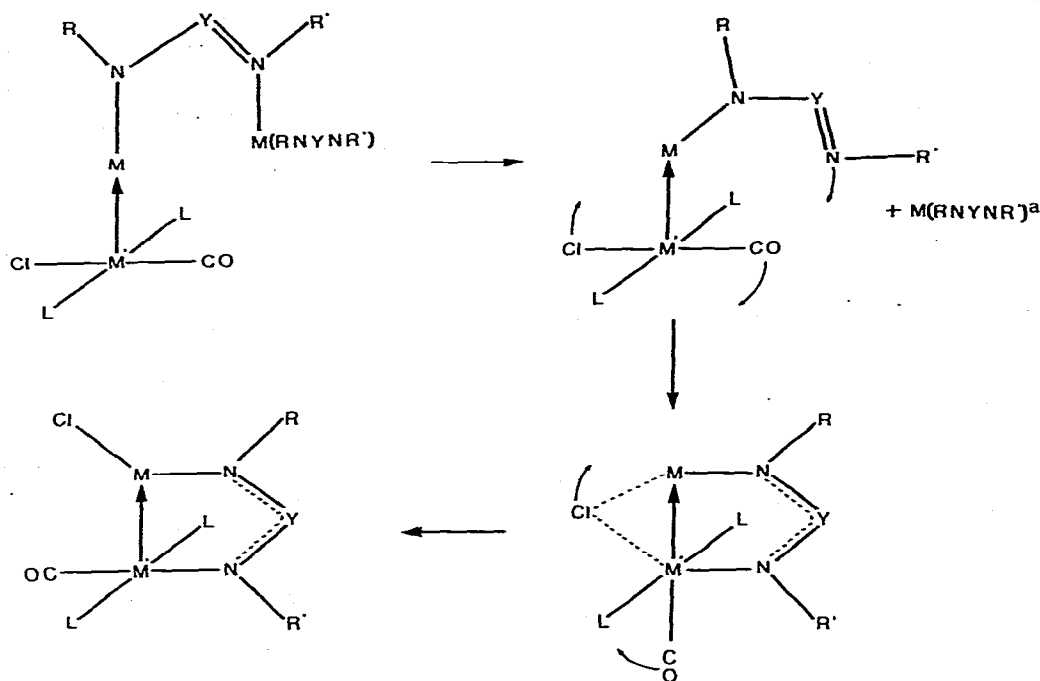


Fig. 4. Reaction mechanism for the M' -to- M bonded triazenido and formamidino compounds. a. Recombination to a dimer (tetramer) or direct reaction with $[L_2(CO)M'X]$.

via $M-N$ bond breaking at one side of the dimer. The coordinative unsaturated $Cu(Ag)$ atom is then attached to the Ir^I atom. Subsequently a second $M-N$ bond is broken after which the formamidino group is linked as a ligand bridging the $M'-M$ pair, with concomitant migration of the halide atom from M' to M (Fig. 4).

A second mechanism in which the Cu atom attacks the halide atom on M is not excluded, but appears less likely.

The reactions of the complexes with Ph_3P , pyridine and formamidines are a clear reflection of the stability of the $M'-M$ bond in these complexes. The reaction with CO is of particular interest in view of the recent work on the insertion of CO into $M-M$ bonds [8,10,13,14,17]. It has been reported that $[(Ph_3P)_2(CO)IrAg(RN_3R')Cl]$ reacts with CO to give $[(Ph_3P)(CO)_2Ir(OCN(R)-N=NR')]$, and Ph_3PAgCl [7]. One of the incoming CO groups was shown to insert between Ir and N and to give rise to a chelating acyltriazenido group.

We have discussed above the formation of $[(Ph_3P)_2(CO)(OCN(R)C(H)NR')-IrAg(CO)Cl]$ with an unstable $Ir-Ag$ bond and an acyltriazenido group bonded to Ir . Of special interest in these complexes is the possible carbon monoxide-to-silver bond, which to our knowledge would be the first example of such a bond in an organometallic compound [12]. These complexes are unstable and decompose even at low temperatures. It could well be that this type of compound is an intermediate in the formation of the previously discussed acyltriazenido complexes $[(Ph_3P)(CO)_2Ir(OCN(R)N=NR')]$ [7].

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