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METAL—METAL BONDED TRIAZENIDO COMPOUNDS

I. COMPLEXES $[L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R)X]$ WITH M = Rh^I, Ir^I; L = AsR_3, PR_3; R = Me, Aryl and X = Cl, Br, I

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Summary

Reactions of $L_2M(CO)X$ (L = Ph_3P, $PhMe_2P$, Ph_3As; M = Rh^I, Ir^I and X = Cl, Br, I) with $[Cu(R{-}N{\cdots}N{\cdots}N{-}R')]_n$ ($n = 4$ for $R = R' = CH_3$; $n = 2$ for $R = R'$ = *p*-tolyl and for $R = CH_3$ and R' = *p*-tolyl) afford the novel complexes $[L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R')X]$ in which three-coordinate Cu^I is directly bonded to the five-coordinate metal atom M^I. The $M^I \rightarrow Cu^I$ donor bond is bridged by the azenido group. The halide atom X has migrated from the metal atom to the copper atom.

Possible mechanisms for the formation of these complexes and of related new formamidine and trifluoroacetate compounds are considered and the properties of the complexes are discussed.

Introduction

Our interest has recently focussed on the coordinating properties of pseudo-allenic and -allylic ligands, such as sulfurdiimines [1-3] and carbodiimines, in complexes of Pt^{II} and Rh^I. In this connection we began to investigate the chemistry of metal—triazenido complexes. Although little is known about them, it has been reported that the triazenido group can act as a monodentate [4,5], as a bidentate bonded to one metal atom [4-6], or as a bridging ligand [7,8] (e.g. $[Cu(RN_3R)]_4$ [7]) (Fig. 1).

The preparations involved reactions of transition metal compounds with triazenes in the presence of a base [9,10], reactions of triazenes with transition metal hydrides with the evolution of hydrogen [5], oxidation-reduction reactions of e.g. $Pt(PPh_3)_3$ with triazenes [5], and finally metathesis reactions of lithiumtriazenido compounds with suitable metal complexes [4].

A new method of preparation, involving reactions with copper-triazenes, is now reported. By this type of reaction a new class of compounds is formed,

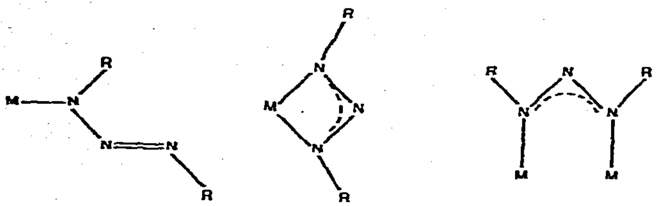

Fig. 1. Coordination modes of the triazenido ligand.

which contains a five membered ring in which a metal—copper bond occurs stabilized by a bridging triazenido group.

The scope of this reaction will be demonstrated in subsequent papers on analogous silver and mercury compounds, and it will be shown below that the azenido group may be replaced in some cases by other groups such as formamidine and trifluoroacetate.

Experimental

The preparations were carried out under argon. The copper triazenes [9, 10], copper di(*p*-tolyl)formamidine [11] and (triphenylphosphine)copper chloride [12] were prepared according to published methods. (Dimethylphenylphosphine)copper chloride was prepared as described for the triphenylphosphine derivative.

Copper trifluoroacetate [13] was prepared by modification of an established procedure. A suspension of excess of cuprous oxide in 20 ml of a 1/1 mixture of trifluoroacetic acid anhydride and benzene was refluxed. After 4 h 20 ml oxygen-free benzene was added and the mixture filtered hot. Oxygen-free hexane was then added and the solution cooled to —20°C. White needles of copper trifluoroacetate were obtained in about 90% yield.

The compounds $L_2Ir(CO)Cl$ ($L = PhMe_2P, Ph_3As$) were prepared according to a novel procedure starting from the easily obtainable bis(cyclooctene)iridium chloride dimer [14]. This is a very general and simple method, which gives high yields and needs only very short reaction times. An example is:

Preparation of $(Ph_3As)_2(CO)IrCl$ [15]

Bis(cyclooctene)iridium chloride dimer (0.9 g) was suspended in oxygen-free benzene (50 ml) and triphenylarsin (1.25 g) added immediately with rapid stirring. After dissolution of the arsine, carbon monoxide was bubbled through the well-stirred, orange suspension. After about two minutes the solution became clear and the colour turned to yellow. The carbon monoxide stream was continued for one minute. After refluxing for another two minutes, the solution was filtered hot to remove traces of colloidal impurities. After 24 h at 5°C yellow crystals of $(Ph_3As)_2(CO)IrCl$ were obtained, and were vacuum dried to remove benzene (yield 95%).

Preparation of $(Ph_3P)_2(CO)MX$ ($M = Rh, Ir; X = Br, I$)

A solution of $(Ph_3P)_2(CO)MCl$ (3.0 mmol) in boiling tetrahydrofuran (75 ml) was refluxed and 30 mmol of LiBr or NaI added slowly. The dark solution was concentrated to about 10 ml, and 100 ml of oxygen-free water was added under vigorous stirring. The precipitate was filtered off, and washed carefully with water at 50°C and subsequently with acetone. Bright yellow compounds were obtained in about 90% yield.

Preparation of $(Me_2Y)_2(CO)PhCl$ $(Y = S, Se, Te)$

To a hot solution of 2.0 mmol $[(CO)_2RhCl]_2$ in 50 ml hexane was added R_2Y (4.0 mmol for Y = Se, Te and 40.0 mmol for Y = S). Cream-yellow crystals were obtained in about 80-85% yield.

Preparation of $[L_2(CO)MCu(R{-}\underline{N{-}N{-}N}{-}R)X]$

As an example the preparation of $[(Ph_3P)_2(CO)RhCu(R{-}\underline{N{-}N{-}N}{-}R)Cl]$ is given.

Tetrameric copper dimethyltriazene (0.5 mmol) was added to a suspension of $(Ph_3P)_2(CO)RhCl$ (2 mmol) in 30 ml tetrahydrofuran. The mixture was refluxed until a clear solution was obtained (about 15 min). After another ten minutes of refluxing the solution was cooled to 0°C. After 24 h orange-yellow crystals were obtained. A second pure fraction may be obtained by concentration to 10 ml and addition of 20 ml ether (yield 75%). This compound and the other members of this series are air stable solids, which decompose slowly in solution when air is admitted.

Preparation of $(Ph_3P)_2(CO)M(O_2CCF_3)$ *(M = Rh [16], Ir [17])*

$[Cu(O_2CCF_3)]_4$ (0.5 mmol) was added to a suspension of $(Ph_3P)_2(CO)MCl$ (2 mmol) in 30 ml of boiling benzene. A precipitate of CuCl appeared, and the mixture was subsequently refluxed for ten minutes. After cooling and filtration, the filtrate was concentrated under vacuum to about 10 ml. After addition of 40 ml of hexane and subsequent cooling yellow crystals were obtained in almost quantitative yield.

Preparation of $[(Ph_3P)_2(CO)IrCu(O_2CCF_3)_2]$

$[Cu(O_2CCF_3)]_4$ (0.5 mmol) was added to a solution of $(Ph_3P)_2(CO)Ir(O_2CCF_3)$ (2 mmol) in 20 ml of benzene. The colour changed from yellow to orange-red. The solution was concentrated under vacuum, and addition of 30 ml of hexane precipitated the orange compound in about 80% yield. The complex is slightly air-sensitive.

The rhodium complex $(Ph_3P)_2(CO)RhCu(O_2CCF_3)_2$ could not be obtained pure. It is likely that it is formed, as indicated by the IR spectra of the precipitates (Nujoll mull).

Reaction of $(PPh_3)_2(CO)IrCl$ *with* $(Ph_3P)_2(CO)IrCu(O_2CCF_3)_2$

Addition of $(Ph_3P)_2(CO)IrCl$ (1 mmol) to a benzene solution of $(Ph_3P)_2(CO)IrCu(O_2CCF_3)_2$ (1 mmol, 10 ml) gave a precipitate of CuCl. After filtration $(Ph_3P)_2(CO)Ir(O_2CCF_3)$ was obtained in almost quantitative yield.

Reactions of $(Ph_3P)_2(CO)MCl$ *with* $LCuCl$ $(L = Ph_3P, PhMe_2P)$

Mixtures of $(Ph_3P)CuCl$ and $(Ph_3P)_2(CO)MCl$ (M = Rh, Ir) in tetrahydrofuran, benzene, acetone, toluene or chloroform (as suspensions or solutions) did not give any observable reaction even after 24 h of refluxing. This was confirmed by analysis and IR spectroscopy of the products after careful recrystallization. The reaction with $(PhMe_2P)CuCl$ (2 mmol) involved its addition to $(Ph_3P)_2(CO)IrCl$ (1 mmol) suspended in 10 ml of benzene at 20°C with stirring. A clear yellow solution was obtained, and a white compound slowly precipitated. Diethyl ether (20 ml) was added, and the precipitate, which was filtered off and washed with ether, analysed as $(PPh_3)CuCl$. After concentration of the filtrate to 5 ml, ether (20 ml) was added. It was kept at −35°C and yellow crystals of $(PPhMe_2)_2(CO)IrCl$ were obtained in 70% yield.

TABLE 1

ANALYTICAL DATA FOR $L_2(CO)MCu(T)X$[a]

Compound[b]	Mol. wt.[c] found (calcd.)	Analysis found (calcd.) (%)				
		C	H	Cl	Cu	N
$(Ph_3P)_2(CO)RhCu(DMT)Cl$	801	56.46	4.30	4.20	6.91	5.22
	(826.5)	(56.66)	(4.39)	(4.29)	(7.68)	(5.08)
$(Ph_3P)_2(CO)RhCu(M_pTT)Cl$	832	59.63	4.48	3.87	5.43	4.09
	(902.7)	(59.88)	(4.47)	(3.93)	(7.04)	(4.66)
$(Ph_3P)_2(CO)RhCu(D_pTT)Cl$	952	61.89	4.48	3.67	6.56	4.66
	(978.7)	(62.58)	(4.53)	(3.62)	(6.49)	(4.29)
$(Ph_3P)_2(CO)RhCu(DMT)I$	895	51.69	4.34		6.25	4.66
	(918.0)	(51.02)	(3.95)		(6.92)	(4.58)
$(Ph_3As)_2(CO)RhCu(DMT)Cl$	925	50.93	4.08	3.83	6.30	4.62
	(914.5)	(51.22)	(3.97)	(3.87)	(6.94)	(4.60)
$(PhMe_2P)_2(CO)RhCu(DMT)Cl$	531	39.54	4.96	6.11	10.74	7.11
	(578.3)	(39.46)	(4.87)	(6.13)	(10.98)	(7.26)
$(Ph_3P)_2(CO)IrCu(DMT)Cl$	914	51.85	4.12	3.59	7.39	4.47
	(915.8)	(51.14)	(3.96)	(3.87)	(6.94)	(4.59)
$(Ph_3P)_2(CO)IrCu(M_pTT)Cl$	995	53.25	3.99	3.59	7.11	4.14
	(991.9)	(54.49)	(4.06)	(3.57)	(6.41)	(4.24)
$(Ph_3P)_2(CO)IrCu(D_pTT)Cl$	1011	56.73	4.12	3.42	5.28	2.95
	(1068)	(57.35)	(4.15)	(3.32)	(5.95)	(3.93)
$(Ph_3P)_2(CO)IrCu(DMT)I$	1015	47.02	3.82		6.14	4.14
	(1007.3)	(46.50)	(3.60)		(6.30)	(4.17)
$(Ph_3As)_2(CO)IrCu(DMT)Cl$	990	46.84	3.69		6.14	4.08
	(1003.7)	(46.66)	(3.62)		(6.33)	(4.19)
$(PhMe_2P)_2(CO)IrCu(DMT)Cl$	624	34.58	4.30		10.63	6.30
	(667.6)	(34.18)	(4.23)		(9.52)	(6.30)
$(Ph_3P)_2(CO)IrCu(D_pTF)Cl$	1031	58.20	4.24		5.28	2.63
	(1067.0)	(58.53)	(4.25)		(5.95)	(2.63)
$(Ph_3P)_2(CO)IrCu(O_2CCF_3)_2$	930	47.41	2.94		5.70	
	(1034.3)	(47.61)	(2.92)		(6.14)	
$(PPh_3)_2(CO)IrO_2CCF_3$		54.30	3.51			
		(54.60)	(3.53)			
$(PPh_3)_2(CO)RhO_2CCF_3$		61.00	3.98			
		(60.95)	(3.93)			
$(PhMe_2P)_2(CO)IrCl$		38.63	4.16			
		(38.38)	(4.17)			

[a] T = Dimethyltriazene (DMT), methyl(p-tolyl)triazene (M_pTT), di(p-tolyl)triazene (D_pTT), di(p-tolyl)formamidine (D_pTF), or trifluoroacetate. [b] The rhodium—copper complexes are yellow-orange to cream coloured crystalline compounds, the iridium—copper complexes are red except for the orange trifluoroderivate. [c] The experimental error is ±10%.

Reactions of $[\mathrm{Cu(Me{-}\underline{N{-}N{-}N}{-}Me)}]_4$ with $(L)_2(CO)RhCl$ ($L = Me_2S, Me_2Se, Me_2Te, PhMe_2As$)

Addition of $[\mathrm{Cu(Me{-}\underline{N{-}N{-}N}{-}Me)}]_4$ (0.25 mmol) to a solution of $\mathrm{L_2(CO)RhCl}$ (1.0 mmol) in tetrahydrofuran or benzene gave a red solution. In the case of L = $\mathrm{PhMe_2As}$ a copper mirror was slowly formed along with black decomposition products. The other ligands L (= $\mathrm{Me_2S}$, $\mathrm{Me_2Se}$, $\mathrm{Me_2Te}$) also gave black decomposition products. No compounds of the formula $\mathrm{(L)_2(CO)RhCu(Me{-}\underline{N{-}N{-}N}{-}Me)Cl}$ could be isolated.

Proton NMR spectra were recorded on a HA 100 Varian spectrometer, and ^{13}C NMR spectra on a Varian XL-100 and a Varian CFT 20. The infrared spectra were recorded on Beckman IR 11 and IR 7 spectrometers. Molecular weights were measured with a Hewlett Packard vapour pressure osmometer Model 320 B.

C, H and Cl analyses were carried out in this laboratory, while N, P and Cu analyses were carried out at the organic laboratory of the TNO in Utrecht (see Table 1).

Results

A. Structural characterization of the azenido compounds

Reactions of $[\mathrm{Cu(R{-}\underline{N{-}N{-}N}{-}R')}]_n$ with $\mathrm{L_2(CO)MX}$ (M = Rh, Ir) gave high yields of complexes of the composition $[\mathrm{L_2(CO)MCu(R{-}\underline{N{-}N{-}N}{-}R')X}]$ (X = Cl, Br, I) in the case of L = $\mathrm{Ph_3P}$, $\mathrm{PhMe_2P}$ and $\mathrm{Ph_3As}$, according to reaction 1:

$$\mathrm{L_2(CO)MX} + \frac{1}{n}[\mathrm{Cu(R{-}\underline{N{-}N{-}N}{-}R')}]_n \rightarrow \mathrm{L_2(CO)MCu(R{-}\underline{N{-}N{-}N}{-}R')X} \qquad (1)$$

R = $\mathrm{CH_3}$, tolyl; R′ = $\mathrm{CH_3}$, tolyl.

$n = 4$ for R = R′ = $\mathrm{CH_3}$ and $n = 2$ for the other combinations. For L = $\mathrm{PhMe_2As}$, $\mathrm{Me_2S}$, $\mathrm{Me_2Se}$ and $\mathrm{Me_2Te}$ decomposition products were formed, and no product could be isolated.

A single crystal X-ray structural determination [16] on $\mathrm{(Ph_3P)_2(CO)RhCu(Me{-}\underline{N{-}N{-}N}{-}Me)Cl}$ showed the existence of a direct Rh—Cu bond (Rh—Cu = 2.73 Å*) bridged by the triazenido group (Fig. 2). The two metal atoms and the three nitrogen atoms lie approximately in one plane.

The crystal structure shows that the rhodium atom is five-coordinate, while the copper atom is three-coordinate. The migration of the chloride atom from rhodium to copper is unusual.

The solid state molecular structure also persists in solution, as is shown by ^{1}H and ^{13}C NMR (Tables 2 and 3). From the NMR spectrum it is clear that the two equivalent phosphine groups are *trans* to each other. It is evident from the non-equivalence of the two methyl groups of $\mathrm{PhMe_2P}$ that there is no plane of symmetry through the P—Rh—P bonds, and this is confirmed by the crystal structure.

From Table 2 it is concluded that the methyl groups of the $\mathrm{Me{-}\underline{N{-}N{-}N}{-}Me}$ ligand are non-equivalent and resonate at quite different fields when L = $\mathrm{PhMe_2P}$.

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* The Ir—Cu distances in $\mathrm{Ir_2Cu_4(C{\equiv}C{-}Ph)_8(PPh_3)_2}$ range from 2.77 to 2.96 Å [17].

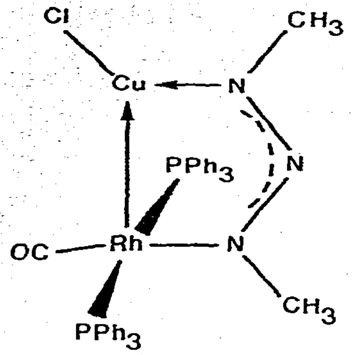

Fig. 2. Structure of [bis(triphenylphosphine)carbonylrhodiumcopperdimethyltriazenidochloride].

For L = Ph_3P and L = Ph_3As, the low field absorption is moved to a much higher field and lies close to the other methyl absorption. This upfield shift can be explained if the low field methyl absorption in the case of [$(PhMe_2P)_2(CO)MCu$-

TABLE 2

^{1}H NMR DATA FOR $L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R)X$[a] AND FOR SOME RELEVANT STARTING COMPOUNDS IN $CDCl_3$ (ppm RELATIVE TO TMS)

Compound	Aryl protons of the tolyl group on the side[b] of		Methyl protons[c] on the side[b] of		Resonances of L
	Cu	Rh, Ir	Cu	Rh[d], Ir	
DMT			3.06		
$[Cu(DMT)]_4$			3.34		
$(Ph_3P)_2(CO)RhCu(DMT)Cl$			2.66	2.54	7.80m: 7.41m
$(Ph_3P)_2(CO)RhCu(DMT)I$			2.70	2.49	7.80m: 7.42m
$(Ph_3As)_2(CO)RhCu(DMT)Cl$			2.55	2.52	7.74m: 7.41m
$(PhMe_2P)(CO)RhCu(DMT)Cl$			3.28	2.82	7.75m; 7.42m 1.94dt[e]; 1.75dt[e]
$(Ph_3P)_2(CO)IrCu(DMT)Cl$			2.59	2.51	7.83m: 7.42m
$(Ph_3P)_2(CO)IrCu(DMT)Br$			2.61	2.50	7.82m: 7.41m
$(Ph_3P)_2(CO)IrCu(DMT)I$			2.63	2.48	7.83m: 7.43m
$(Ph_3As)_2(CO)IrCu(DMT)Cl$			2.60	2.60	7.77m: 7.41m
$(PhMe_2P)_2(CO)IrCu(DMT)Cl$[f]			3.21	2.75	7.58m: 7.08m: 7.03m 1.83t[e]; 1.59t[e]
M_pTT	7.27: 7.12		3.26: 2.32		
$[Cu(M_pTT)]_2$	7.30: 7.06		3.13: 2.30		
$(PPh_3)_2(CO)RhCu(M_pTT)Cl$		6.96: 6.85	2.61	2.22	7.75m: 7.36m
$(PPh_3)_2(CO)IrCu(M_pTT)Cl$		6.93: 6.85	2.60	2.22	7.78m: 7.36m
DpTT	7.30: 7.15		2.33		
$[Cu(D_pTT)]_2$	7.17; 6.77		2.16		
$(PPh_3)_2(CO)RhCu(D_pTT)Cl$	7.06;6.43	6.96: 6.85	2.07	2.22	7.65m: 7.27m
$(PPh_3)_2(CO)IrCu(D_pTT)Cl$	7.12: 6.46	6.94; 6.86	2.08	2.22	7.69m: 7.30m
$(PPh_3)_2(CO)Ir(D_pTT)$		6.89: 6.74		2.19	7.62m: 7.25m
$(PPh_3)_2(CO)IrCu(D_pTF)Cl$	6.83; 6.37	6.38; 6.38	2.07	2.20	7.71m: 7.33m

[a] See note [a] of Table 1. [b] This denotes the aryl or methyl group bonded to the nitrogen atom attached to copper, rhodium or iridium (except in the case of the pure ligands). [c] In the case of DMT a methyl—methyl coupling is observed of $J(H{-}H) \approx 0.8$ Hz. [d] In the rhodium(DMT) compounds a rhodium—methyl coupling is observed for these resonances $J(Rh{-}H) \approx 0.6$ Hz. [e] dt = double triplet $J(Rh{-}H) = 1.4$ and 1.2, and $J(P{-}H) = 3.2$ Hz. t = triplet, $J(P{-}H) = 3.5$ Hz. [f] In C_6D_6.

TABLE 3

^{13}C NMR DATA FOR SOME L_2(CO)MCu(DMT)Cl COMPOUNDS IN $CDCl_3$ (ppm RELATIVE TO TMS)

Compound	DMT	Resonances of L (*J*P is noted in brackets in Hz)			
		ortho	*meta*	*para*	C—P, As
$(Ph_3P)_2$(CO)RhCu(DMT)Cl	47.00; 46.33[a]	134.5t(6.6)	128.3t(5)	130.5	132.7t(22.3)
$(Ph_3As)_2$(CO)RhCu(DMT)Cl	46.96[b]: 46.73	133.8	128.8	130.3	133.9
$(Ph_3P)_2$(CO)IrCu(DMT)Cl	48.82: 47.06	134.6t(6.2)	128.3t(5.4)	130.8	132.1t(23)

[a] This resonance is broadened, probably by coupling with Rh. [b] $J(^{103}Rh—^{13}C)$ = 2.2 Hz.

$(\mathrm{Me{-}\underline{N}{\cdots}\underline{N}{\cdots}\underline{N}{-}Me})\mathrm{Cl}]$ is assigned to the —N—Me group coordinated to the copper atom, since in the case of $[(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{RhCu}(\mathrm{Me{-}\underline{N}{\cdots}\underline{N}{\cdots}\underline{N}{-}Me})\mathrm{Cl}]$ the Me group is known to lie above the center of one of the phenyl rings, as shown by the X-ray structural determination [16]. This methyl group will experience additional screening in the last compound, which will cause an upfield shift. A tentative assignment of the NMR absorptions is shown in Table 2.

TABLE 4

IR DATA FOR L_2(CO)MCu(T)X[a] AND SOME RELEVANT COMPOUNDS (NUJOLL MULL AND C_4Cl_6) IN CM^{-1}

Compound	ν_{CO}	ν_{CuX}	$\nu_{triazenido}$[b], acetate	δ_{nnn}[b]
$[Cu(DMT)]_4$			1358 ν_{as}; 1340; 1190 ν_s	635, 620
$(Ph_3P)_2$(CO)RhCu(DMT)Cl	2002	339	1353 ν_{as}; 1333	626
$(Ph_3P)_2$(CO)RhCu(DMT)I	1993	199	1350 ν_{as}; 1328	620
$(Ph_3As)_2$(CO)RhCu(DMT)Cl	1999	340[c]	1351 ν_{as}; 1335	625
$(PhMe_2P)$(CO)RhCu(DMT)Cl	1976	347	1355 ν_{as}; 1325	619
$(Ph_3P)_2$(CO)IrCu(DMT)Cl	1992	336	1356 ν_{as}; 1333	630
$(Ph_3P)_2$(CO)IrCu(DMT)Br	1980	217?	1354 ν_{as}; 1335	625
$(Ph_3P)_2$(CO)IrCu(DMT)I	1984	201	1354 ν_{as}; 1335	618
$(Ph_3As)_2$(CO)IrCu(DMT)Cl	1984	338[c]	1356 ν_{as}; 1332	625
$(PhMe_2P)$(CO)IrCu(DMT)Cl	1964	340	1350 ν_{as}; 1329	611
$[Cu(M_pTT)]_2$			1368 ν_{as}; 1282 ν_s(br); 1316	598
$(Ph_3P)_2$(CO)RhCu(M_pTT)Cl	1985	334	1371 ν_{as}; 1274 ν_s; 1318	603
$(Ph_3P)_2$(CO)IrCu(M*p*TT)Cl	1978	331	1369 ν_{as}; 1278 ν_s; 1319	
$[Cu(D_pTT)]_2$			1361 ν_{as}; 1215 ν_s	600
$(Ph_3P)_2$(CO)RhCu(D_pTT)Cl	1998	345	1370 ν_{as}; 1205 ν_s	
$(Ph_3P)_2$(CO)IrCu(D_pTT)Cl	1992	345	1375 ν_{as}; 1208 ν_s	
$[Cu(D_pTF)]_2$			1575 ν_{as}; 1353 ν_s; 1225	634
$(Ph_3P)_2$(CO)IrCu(D_pTF)Cl	1984	355?	1564 ν_{as}; 1373 ν_s	
$[Cu(O_2CCF_3)]_4$[d]			1665 ν_{as}; 1425 ν_s	675
$(Ph_3P)_2$(CO)Ir(O_2CCF_3)[d]	1976		1701 ν_{as}; 1404 ν_s	620
$(Ph_3P)_2$(CO)IrCu$(O_2CCF_3)_2$[d]	1988		1685 ν_{as}(1); 1650 ν_{as}(2); 1420 ν_s	617
$(Ph_3P)_2$(CO)RhCu$(O_2CCF_3)_2$	2000		1685 ν_{as}(1); 1645 ν_{as}(2); 1416 ν_s	
$(Ph_3P)_2$(CO)Rh(D_pTT)	1940		1274 ν_{as}[e]; 1211 ν_s	627
$(Ph_3P)_2$(CO)Ir(D_pTT)	1930		1276 ν_{as}[e]; 1211 ν_s	

[a] See note [a] of Table 1. [b] A tentative assignment is given. ν_{as} is very strong in the range 1350-1375 cm^{-1} and might be associated with the bridging triazenido group. [c] Obscured by ν(Rh—As) and ν(Ir—As). [d] Vibrations between 1680-1710 cm^{-1} belong to a monodentate acetato group whereas vibrations below 1670 cm^{-1} belong to a chelate acetato group [19]. [e] Unidentate triazenido group [5].

The infrared spectra (Nujoll mulls) show one CO vibration at around 1985 cm^{-1}, as expected for complexes of Rh^I and Ir^I [15,18,19] (see Table 4).

In the region of 300-330 cm^{-1} the Rh—Cl and Ir—Cl stretching frequencies are absent, while the appearance of a new vibration in the range of 330-345 cm^{-1} can probably be assigned to the Cu—Cl stretch [20,21]. In the case of the iodides, a relative strong vibration appears at 199 and 200.5 cm^{-1} for M = Rh^I and M = Ir^I respectively, which is probably due to the Cu—I stretch. No useful information could be obtained from the Raman spectra owing to their poor quality.

The frequencies which could be assigned to the skeletal vibrations of the azenido group are also listed in Table 4. It has been proposed by others [4,5] that in the case of the four membered metal azenido ring, in which the azenido group acts as a bidentate ligand, the skeletal vibrations occur in the ranges 1260-1300 cm^{-1} and 1580-1600 cm^{-1} *. In the case of the monodentate or the bridging azenido group vibrations were found in the ranges 1150, 1190-1210, 1260-1300 cm^{-1} and 1580-1600 cm^{-1} *. Comparison of the few literature data [4,5] with our results indicate that much more work is needed before definite assignments can be made and used as diagnostic tests.

B. Reactions of $L_2(CO)MX$ with other Cu^I compounds

Treatment of $(Ph_3P)_2(CO)IrCl$ with the complex $[Cu(p\text{-tolyl-}\underline{N{-}C(H){-}N}\text{-}p\text{-tolyl})]_2$ yielded $[(Ph_3P_2(CO)IrCu(p\text{-tolyl-}\underline{N{-}C(H){-}N}\text{-}p\text{-tolyl})Cl]$. The corresponding rhodium complex could not be prepared in this way. An alternative route to both the rhodium (impure) and iridium compounds is the exchange reaction 2:

$$[(Ph_3P)_2(CO)MCu(Me{-}\underline{N{-}N{-}N}{-}Me)Cl] + p\text{-tolyl}{-}N{=}C(H){-}N(H){-}p\text{-tolyl} \rightarrow$$
$$\rightarrow [(Ph_3P)_2(CO)MCu(p\text{-tolyl}{-}\underline{N{-}C(H){-}N}{-}p\text{-tolyl})Cl] + Me{-}N(H){-}N{=}N{-}Me \qquad (2)$$

Reactions with the tetrameric copper trifluoroacetate proceeded by two steps (reactions 3 and 4):

$$(PPh_3)_2(CO)MCl + \tfrac{1}{4}[Cu(O_2CCF_3)]_4 \rightarrow (PPh_3)_2(CO)M(O_2CCF_3) + CuCl\downarrow \qquad (3)$$

$$(Ph_3P)_2(CO)M(O_2CCF_3) + \tfrac{1}{4}[Cu(O_2CCF_3)]_4 \rightarrow [(Ph_3P)_2(CO)MCu(O_2CCF_3)_2] \qquad (4)$$

In the case of M = Ir^I, reaction 4 goes to completion, while for M = Rh^I an equilibrium exists, so that the rhodium compound cannot be isolated pure (see Experimental).

Finally an attempt was made to form compounds by treating $(Ph_3P)_2(CO)$-IrCl with LCuCl (L = Ph_3P, PMe_2P). No reaction was observed for $(Ph_3P)CuCl$**, while an interesting ligand exchange was found for $(PhMe_2P)CuCl$ (reaction 5):

$$2\,(PhMe_2P)CuCl + (Ph_3P)_2(CO)IrCl \rightarrow (PhMe_2P)_2(CO)IrCl + 2\,(PPh_3)CuCl\downarrow \qquad (5)$$

This reaction is of preparative value, as $(PhMe_2P)_2(CO)IrCl$ was readily obtained pure and in high yield.

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* In our opinion this frequency must be assigned to aryl group vibrations.

** A reaction has been reported [22], but we were unable to find any evidence for it (see Experimental).

C. Chemical properties

The azenido group in $[(Ph_3P)_2(CO)RhCu(Me{-}N{\cdots}N{\cdots}N{-}Me)Cl]$ can be rapidly replaced by a reaction in chloroform with triazenes, which are more acidic than dimethyltriazene and, as we have noted before, also with di(*p*-tolyl)formamidine. The order of reactivity is: dimethyltriazene < di(*p*-tolyl)formamidine < methyl(*p*-tolyl)triazene ≈ di(*p*-tolyl)triazene. In the case of the iridium compounds, the exchange reactions are very slow.

In mixtures of $[L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R)X]$ and $[L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R)X']$ in chloroform at 30°C a rapid exchange of X and X′ ($X = X' = Cl, Br, I$) occurs. This may indicate some dissociation to X and X′ as halide ions in solution. Exchange might also occur via polynuclear intermediates [23].

The metal—metal bonded triazenido compounds do not react with donor ligands such as Ph_3P, Ph_3As, and pyridine. However $[(Ph_3P)_2(CO)IrCu(O_2CCF_3)_2]$ decomposes rapidly in the presence of Ph_3P, pyridine and *p*-toluidine.

Discussion

Although many metal—metal bonded compounds are known [25-28] there are relatively few with a covalent metal—copper bond [e.g. (*o*-triarsine)Cu—Mn$(CO)_5$], while no compounds have been prepared containing a metal→copper donor bond analogous to the cobalt→mercury bond in $(h^5\text{-}C_5H_5)(CO)_2Co{\rightarrow}HgCl_2$ [30]. A probable reason is the lower electronegativity of Cu^I compared with Hg^{II}.

The complexes described in this paper are the first examples of compounds formally containing a metal→Cu^I donor bond in which Rh^I or Ir^I donates an available electron pair to the Cu^I atom. This formulation seems appropriate, as the Rh^I and Ir^I metal atoms are five-coordinated, while Cu^I is three-coordinated. Furthermore, the carbonyl stretching frequencies (Table 4) are in the normal frequency region for Rh^I and Ir^I complexes.

An important feature stabilizing the metal→Cu^I bonds is no doubt the bridging azenido (formamidino and trifluoroacetato) group, which holds the metal—metal bond together in a five-membered ring, in which some electron delocalization may be assumed to occur.

It is clear that the formation and stability of the compounds are strongly influenced by the type of ligands L, by the type of bridging group and by the type of metal atom M. This is illustrated by the observation that the azenido compounds are formed if $L = Ph_3P$, $PhMe_2P$ or Ph_3As, but not if $L = PhMe_2As$, Me_2S, Me_2Se or Me_2Te, facts for which we have no satisfactory explanation. In the case of the azenido and formamidino complexes, the complexes are stable towards reaction with ligands such as phosphines, arsines and pyridine, but this is not the case for the trifluoroacetate analogue. This may indicate that strongly electron donating atoms such as N are needed to stabilize the bridged metal—metal bond. Finally the compounds can be more easily formed and seem to be less reactive when $M = Ir^I$. This is probably because Ir^I is a stronger electron donor than Rh^I [24].

The mechanism leading to the formation of the metal—metal bonded compounds and the migration of the halide atom, is as yet not very well under-

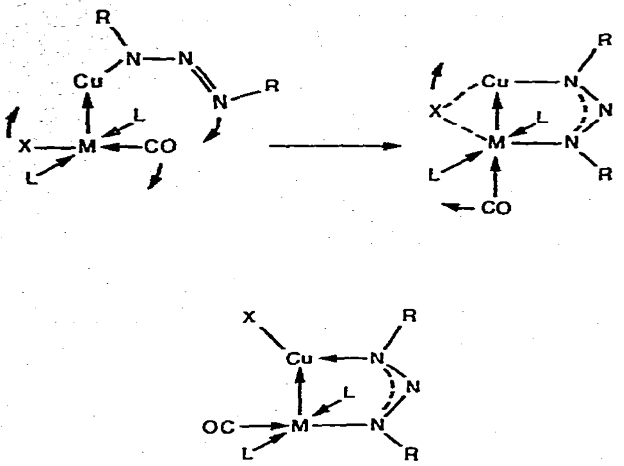

Fig. 3. Reaction mechanism I for the formation of $[L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R)X]$.

stood. The tetramer $[Cu(RN_3R)]_4$ may dissociate into dimers (mass spectrometric results), $[Cu(RN_3R)]_2$, which involves breaking of copper—nitrogen bonds. This implies that singly coordinate copper atoms, either in the dimer in an intermediate stage, or even in an intermediate monomer species Cu(R—N—N=N—R), may be available for attack on $L_2(CO)MCl$*. In principle the copper atom may attach itself directly to the metal atom M, after which the reaction may then proceed as shown in Fig. 3. An alternative mechanism may involve an attack of the copper atom on the halide atom, as in Fig. 4. Both mechanisms seem equally possible in the light of the available evidence.

In subsequent papers analogous addition compounds involving other metal atoms such as Ag^I and Hg^{II} will be described.

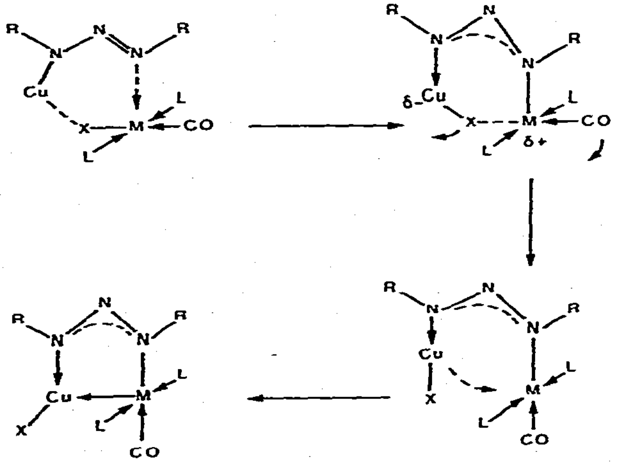

Fig. 4. Reaction mechanism II for the formation of $[L_2(CO)MCu(R{-}N{\cdots}N{\cdots}N{-}R)X]$.

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* A possible alternative is an attack of the dimer $[Cu(RN_3R)]_2$ on the metal complex, as the copper atoms have vacant coordination sites.

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