Journal of Organometallic Chemistry, 105 (1976) 379—387

METAL—METAL BONDED TRIAZENIDO COMPOUNDS

II *. COMPOUNDS $[(Ph_3P)_2(CO)M—Ag(R—N—N—N—R')X]$ WITH M = Rh^I, Ir^I; R = Me, ARYL AND X = Cl, Br, I

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(Received August 15th, 1975)

Summary

Complexes $[(Ph_3P)_2(CO)MAg(R—N—N—N—R')X]$ (M = Rh, X = Cl; M = Ir, X = Cl, Br, I and R = CH_3, R' = CH_3, *p*-tolyl) have been made by the reaction of $(Ph_3P)_2(CO)MX$ with $[Ag(R—N—N—N—R')]$. The proposed structure is analogous to that of the related copper derivatives and contains a five-membered ring in which an M^I to Ag^I donor bond is bridged by an azenido group, while the halide atom X has migrated from M^I to Ag^I.

Carbon monoxide at 1 atm reacts rapidly and quantitatively with the iridium compounds to give novel acyltriazenido compounds $\{Ph_3P(CO)_2\text{-}Ir[OC—N(—R)—N{=}N—R']\}$ (R = CH_3, *p*-tolyl; R' = CH_3, *p*-tolyl).

Introduction

In the first part of this series [1] the preparation, structure and some properties were reported of compounds of a new type, $[L_2(CO)MCu(R—N—N—N—R')X]$ (L = Ph_3P, $PhMe_2P$, Ph_3As; M = Rh, Ir; X = Cl, Br, I) which contain a five-membered ring in which a metal-to-Cu^I donor bond is bridged by an azenido group; it was shown that formamidino and trifluoroacetato groups are also able to stabilize the M^I to Cu^I donor bond, which were previously unknown. The structure [2] was also surprising in that the halide ion had migrated from the metal atom M to the Cu atom, which is three-coordinate, while M is five-coordinate.

It was noted that the ease of formation and the stability of the compounds are critically dependent on M, the type of bridging group and the nature of the ligands L. Therefore it was of interest to compare the Cu compounds with the

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* For part I, see ref. 1.

Ag compounds, and the preparation, structural characterization and properties of the latter are described below.

Experimental

All preparations were carried out under argon. Silver diaryltriazenes [3] and silver methylaryltriazenes [4] were prepared by published methods.

Preparation of silver dimethyltriazene [Ag(DMT)]

To an icecold solution of $AgNO_3$ (0.1 mol) in water (60 ml), covered with an ether layer (80 ml), was added a solution of NaOH (0.075 mol) in water (40 ml) with rapid stirring. Subsequently a solution of aluminium tris(dimethyltriazene) [5] (0.022 mol) in dry ether (40 ml) was added dropwise during 3 min. After the reaction had ceased, vigorous stirring was continued for 3 min. Icecold chloroform (300 ml) was added and the mixture shaken vigorously for 1 min. The organic layer was separated, and the water layer again extracted with 100 ml of chloroform. The organic layers were combined, and dried over Na_2SO_4 (5 min) with stirring. After filtration, concentration and addition of hexane white needles were obtained at —30° C in 90% yield.

Preparation of $[L_2(CO)MAg(R{-}\underline{N{-}N{-}N}{-}R')X]$ ($R = CH_3$, p-tol; $R' = CH_3$; $M = Rh$, $X = Cl$; $M = Ir$, $X = Cl, Br, I$; $L = Ph_3P$, $(p\text{-}tol)_3P$

As an example the preparation of $[(Ph_3P)_2(CO)RhAg(CH_3{-}\underline{N{-}N{-}N}{-}CH_3)Cl]$ is given. Ag(DMT) (1 mmol) was added to a stirred suspension of $(Ph_3P)_2(CO)$-RhCl (1 mmol) in warm benzene (20 ml, 40°C). After 10 min, the mixture was filtered and hexane was added. The yellow compound was obtained in 50% yield at —10° C. The yields of the orange Ir compounds were about 80—90%. The corresponding tri-*p*-tolylphosphine compounds are much more soluble than the triphenylphosphine compounds.

Preparation of $[(Ph_3P)_2(CO)M(DpTT)]$ ($M = Rh, Ir$)

Silver di-*p*-tolyltriazene (Ag(DpTT)) (1 mmol) was added to a suspension of $(Ph_3P)_2(CO)MCl$ (1 mmol) in dichloromethane (20 ml) and the mixture stirred for 14 h. After filtration and concentration to 5 ml under vacuum, 15 ml hexane was added. When necessary, any precipitate was filtered off. Orange crystals were obtained at —35° C in 70 or 90% yield for M = Rh or Ir respectively.

Reactions of Ag(DMT) with $L_2M(CO)Cl$ ($L = PhMe_2P$, Ph_3As, $(p\text{-}tol)_3As$; $M = Rh, Ir$)

These reactions in $CHCl_3$, C_6H_6 or THF resulted in the formation of black products or silver mirrors from which no metal—metal bonded complexes could be obtained.

Reactions of $[(Ph_3P)_2(CO)MAg(DMT)Cl]$ with MpTT, DpTT and DpTA

In the case of M = Rh a replacement of the weaker acid DMT by the stronger acid MpTT or DpTT was observed (NMR) in $CHCl_3$. In the case of M = Ir a reaction took place in $CHCl_3$ or C_6H_6, but it did not give the expected substitution products.

Reactions of [(Ph$_3$P)$_2$(CO)MAg(R—N—N—N—R')Cl] with Ph$_3$P

When Ph$_3$P was added to chloroform solutions of the compounds (M = Rh, Ir) decomposition was observed (NMR) except in the case of [(Ph$_3$P)$_2$(CO)-RhAg(MpTT)Cl].

Reaction of [(Ph$_3$P)$_2$(CO)Ir(DpTT)] with CO

The NMR spectrum shows that the compound (Ph$_3$P)$_2$(CO)Ir(DpTT) reacts rapidly and quantitatively in CH$_2$Cl$_2$ with CO when exposed to a CO atmosphere. The reaction is reversible, since only the starting compound is obtained if CO is removed by vacuum or if argon is introduced. The isolation of the pure product is thus difficult, and a CO atmosphere must be maintained throughout the preparation, which is described below.

Preparation of {Ph$_3$P(CO)$_2$Ir[OC—N(p-tolyl)—N=N—p-tolyl)]·$\frac{1}{2}$ CH$_2$Cl$_2$}

(Ph$_3$P)$_2$(CO)Ir(DpTT) (800 mg) was dissolved in CH$_2$Cl$_2$ (6 ml) and exposed to a Co atmosphere. After 20 min the dark red solution was cooled (0° C) and cold pentane (20 ml) saturated with CO was slowly added with rapid stirring. Red crystals were obtained at —35° C in 40% yield (in some preparations the product was contaminated with crystals of (Ph$_3$P)$_2$(CO)Ir(DpTT)). Solutions of the product are only stable under a CO atmosphere. (N.B. (Ph$_3$P)$_2$(CO)-Rh(DpTT) did not react with CO).

The compound was also obtained when a well stirred suspension of (Ph$_3$P)$_2$-(CO)IrCl and Ag(DpTT) in CH$_2$Cl$_2$ is exposed to a CO atmosphere. After 1 h a dark red solution was obtained. Fractional crystallization from CH$_2$Cl$_2$ /pentane gave first Ph$_3$PAgCl, and then {Ph$_3$P(CO)$_2$Ir[OC—N(*p*-tolyl)—N=N—*p*-tolyl]·$\frac{1}{2}$ CH$_2$Cl$_2$} in about 40% yield. A blue green insoluble product was formed when a CH$_2$Cl$_2$ solution of the compound was kept under argon, but most of this product dissolved slowly under a CO atmosphere to reform the original complex.

Reaction of [(Ph$_3$P)$_2$(CO)IrAg(MpTT)Cl] and [(Ph$_3$P)$_2$(CO)IrAg(DMT)Cl] with CO

Under the conditions described above, similar products were obtained when the compounds were exposed to CO. The NMR spectrum indicated that the reaction is quantitative. With MpTT the reaction is reversible to some extent, but with DMT it is irreversible. Unfortunately the product in the case of DMT, which the NMR spectrum suggests is probably {Ph$_3$P(CO)$_2$Ir[OC—N(CH$_3$)—N=N—CH$_3$]}, is extremely labile even under a CO atmosphere, and this prevents the isolation of this compound.

The analogous Rh compounds also react with CO as shown by NMR; however, other unidentifiable products are also formed.

Preparation of {Ph$_3$P(CO)$_2$Ir[OC—N(p-tolyl)—N=N—CH$_3$]·CH$_2$Cl$_2$}

(Ph$_3$P)$_2$(CO)IrAg(MpTT)Cl (800 mg) was suspended in CH$_2$Cl$_2$ (6 ml) under CO. After 1 h stirring a dark red solution was obtained. Fractional crystallization under CO from CH$_2$Cl$_2$ /pentane gave first, a fraction of mainly Ph$_3$PAgCl, and then dark red crystals of {Ph$_3$P(CO)$_2$Ir[OC—N(*p*-tolyl)—N=N—CH$_3$]·CH$_2$Cl$_2$]} (40% yield). When a CH$_2$Cl$_2$ solution of this compound was

TABLE 1

ANALYTICAL DATA FOR $[(Ph_3P)_2(CO)MAg(R{-}\underline{N{\cdots}N{\cdots}N}{-}R')X]$ [a] AND $\{Ph_3P(CO)_2Ir[OC{-}N(R){-}N{=}N{-}R']\}$

Compound [b]	Analysis found (calcd.) (%)									
	C		H		N		P		Cl	
$(Ph_3P)_2(CO)RhAg(DMT)Cl$	53.81	(53.78)	4.13	(4.17)	4.45	(4.83)	6.86	(7.11)	3.80	(4.07)
$(Ph_3P)_2(CO)RhAg(MpTT)Cl$	57.54	(57.07)	4.32	(4.26)	4.41	(4.44)	6.31	(6.54)	3.70	(3.74)
$(Ph_3P)_2(CO)Rh(DpTT)$	69.31	(69.63)	4.94	(5.04)						
$(Ph_3P)_2(CO)IrAg(DMT)Cl$	49.75	(48.78)	3.85	(3.78)	3.80	(4.37)	5.86	(6.45)	3.47	(3.69)
$(Ph_3P)_2(CO)IrAg(MpTT)Cl$	51.76	(52.16)	3.71	(3.89)	3.65	(4.06)	6.05	(5.98)	3.85	(3.42)
$(Ph_3P)_2(CO)Ir(DpTT)$	63.42	(63.21)	4.48	(4.58)						
$Ph_3P(CO)_2Ir(OC{\cdot}MpTT){\cdot}CH_2Cl_2$	46.76	(46.69)	3.42	(3.53)	5.24	(5.45)	4.20	(4.01)		
$Ph_2P(CO)_2Ir(OC{\cdot}DpTT){\cdot}\frac{1}{2}CH_2Cl_2$	52.76	(52.94)	3.67	(3.75)	5.00	(5.22)	3.80	(3.84)		

[a] The experimental molecular weights are within 10% of the theoretical value. [b] DMT = di-methyltriazene, MpTT = methyl-*p*-tolyltriazene, DpTT = di-*p*-tolyltriazene, OC·MpTT = $OC{-}N(p\text{-tolyl}){-}N{=}N{-}CH_3$, OC·DpTT = $OC{-}N(p\text{-tolyl}){-}N{=}N{-}p\text{-tolyl}$.

kept under argon a blue-green insoluble product was formed. This dissolved slowly under a CO atmosphere, and the original complex was reformed almost completely.

Proton NMR spectra were recorded on a HA 100 Varian spectrometer. Infrared spectra were measured with a Beckman 4250 spectrometer. Molecular weights were recorded with a Hewlett—Packard vapour pressure osmometer Model 320 B.

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

Results

Structural characterization of the azenido halogen complexes

As with the analogous copper complexes [1] the compounds $[(Ph_3P)_2(CO)MAg(R\text{—}\underline{N\text{—}N\text{—}N}\text{—}R')X]$ have been prepared by the following reaction:

$$(Ph_3P)_2(CO)MX + Ag(R\text{—}\underline{N\text{—}N\text{—}N}\text{—}R') \rightarrow (Ph_3P)_2(CO)MAg(R\text{—}\underline{N\text{—}N\text{—}N}\text{—}R')X \quad (1)$$

($R = CH_3$, *p*-tolyl; $R' = CH_3$; M = Rh; X = Cl; M = Ir; X = Cl, Br, I)

Unlike the copper compounds, no complexes with $PhMe_2P$ or Ph_3As instead of Ph_3P or *p*-tol_3P as ligands could be obtained. The NMR-spectra (Table 2) are very similar to those of the analogous copper compounds. This, together with the infrared results (Table 3), strongly indicates that the structure of the complexes are as determined for $[(Ph_3P)_2(CO)RhCu(CH_3\text{—}\underline{N\text{—}N\text{—}N}\text{—}CH_3)Cl]$ and $[(PhMe_2P)_2(CO)IrCu(CH_3\text{—}\underline{N\text{—}N\text{—}N}\text{—}CH_3)Cl]$ * by a single crystal X-ray investigation [2]. The molecule therefore contains a metal-to-Ag^I donor bond, bridged by an azenido group. The halide atom has migrated from M^I to Ag^I. The Ag^I atom is three-coordinate while the Rh^I or Ir^I atom is five-coordinate.

The skeletal vibrations of the coordinated azenido group require special comment, as they are used for the characterization of the bonding mode of the azenido group. Previously, on the basis of IR data, the azenido compounds have been divided in two classes of compounds [6,7]. Class A compounds, in which the azenido group acts as a chelate ligand and having IR vibrations in the ranges 1260—1300 and 1580—1600 cm^{-1} and Class B compounds, in which the azenido group acts as a monodentate or bridging ligand with IR vibrations in the ranges 1150, 1190—1210, 1260—1300 and 1580—1600 cm^{-1}. In addition to the vibrations in the range 1580—1600 cm^{-1}, which to our opinion [1] must be assigned to aryl vibrations, the IR data, in this and previous [1] work, indicate that a bridging triazenido group has a characteristic azenido skeletal vibration in the range 1350—1375 cm^{-1} (Class C), and can therefore be distinguished from monodentate and chelate azenido groups. More information is necessary before the accuracy of this suggestion can be assessed.

Reactions of $Ag(p\text{-}tolyl\text{—}\underline{N\text{—}N\text{—}N}\text{—}p\text{-}tolyl)$ with $(Ph_3P)_2(CO)MCl$

Unlike the reactions of Ag(MpTT) and Ag(DMT) with $(Ph_3P)_2(CO)MCl$ (M = Rh, Ir) in which metal—metal bonded triazenido compounds are formed, the

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* The Ir—Cu distance is 2.70 Å.

TABLE 2

^{1}H NMR DATA FOR $L_2(CO)MAg(R{-}\underline{N{-}N{-}N}{-}R')X$ AND $Ph_3P(CO)_2Ir(OC{-}N(R){-}N{=}N{-}R')$ in $CDCl_3$ (ppm relative to TMS)

Compound [a]	Aryl protons of the triazene	Methyl protons on the side of [b]		Resonances of L
		Ag [c]	Rh, Ir	
Ag(DMT)		3.40		
$(Ph_3P)_2(CO)RhAg(DMT)Cl$		2.60	2.55	7.72 m ; 7.38 m
$(tol_3P)_2(CO)RhAg(DMT)Cl$ [d]		2.62	2.85	7.97 dt [e]; 6.98 d; 1.97
$(Ph_3P)_2(CO)RhAg(MpTT)Cl$	7.82; 7.82	2.22	2.65	7.73 m ; 7.38 m
$(Ph_3P)_2(CO)IrAg(DMT)Cl$		2.55	2.52	7.75 m ; 7.40 m
$(tol_3P)_2(CO)IrAg(DMT)Cl$		2.55	2.53	7.68 dt [e]; 7.23 d; 2.35
$(Ph_3P)_2(CO)IrAg(DMT)Br$		2.55	2.51	7.74 m ; 7.40 m
$(Ph_3P)_2(CO)IrAg(DMT)I$		2.57	2.52	7.80 m ; 7.44 m
$(tol_3P)_2(CO)IrAg(MpTT)Cl$	6.83; 6.68	2.19	2.70	7.67 dt [e]; 7.16 i; 2.27
$(Ph_3P)_2(CO)Ir(DpTT)$ [f]	6.92; 6.73		2.17	7.62 m ; 7.27 m
$Ph_3P(CO)_2Ir(OC{\cdot}DpTT){\cdot}\frac{1}{2}CH_2Cl_2$ [g]	7.10, 6.96; 7.06, 7.02		2.32; 2.30	7.38 m ; 7.23 m (*para*)
$Ph_3P(CO)_2Ir(OC{\cdot}PmTT){\cdot}CH_2Cl_2$	6.99; 6.99		3.26; 2.33	7.37 m ; 7.20 m (*para*)
$Ph_3P(CO)_2Ir(OC{\cdot}DMT)$			3.97; 2.93	7.38 m ; 7.16 m (*para*)

[a] See note [a] of Table 1. [b] This denotes the methyl group, or the methyl of the tolyl group bonded to the nitrogen atom attached to silver or rhodium, iridium. [c] This resonance of the DMT group, except for Ag(DMT), is broadened. Probably by silver coupling. [d] In C_6D_6. [e] dt = double triplet, $J(P{-}H) = 5.5$ Hz. [f] See also ref. 6 and 7. [g] At −45°C the resonances of the tolyl groups are better resolved; 7.13, 6.85; 7.12, 7.01 and 2.33, 2.31 ppm.

analogous reaction with Ag(DpTT) results in the formation of AgCl and the triazenido compounds $(Ph_3P)_2(CO)M(DpTT)$. These compounds were identical with the reported compounds [6,7], as confirmed by NMR and IR spectra and analysis.

Reactions of triazenido complexes with CO

The compound $[(Ph_3P)_2(CO)Ir(R{-}\underline{N{-}N{-}N}{-}R)]$ (R = *p*-tolyl) in dichloromethane solution reacts reversibly with CO according to reaction 2:

$$(Ph_3P)_2(CO)Ir(R{-}\underline{N{-}N{-}N}{-}R) \underset{\text{argon atmosphere}}{\overset{\text{CO atmosphere}}{\rightleftharpoons}} Ph_3P(CO)_2Ir\{OC{-}N(R){-}N{=}N{-}R\} + Ph_3P \tag{2}$$

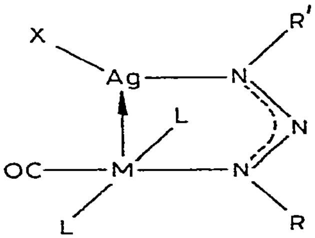

Fig. 1. Proposed structure for $[L_2(CO)MAg(R{-}\underline{N{-}N{-}N}{-}R')X]$.

TABLE 3

IR DATA FOR $[(Ph_3P)_2(CO)MAg(R-\underline{N-N-N}-R')]$ AND $\{Ph_3P(CO)_2Ir[OC-N(R)-N{=}N-R']\}$ (in cm^{-1}, nujoll and C_4Cl_6)

Compound [a]	ν(CO)	ν(NNN)	ν(AgCl)	Other vibrations
Ag(DMT)		1354; 1183		1324
Ag(MpTT)		1370; 1290		1318
$(Ph_3P)_2(CO)RhAg(DMT)Cl$	2003	1356	288	1326
$(Ph_3P)_2(CO)RhAg(MpTT)Cl$	1997	1367; 1286	296	1313
$(Ph_3P)_2(CO)IrAg(DMT)Cl$	1994	1361	286	1324
$(Ph_3P)_2(CO)IrAg(DMT)I$	1984	1358		1326
$(Ph_3P)_2(CO)IrAg(MpTT)Cl$	1985	1367; 1293		1319
$Ph_3P(CO)_2Ir(OC{\cdot}MpTT){\cdot}CH_2Cl_2$	2016; 1972; 1601 [b]	1375; 1250		1327; 929
$Ph_3P(CO)_2Ir(OC{\cdot}DpTT){\cdot}\frac{1}{2}CH_2Cl_2$	2027; 1979; 1635 [b]	1380; 1193		1322; 1220; 915
$Ph_3P(CO)_2Ir(OC{\cdot}DMT)$ [c]	2008; 1976; 1610 [b]	1329; 1247		

[a] See note [a] of Table 1. [b] Acyltriazenido frequency. [c] $CDCl_3$. Also a frequency at 2052 cm^{-1} is found.

The NMR spectra indicate that the reaction goes to completion in a CO atmosphere. The same product was obtained by reaction 3:

$$(Ph_3P)_2(CO)IrCl + Ag(R-\underline{N-N-N}-R) \xrightarrow{\text{CO atmosphere}} Ph_3P(CO)_2Ir[OC-N(R)-N{=}N-R] + Ph_3PAgCl \quad (3)$$

(R = *p*-tolyl)

This reaction is relatively rapid, since under argon the product $(Ph_3P)_2(CO)$-Ir(DpTT) is obtained only after 14 h (see Experimental). A somewhat similar reaction (eq. 4) was observed with the compounds $(Ph_3P)_2(CO)IrAg(R-\underline{N-N-N}-R')Cl$ (R = CH_3, *p*-tolyl; R′ = CH_3).

$$(Ph_3P)_2(CO)IrAg(R-\underline{N-N-N}-R')Cl \xrightarrow{\text{CO atmosphere}} Ph_3P(CO)_2Ir[OC-N(R)-N{=}N-R'] + Ph_3PAgCl \quad (4)$$

In the case of R = *p*-tolyl the reaction is reversible to some extent but not when R = CH_3. The NMR spectra show that both reactions go to completion in a CO atmosphere. The compounds $\{Ph_3P(CO)_2Ir[OC-N(R)-N{=}N-R']\}{\cdot}xCH_2Cl_2\}$(R = R′ = *p*-tolyl, $x = \frac{1}{2}$; R = *p*-tolyl, R′ = CH_3, $x = 1$) were identified by analyses, NMR and IR. Two CO vibrations at around 2000 cm^{-1} belong to terminal CO groups whereas the IR frequency at 1635 or 1601 cm^{-1} must be ascribed to a "ketonic" CO in which the carbon atom is probably bonded to Ir and N. Although many isomeric structures are possible, the following structure is proposed (see Fig. 2) on basis of IR and NMR data (Tables 2 and 3).

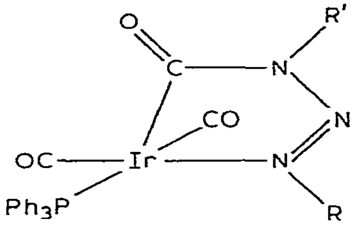

Fig. 2. Proposed structure for $\{Ph_3P(CO)_2Ir[OC-N(R)-N{=}N-R']\}$.

Unfortunately the compound $\{Ph_3P(CO)_2Ir[OC-N(CH_3)-N{=}N-CH_3]\}$, which the NMR spectrum shows to be clearly formed, decomposes slowly in solution under CO and could not be isolated.

Other reactions of metal—metal bonded complexes

The dimethyltriazene group in $[(Ph_3P)_2(CO)RhAg(DMT)Cl]$ is easily replaced in solution by methyl-*p*-tolyltriazene and di-*p*-tolyltriazene. However, in the case of the Ir compound only decomposition is observed. Similar behaviour is found in the reaction of $(Ph_3P)_2(CO)MAg(MpTT)Cl$ with an excess of di-*p*-tolyltriazene.

Addition of Ph_3P to the metal—metal bonded complexes results in decomposition except in the case of $[(Ph_3P)_2(CO)RhAg(MpTT)Cl]$. In this case a rapid phosphine exchange is observed and the resonances of the methyl-*p*-tolyltriazenido group show small upfield shifts of 0.05—0.10 ppm.

Discussion

The compounds $[L_2(CO)MAg(R-\underline{N-N-N}-R')X]$, described in this paper, are the first examples of complexes containing formally a metal-to-Ag^I donor bond analogous to the previously reported Cu^I complexes [1]. Although they are obviously formed in a very similar way, it is clear that the number of compounds which could be prepared is smaller than for the copper analogues. Although one of the reasons may be the greater ease of formation of AgCl, relative to CuCl, it is apparent that, while the silver compounds are more rapidly formed, they are inherently less stable than the analogous copper compounds. Evidence for this is for example that only for $L = Ph_3P$, $p\text{-tol}_3P$ could stable silver compounds be prepared, and furthermore the isolated complexes are more easily decomposed by suitable reagents than the Cu compounds.

In the case of the Rh compounds the yields of the preparations (~50%) are much lower than those of the Ir compounds (80—90%) and side products are formed. The Ir compounds are also much more stable in chlorinated solvents (CH_2Cl_2, $CHCl_3$). This is probably because Ir^I is a stronger electron donor than Rh^I, and so a stronger metal donor bond is formed, as in the case of the analogous Cu^I compounds [1].

The reactions with carbon are of special interest since they are the first examples of the reversible formation of acyltriazenido metal complexes. The formation of the Ir—C(O)—N part of the molecule in the case of $(Ph_3P)_2(CO)Ir(DpTT)$ might involve coordination of CO, followed by either an insertion of CO in the iridium—nitrogen bond or by an attack of the uncoordinated nitrogen atom of the triazene molecule on one of the coordinated carbonyl groups. The nature of the first step, the coordination of CO to the molecule, may be the reason why $(Ph_3P)_2(CO)Rh(DpTT)$ does not react with CO, since rhodium has much less tendency to coordinate an extra CO.

It is of interest to consider the related carbamoyl type compounds of manganese, which were obtained from $Mn(CO)_5Br$ and lithium amidines [8]. In the case of the compounds $[(Ph_3P)_2(CO)IrAg(R-\underline{N-N-N}-R')Cl]$ ($R = CH_3$, *p*-tolyl; $R' = CH_3$) the Ir—Ag bond might be broken by CO which then is attached to Ir. Subsequently a reaction of the type suggested above takes place.

The phosphine ligand which is also displaced in the reaction with CO reacts with AgCl to give the complex Ph_3PAgCl.

However another interpretation is that a phosphine is replaced by CO and forms Ph_3PAgCl. Then a similar reaction as with $(Ph_3P)_2(CO)Ir(DpTT)$ occurs. The reversible formation of a blue-green precipitate (with the DpTT and MpTT compounds, not with the DMT compounds) when argon is introduced into CH_2Cl_2 solutions of the carbamoyl type compounds might be the reversible loss of CO.

In a following paper [9] are reported the preparation and properties of a series of metal—metal bonded compounds in which the metal—metal bond is stabilized by bridging oxygen donor ligands.

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