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METAL—METAL BONDED COMPOUNDS

I. COMPOUNDS WITH $\mathrm{MAg^I}$ PAIRS ($\mathrm{M = Rh^I, Ir^I}$) BRIDGED BY OXYGEN ACID ANIONS $\mathrm{O_2CCF_3^-}$, $\mathrm{ClO_4^-}$, $\mathrm{O_2CCHC(CH_3)_2^-}$

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Summary

Novel metal—metal bonded compounds $[\mathrm{L_2(CO)MAgOx_2}]$ ($\mathrm{L = Ph_3P}$, p-$\mathrm{tol_3P}$; $\mathrm{M = Rh^I, Ir^I}$; $\mathrm{Ox = O_2CCF_3, ClO_4}$) have been isolated. The proposed structure contains a five membered ring in which an $\mathrm{M^I}$ to $\mathrm{Ag^I}$ donor bond is bridged by an oxygen acid anion (= Ox) group. This structure is analogous to that of the metal—metal bonded triazenido compounds $[\mathrm{L_2(CO)MM'(R{-}N{\cdots}N{\cdots}N{-}R)X}]$ ($\mathrm{M = Rh^I, Ir^I}$; $\mathrm{M' = Cu^I, Ag^I}$). The analogous isobutyrato complexes, however, are formulated as $\{\mathrm{L(CO)M[O_2CCH(CH_3)_2]_2AgL}\}$ ($\mathrm{L = Ph_3P}$, p-$\mathrm{tol_3P}$, p-$\mathrm{tol_3As}$). One of the ligands L has migrated from the metal to the silver atom. A metal—metal bond may be present. Compounds in which the bridging Ox group ($\mathrm{O_2CCF_3}$, $\mathrm{O_2CCH(CH_3)_2}$) is replaced by a triazenido or an acetamidino group have also been obtained.

Introduction

In two previous publications [1,2] the preparation, structure and some properties have been reported for a new class of compounds $[\mathrm{L_2(CO)M{-}M'(R{-}N{\cdots}N{\cdots}N{-}R')X}]$ ($\mathrm{L = R_3P, R_3As}$; $\mathrm{M = Rh^I, Ir^I}$; $\mathrm{M' = Ag^I, Cu^I}$; X = Cl, Br, I) which contain a five-membered ring [3] in which an M-to-M′ donor bond is bridged by an azenido group. The M atom is five-coordinate while M′ is three-coordinate. It was shown in the case of copper that formamidino and trifluoroacetato groups are also able to support the metal-to-metal donor bond [1].

It was noticed that the ease of formation and the stability of the compounds are dependent on M and M′, the type of bridging group and the nature of the ligand L. In the case of $\mathrm{Ag^I}$ we have already described the triazenido complexes [2]. In this article the oxygen acid anion analogues are discussed; in some instances the products are different in structure from the triazenido compounds.

Experimental

All preparations involving Rh^I or Ir^I complexes were carried out under argon. For the preparation of the silver triazenes see ref. 2.

Preparation of silver di-p-tolylacetamidine [Ag(DTA)]

A solution of di-*p*-tolylacetamidine [4] (10 mmol) in methanol followed by a solution of K(O-t-Bu) (10 mmol) in methanol was added to a stirred solution or suspension of $AgNO_3$ (10 mmol) in methanol. The white precipitate was washed with methanol and recrystallized from dichloromethane/hexane (yield 70%).

Preparation of $[(Ph_3P)_2(CO)IrAg(ClO_4)_2]$

$AgClO_4$ (0.25 mmol) was added to a hot freshly prepared solution of $(Ph_3P)_2(CO)Ir(ClO_4)$ [5] (0.25 mmol) in benzene (10 ml) and the mixture was refluxed for 5 min. Hexane (10 ml) was added, and the orange precipate formed was isolated by decanting the liquid. After washing with benzene and hexane the compound was obtained in 75% yield.

The compound is highly explosive and is detonated by heat or shock, and extreme care has to be taken. It is practically insoluble in benzene, ether, chloroform or acetone. The tri-*p*-tolylphosphine derivative was prepared similarly; it is soluble in chloroform.

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

AgO_2CCF_3 (1 mmol) was added to a stirred suspension of $(Ph_3P)_2(CO)MCl$ (1 mmol) in benzene (15 ml). The AgCl (95—100%) was filtered off after 10 min and another equivalent of AgO_2CCF_3 was added to this freshly prepared solution of $(Ph_3P)_2(CO)M(O_2CCF_3)$. The mixture was refluxed for 5 min to give a clear solution, from which a yellow compound precipitated in about 50% yield at ambient temperature.

Preparation of $[(Ph_3P)_2(CO)IrAg(DpTT)O_2CCF_3]$

Silver di-*p*-tolyltriazene (= Ag(DpTT)) (1 mmol) was added to a freshly prepared solution of $(Ph_3P)_2(CO)Ir(O_2CCF_3)$ as described above, and the mixture was refluxed for 10 min to give an orange solution.

The solution was filtered and evaporated under vacuum until the residue solidified. The residue was dissolved in 10 ml. ether and cooled to 0°C to give orange crystals (70% yield). The analogous reaction with $(Ph_3P)_2(CO)Rh(O_2CCF_3)$ did not yield the Rh analogue and most of the AgDpTT remained unchanged. The compounds $[(Ph_3P)_2(CO)MAg(DpTA)O_2CCF_3]$ (DpTA = di-*p*-tolylacetamidine) (M = Rh, Ir) were prepared similarly at ambient temperature (70—80% yield).

Preparation of $\{(Ph_3P)_2(CO)M[O_2CCH(CH_3)_2]\}$, (M = Rh, Ir)

$Ag[O_2CCH(CH_3)_2]$ (1 mmol) was added to a stirred suspension of $(Ph_3P)_2(CO)MCl$ (1 mmol) in benzene (15 ml). A white precipitate of AgCl formed rapidly. After 10 min the AgCl (95—100%) was filtered off and washed with benzene. The solution was concentrated under vacuum and as soon as the residue solidified ether (25 ml) was added with stirring and the mixture was set aside at —20°C. After 24 h the yellow precipitate was filtered off, washed twice with ether (5 ml), and vacuum dried at 50°C for 2 h (yield ~70%). The tri-*p*-tolylphosphine derivate was obtained similarly.

Preparation of $\{Ph_3P(CO)M[O_2CCH(CH_3)_2]_2AgPPh_3\}$ $(M = Rh, Ir)$

$Ag[O_2CCH(CH_3)_2]$ (M = Rh, 1.0 mmol; M = Ir, 1.3 mmol), is added to a solution of $(Ph_3P)_2(CO)M[O_2CCH(CH_3)_2]$, obtained as in the preceding reaction. After 5 min the filtered solution was evaporated under vacuum until the residue solidified. The residue was dissolved in ether (10 ml) and the solution set aside at —30°C. Yellow crystals were obtained in about 75% yield. The *p*-tol_3P and *p*-tol_3As derivatives were prepared similarly.

The same procedure was followed for the orange compounds $[(Ph_3P)_2(CO)IrAg(MpTT)O_2CCH(CH_3)_2]$ and $[(Ph_3P)_2(CO)RhAg(DpTA)O_2CCH(CH_3)_2]$.

Preparation of $\{(Ph_3P)_2(CO)IrAg(MpTT)[((CH_3)_2CHCO_2)_2H] \cdot \frac{1}{2}O(C_2H_5)_2\}$

Methyl-*p*-tolyltriazene (1 mmol) (= MpTT) was added to a solution of $\{Ph_3P(CO)Ir[O_2CCH(CH_3)_2]_2AgPPh_3\}$ (1 mmol) in benzene (15 ml) and the orange solution was worked up as before. Red-brown crystals were obtained in 75% yield. A yellow compound of apparent composition $\{(Ph_3P)_2(CO)RhAg(DpTT)[((CH_3)_2CHCO_2)_2H]\}$ was obtained similarly. Redissolution of this complex (or the Ir analogue) (in $CHCl_3$ or C_6H_6), however, resulted in the rapid precipitation of Ag(DpTT) and the formation of $(Ph_3P)_2(CO)Rh\{[O_2CCH(CH_3)_2]_2H\}$.

Reactions of Ag(DMT) with $(Ph_3P)_2(CO)MOx$ $(M = Rh, Ir; Ox = O_2CCF_3, O_2CCH(CH_3)_2)$

Although clear orange C_6H_6 or THF solutions were obtained, the decomposition was too rapid to allow the isolation of identifiable products, except for M = Ir and Ox = O_2CCF_3. The compound $(Ph_3P)_2(CO)IrAg(DMT)O_2CCF_3$ was isolated as red crystals.

Reactions of $L_2(CO)MO_2CCH(CH_3)_2$ $(L = Ph_3P, Ph_3As; M = Rh, Ir)$

No reaction was observed (NMR) when MpTT or DpTT was added to $CHCl_3$ or C_6H_6 solutions of these compounds. When L was added a rapid exchange between free and coordinated L was observed and the $O_2CCH(CH_3)_2$ resonances (NMR) remained practically unchanged.

Reactions of $\{L(CO)M[O_2CCH(CH_3)_2]_2AgL\}$, $(L = Ph_3P$, *p*-tol_3P, Ph_3As, *p*-tol_3As $M = Rh, Ir)$

A rapid replacement of one of the $O_2CCH(CH_3)_2$-groups took place when MpTT was added to benzene solutions of the compounds. Addition of an excess of MpTT did not lead to further substitution. However for L = Ph_3As only impure (specially if M = Rh) yellow products could be obtained.

When *p*-tol_3P was added to benzene solutions of the compounds (L = *p*-tol_3P, M = Rh, Ir) the molecule was split into two fragments $L_2(CO)MO_2CCH(CH_3)_2$ and $LAg[O_2CCH(CH_3)_2]$ (NMR). When *p*-tol_3P is added to chloroform solutions of $(p\text{-}tol_3P)_2(CO)MAgOx_2$ (Ox = ClO_4, O_2CCF_3) a similar splitting occurred to give the fragments $(p\text{-}tol_3P)_2(CO)MOx$ and *p*-tol_3PAgOx (NMR).

Similar reactions were observed with other donor ligands such as pyridine, butylamine and *p*-toluidine.

TABLE 1

ANALYTICAL DATA

Compound [a,b]	Analysis found (calcd.) (%)		
	C	H	P [c]
AgDpTA	54.92(55.66)	4.93(4.96)	
$(Ph_3P)_2(CO)RhB$	65.92(66.31)	5.08(5.02)	
$(Ph_3P)_2(CO)RhB_2H$	64.83(65.06)	5.43(5.46)	
$(p\text{-tol}_3P)_2(CO)RhB$	68.93(68.27)	6.14(5.93)	
$p\text{-tol}_3P(CO)RhB_2AgP(p\text{-tol})_3$	59.54(59.95)	5.82(5.52)	
$Ph_3P(CO)IrB_2AgPPh_3$	52.89(52.63)	4.38(4.32)	5.81(6.03)
$(Ph_3P)_2(CO)RhAg(O_2CCF_3)_2$	50.65(49.77)	3.34(3.06)	
$(Ph_3P)_2(CO)IrAg(O_2CCF_3)_2$	44.69(45.65)	2.73(2.80)	5.90(5.74)
$(Ph_3P)_2(CO)RhAg(DpTT)B_2H$	61.59(60.99)	5.08(5.03)	
$(Ph_3P)_2(CO)RhAg(DpTA)B$	62.46(62.94)	5.12(5.00)	
$(Ph_3P)_2(CO)IrAg(DpTT)O_2CCF_3$	53.20(53.49)	3.70(3.73)	5.34(5.21)
$(Ph_3P)_2(CO)IrAg(DpTA)O_2CCF_3$	53.97(54.91)	4.03(3.94)	5.35(5.15)
$(Ph_3P)_2(CO)IrAg(MpTT)B$	54.62(54.09)	4.43(4.36)	5.14(5.69)
$(Ph_3P)_2(CO)IrAg(MpTT)B_2H \cdot \frac{1}{2}$ ether	54.11(54.45)	4.74(4.99)	5.00(5.11)

[a] DpTA = di-*p*-tolylacetamidine, B = $O_2CCH(CH_3)_2$, DpTT = di-*p*-tolyltriazene, MpTT = methyl-*p*-tolyltriazene. [b] No analysis of $(Ph_3P)_2(CO)IrAg(ClO_4)_2$ was obtained (extremely explosive). [c] For all rhodium-compounds the %P was 0.8—1.2% too low, probably owing to the method of analysis (according to Schöniger). Integration of the ¹H NMR spectra (with a reference compound) corresponded always with two phosphine ligands.

TABLE 2.

IR DATA (Nujoll, C_4Cl_6) in cm^{-1}

Compound [a]	ν(CO)	frequencies [b] of MpTT, DpTT, DpTA	frequencies [b] of O_2CCF_3, ClO_4, $O_2CCH(CH_3)_2$ [c]
Ag(DpTA)		1505s; 1254w, 1204w	
AgB			1538s, 1503s; 1408ms, 1288w
AgO_2CCF_3			1635s; 1449w
$(Ph_3P)_2(CO)RhB$	1975		1610ms; 1388m, 1259ms
$(Ph_3P)_2(CO)IrB$	1963		1627ms; 1385m, 1249ms
$Ph_3P(CO)RhB_2AgPPh_3$	1988		1572s; 1404m, 1276w
$Ph_3P(CO)IrB_2AgPPh_3$ [d]	1977		1550s; 1403m, 1283w
$(Ph_3P)_2(CO)RhAg(O_2CCF_3)_2$	2005		1695m, 1651s; 1411w
$(Ph_3P)_2(CO)IrAg(O_2CCF_3)_2$	1997		1707m, 1657s; 1406w
$(Ph_3P)_2(CO)IrAg(ClO_4)_2$	1993		1190, 1150, 1000, 830
$(Ph_3P)_2(CO)IrAg(DpTT)O_2CCF_3$	1993	1384; 1374	1686m; 1418w
$(Ph_3P)_2(CO)IrAg(MpTT)B$	1987	1362; 1296, 1321	1577ms; 1390m, 1250w
$(Ph_3P)_2(CO)IrAg(MpTT)B_2H \cdot \frac{1}{2}$ ether	1987	1361; 1294, 1320	1575m, 1545m; 1427w, 1390, 1250w
$(Ph_3P)_2(CO)RhAg(DpTT)B_2H$	1978	1367; 1215	1609m, 1570m

[a] See note [a] of Table 1. [b] The frequencies characteristic for this group are given (see also ref. 1 and 2). [c] From these data is concluded that frequencies above 1500 cm^{-1} must be assigned as ν_{as}, and the frequencies at about 1390 and 1250 cm^{-1} are characteristic for a unidentate, the frequencies at about 1405 and 1280 cm^{-1} for a bridging $O_2CCH(CH_3)_2^-$ group. [d] Also weak frequencies are observed at 1963, 1630, and 1250 cm^{-1}. These were ascribed to some impurity of $(Ph_3P)_2(CO)IrB$ (as the relative intensities differ in different preparations).

Reaction of $(Ph_3P)_2(CO)IrAg(O_2CCF_3)_2$ with MpTT

When one equivalent MpTT was added to a benzene or $CHCl_3$ solution of $(Ph_3P)_2(CO)IrAg(O_2CCF_3)_2$ rapid gas evolution (N_2) occurred. The NMR spectrum did not show any evidence for the presence of a MpTT group.

Proton NMR spectra were recorded on a HA 100 Varian spectrometer. IR spectra were measured with a Beckman 4250 spectrometer.

C, H, and P analyses were carried out in this laboratory (see Table 1).

Results

Structural characterization of oxygen acid analogues.

Reactions of $L_2(CO)MCl$ (M = Rh, Ir; L = Ph_3P, p-tol$_3$P, Ph_3As, p-tol$_3$As under suitable conditions, with a variety of AgOx (1 equivalent) (AgOx = $Ag[O_2CCH(CH_3)]_2$, AgO_2CCF_3, $AgClO_4$ [5] or $AgNO_3$ [7]) resulted in rapid and quantitative precipitation of AgCl and simultaneous formation of a Rh^I or Ir^I complex with an oxygen ligand, according to equation 1:

$$L_2(CO)MCl + AgOx \rightarrow L_2(CO)MOx + AgCl \qquad (1)$$

From the available IR data (Table 2) it is concluded that the Ox group is monodentate [6].

If subsequently a second equivalent of AgOx (Ox $\neq O_2CCH(CH_3)_2$) is added to a solution of $L_2(CO)MOx$ the following reaction takes place *:

$$L_2(CO)MOx + AgOx \rightarrow L_2(CO)MAg(Ox)_2 \qquad (2)$$

In the case of Ox = O_2CCF_3, the IR spectra show the presence of two asymmetric OCO stretching bands at 1700 and $\simeq$1655 cm^{-1}. The first band indicates that one trifluoroacetato group is bonded as a monodentate, while the second band indicates that the other group is bridging. This was deduced by comparison with the spectra of the bridging O_2CCF_3 groups in $Ag(O_2CCF_3)$. Only one symmetric OCO stretching band could however be observed. The structure is probably as shown in Fig. 1. A further confirmation is given by NMR, which for L = p-tol$_3$P shows a triplet structure for the *ortho* protons of p-tol$_3$P with J(P—H) 5.5 Hz, this indicates that the phosphine groups are *trans* to each other and equivalent.

Because the perchlorato compound is highly explosive no detailed study was carried out. An analogous structure is proposed on the basis of the triplet structure of the *ortho* protons (J(P—H) 5.5 Hz) of the p-tol$_3$P group.

In the case of Ox = $O_2CCH(CH_3)_2$, the composition of the product is again $L_2(CO)MAgOx_2$. However the reaction probably proceeds as follows:

$$L_2(CO)M[O_2CCH(CH_3)_2] + Ag\{O_2CCH(CH_3)_2\} \rightarrow$$
$$\rightarrow L(CO)M[O_2CCH(CH_3)_2]_2AgL \qquad (3)$$

From the NMR data it is clear that both for Rh^I and Ir^I the p-tol$_3$P or p-tol$_3$As ligands are not equivalent (Table 3). Furthermore the low temperature ^{1}H NMR

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* For Ox = NO_3, Cash et al. [7] reported a similar compound, but proposed a different structure with which we do not agree.

TABLE 3

^{1}H NMR DATA (ppm relative to TMS)

Compound [a]	solv.	T (°C)	Resonances [b] of DpTA, MpTT or DpTT	Resonances [b,c] of $O_2CCH(CH_3)_2$		Resonances [b,d] of L (J(P—H) in brackets in Hz)		
				CH	CH_3	*ortho* [i]	*meta*	CH_3
AgDpTA	$CDCl_3$	30	6.93, 6.63; 2.25(2X), 1.61					
p-tol$_3$PAgB	C_6D_6	30		2.90	1.47	7.37dd(11),	6.77dd(1.7);	1.95
	C_7D_8	−15		2.91	1.49	7.52dd(11),	6.83d(1.7);	1.97
p-tol$_3$PAgO$_2$CCF$_3$	$CDCl_3$	30				7.31ds(15),	7.21ds(1.5);	2.37
p-tol$_3$PAgClO$_4$	$CDCl_3$	30				7.26ds(14),	7.15ds(1.5);	2.30
(p-tol$_3$P)$_2$(CO)RhB	C_7D_8	−15			0.58	7.86dt(5.5),	6.91d;	1.97
$(Ph_3P)_2(CO)RhB$	$CDCl_3$	30		1.27	0.20	7.70m,	7.37m	
$(Ph_3P)_2(CO)RhB_2H$	$CDCl_3$	30		1.90	0.66	7.71m,	7.38m	
p-tol$_3$P(CO)RhB$_2$AgP(p-tol)$_3$ [e]	C_7D_8	−35		2.99	1.48	7.62dd(12),	6.75dd(1.7);	1.95
				2.48	1.12, 1.08	7.48dd(12),	6.62dd(1.7);	1.91
p-tol$_3$As(CO)RhB$_2$AgAs(p-tol)$_3$ [f]	C_7D_8	−50		3.03	1.48	7.53d,	6.70d;	1.94
				2.40	1.12, 1.06	7.33d,	6.59d;	1.88
$(Ph_3P)_2(CO)IrB$	$CDCl_3$	30		1.27	0.13	7.77m,	7.46m;	
$Ph_3P(CO)IrB_2AgPPh_3$ [g]	C_7D_8	−65		2.88	1.41, 1.36			
					1.06, 0.96			
(p-tol$_3$P)$_2$(CO)IrO$_2$CCF$_3$	$CDCl_3$	30				7.53dt(5.5),	7.14d;	2.33
(p-tol$_3$P)$_2$(CO)IrAg(O$_2$CCF$_3$)$_2$	$CDCl_3$	30				7.53dt(5.5),	7.24d;	2.37
(p-tol$_3$P)$_2$(CO)IrAg(ClO$_4$)$_2$	$CDCl_3$	30				7.53dt(5.5),	7.25d;	2.36
$(Ph_3P)_2(CO)IrAg(DMT)O_2CCF_3$	$CDCl_3$	30	2.62, 2.48			7.67m,	7.40m	
$(Ph_3P)_2(CO)IrAg(DpTT)O_2CCF_3$	$CDCl_3$	30	7.21, 6.56; 2.11 6.90, 6.90; 2.21			7.57m,	7.30m	
$(Ph_3P)_2(CO)IrAg(MpTT)B$	$CDCl_3$	30	6.88; 2.60, 2.17	2.74	1.35	7.70m,	7.35m	
$(Ph_3P)_2(CO)IrAg(MpTT)B_2H$ · ½ether [h]	$CDCl_3$	−65	6.91; 2.54, 2.21	2.78	1.32	7.74m,	7.43m	
$(Ph_3P)_2(CO)RhAg(DpTA)O_2CCF_3$	$CDCl_3$	30	7.87; 2.17			7.50m,	7.24m	

[a] See note [a] of Table 1, DMT = dimethyltriazene. [b] In the case of two different tolyl- or $O_2CCH(CH_3)_2$-groups, the data are put below each other. [c] CH—CH$_3$ coupling J ~ 7 Hz. [d] d = doublet, m = multiplet, ds = doublet + singulet, dd = double doublet, dt = double triplet; *ortho*—*meta* coupling J ~ 8 Hz. [e] The resonance at 1.48 ppm does not split at −80°C in C_7D_8, $C_7D_8/CDCl_3$ or deuteroacetone at −80°C. The resonances at 1.12 and 1.08 ppm have coalesced at −15°C. At 30°C slow exchange between both $O_2CCH(CH_3)_2$-groups. [f] Similar as note [e] (exchange a bit more rapidly) and at 30°C also a rapid exchange of both p-tol$_3$As-groups. [g] At higher temperatures first the resonances at 1.41 and 1.36 ppm are coalesced (~0°C) then the resonances at 1.06 and 0.96 broaden. At 30°C a sharp doublet and a broadened doublet are obtained (no exchange between both $O_2CCH(CH_3)_2$-groups). [h] Resonances of lattice ether at 3.50 and 1.24 ppm. [i] The apparent constant from the spectra is given. If J(P—H) is ~0 in the relation $J(P—H) + J(P'—H')$ the values of Hz should be doubled for the actual coupling constant.

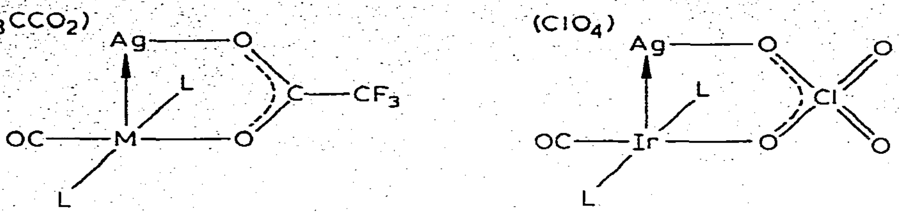

Fig. 1. Proposed structure for $[L_2(CO)MAg(O_2CCF_3)_2]$ (M = Rh, Ir) and $[L_2(CO)IrAg(ClO_4)_2]$ (L = Ph_3P and p-tol_3P).

spectra not only show that the $O_2CCH(CH_3)_2$ groups are not equivalent, but also, that in the case of Ir the two methyl groups of each $O_2CCH(CH_3)_2$ group are not equivalent. In the case of Rh^I the methyl resonances of only one $O_2CCH(CH_3)_2$ group are split. Possibly the two methyl groups of the other $O_2CCH(CH_3)_2$ group remain magnetically equivalent because of a rapid exchange of this group even at −80°C.

Three structures are possible in principle. The first one is as shown in Fig. 1, but the L groups have to be *cis* instead of *trans*, and this, as far as we know, has never been observed for Vaska-type compounds.

The second possibility is a structure in which one of the ligands L has moved to Ag. One isobutyric acid anion is bridging while the other is bonded as a monodentate to M. However IR data (Table 2) indicate that both $O_2CCH(CH_3)_2$ groups are bridging, which is tentatively deduced from the asymmetric OCO stretching frequencies at 1550 and 1572 cm^{-1} resp. (Table 2). Although IR data are certainly not conclusive, in the absence of crystallographic data, we prefer the third possible structure which is shown in Fig. 2.

Compounds with both an oxygen acid anion and a triazenido or acetamidino group

These complexes have been prepared by two methods. The first, which is shown in eq. 4, involves the direct reaction of the silver compounds of triazene or acetamidine with $(Ph_3P)_2(CO)MOx$ (Ox = $O_2CCH(CH_3)_2$, O_2CCF_3):

$$(Ph_3P)_2(CO)M(O_2CCF_3) + Ag(DpTT) \rightarrow (Ph_3P)_2(CO)MAg(DpTT)(O_2CCF_3) \quad (4)$$

(for M = Ir^I, but not if M = Rh^I)

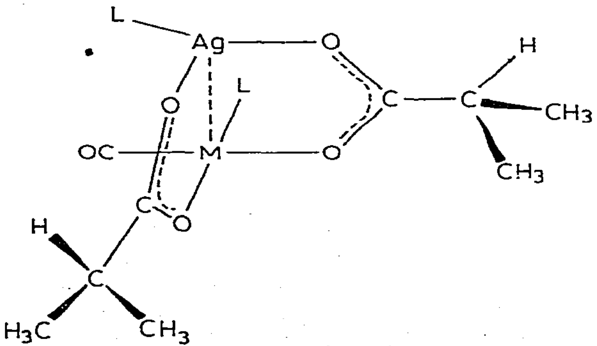

Fig. 2. Proposed structure for $\{L(CO)M[O_2CCH(CH_3)_2]_2AgL\}$ (M = Rh, Ir; L = Ph_3P, p-tol_3P, p-tol_3As).

Analogous compounds were prepared in this way with DMT, MpTT and DpTA instead of DpTT. In the case of DpTA, isomers are obtained, which makes the assignment of the NMR spectra difficult. On the basis of the NMR (Table 3) and IR data (Table 2), the trifluoroacetato compounds formed in reaction 4 probably have a structure analogous to that shown in Fig. 1. In the case of DpTA, however, a different type of structure is certainly also present.

The second reaction involves the replacement of one Ox group in $\{Ph_3P(CO)M[O_2CCH(CH_3)_2]_2AgPPh_3\}$ by a triazenido group, as shown in eq. 5

$$\{Ph_3P(CO)M[O_2CCH(CH_3)_2]_2AgPPh_3\} + MpTT \rightarrow \{(Ph_3P)_2(CO)MAg(MpTT)[(O_2CCH(CH_3)_2)_2H]\} \quad (5)$$

(for M = Rh^I and Ir^I)

The di-*p*-tolylacetamidine complex could not be prepared according to eq. 5.

Preliminary single crystal X-ray data [8] show that in the compound $\{(Ph_3P)_2(CO)IrAg(\mathrm{Me{-}\underline{N}{\cdots}\underline{N}{\cdots}\underline{N}{-}}p\text{-tol})[O_2CCH(CH_3)_2][HO_2CCH(CH_3)_2]\}$ the triazenido group bridges the Ir—Ag bond (Ir—Ag $\simeq$2.8 Å) with the N—Me group coordinating to Ir and the N—tol group to Ag. The $O_2CCH(CH_3)_2$ group is bonded as a monodentate to Ag. The $HO_2CH(CH_3)_2$ part is as yet not fully resolved, but it does not coordinate to Ir or Ag.

The NMR spectra of this type of compound in solution is interesting, as the methyl signals are not split even at −65°C. A fast exchange is probably occurring, as was reported in the case of $(Ph_3P)_2(CO)Rh[(O_2CCH_3)_2H]$ by Robinson et al. [6].

Chemical properties

We attempted unsuccessfully to replace more than one Ox group in the compounds $L_2(CO)MAgOx_2$ and $\{L(CO)M[O_2CCH(CH_3)_2]_2AgL\}$ by triazenido groups.

The compounds $\{L(CO)M[O_2CCH(CH_3)_2]_2AgL\}$ react with one equivalent of L (L = Ph_3P, *p*-tol_3P, *p*-tol_3As) according to eq. 6:

$$\{L(CO)M[O_2CCH(CH_3)_2]_2AgL\} + L \rightarrow L_2(CO)M[O_2CCH(CH_3)_2] + LAg[O_2CCH(CH_3)_2] \quad (6)$$

The compounds $(p\text{-}tol_3P)_2(CO)MAgOx_2$ (Ox = O_2CCF_3, ClO_4) react similarly with *p*-tol_3P to give analogous products. The Ir complexes are more stable in chlorinated solvents than the analogous Rh complexes.

The compounds react with carbon monoxide. However, in contrast to the results for the analogous azenido complexes, for which well defined acyltriazenido compounds were isolated, only unidentified products were obtained.

Discussion

Previously was reported that the M-to-M′ bond (M = Rh^I, Ir^I) in $[L_2(CO)MM'$(bridging ligand)X] can be stabilized in the case of Cu^I and Ag^I by the triazenido group [1,2], and also in the case of Cu^I * by the formamidino and trifluoro-

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* The number of M-to-Cu^I bonded compounds bridged by oxygen acid anions is smaller than in the case of Ag^I, because of the relative inaccessability of suitable starting Cu^I compounds.

acetato groups [1]. We have now shown that for $M' = Ag^I$ a metal-to-metal bond may also be formed with a surprisingly wide range of bridging oxygen acid anions such as the trifluoroacetato, the perchlorato and probably [7] also the nitrato groups *.

It seems clear from the available evidence [1,2] that in general the ease of formation and the stability of the reported compounds decrease in the order $Ir^I > Rh^I$, $Cu^I > Ag^I$, and bridging nitrogen ligands > bridging oxygen ligands. Furthermore, in general, strongly electron donating ligands L seem to favour the formation of M-to-M′ donor bonds. However, while the ease of formation and the stability of the above compounds are fairly critically dependent on M,M′, and in particular on the ligand L bonded to M, in view of the very different bridging groups used, they seem less sensitive to the type of bridging ligand. It seems that the most important stabilizing factor is a large electron density on the metal atom M, while the bridging ligand exerts its stabilizing influence mainly by its capacity to bridge M and M′, although there is of course clearly a difference between strong donors like RN_3R and very weak donors like ClO_4.

An interesting unexpected feature is that the isobutyric acid anion yields a different type of compound i.e. $\{L(CO)M[O_2CCH(CH_3)_2]_2AgL\}$ for $L = Ph_3P$, p-tol_3P, p-tol_3As, in which, instead of the anion [1,2], the neutral ligand L has probably moved from M to Ag. As with the other oxygen donor complexes the first step in the formation of the compounds is the replacement of Cl in $L_2(CO)MCl$ by $O_2CCH(CH_3)_2$. In the second step the addition of $Ag[O_2CCH(CH_3)_2]$ is followed by a migration of one of the L groups to Ag, while both $O_2CCH(CH_3)_2$ groups seem to act as bridging groups (Fig. 2). If so, a metal-to-metal bond may or may not be present. The Ag^I atom is three-coordinate in the absence of such a bond, and four-coordinate if a bond or an interaction between both metal atoms is present.

Reactions involving the replacement of one bridging group by another are of interest. For example, it has been observed that bridging carboxylato ligands in $Hg(OAc)_2$ [9], $Ag(O_2CCH(CH_3)_2$ and $[(\eta^3\text{-}C_4H_7)Pd(OAc)]_2$ [10] are easily substituted by triazenido ligands in reactions with triazene. However the $O_2CCH(CH_3)_2$ group in $\{(Ph_3P)_2(CO)Rh[O_2CCH(CH_3)_2]\}$, which is bonded in a monodentate fashion, cannot be replaced even by use of a large excess of triazene.

It is thus noteworthy that one of the bridging $O_2CCH(CH_3)_2$ groups in $\{Ph_3P(CO)Ir[O_2CCH(CH_3)_2]_2Ag(Ph_3P)\}$ may be replaced by a triazenido group by treatment with metal-p-tolyl-triazene or with di-p-tolyltriazene. At the same time the phosphine group, which is bonded to Ag, moves back to Ir, while the other $O_2CCH(CH_3)_2$ group becomes monodentate and cannot be further replaced. The acid $HO_2CCH(CH_3)_2$ which is formed becomes also part of the complex.

A similar reaction probably takes place when $[(Ph_3P)_2(CO)IrAg(O_2CCF_3)_2]$ is treated with methyl-p-tolyltriazene. However the resulting complex $[(Ph_3P)_2(CO)IrAg(Me{-}\underline{N{-}N{-}N}{-}p\text{-tol})(O_2CCF_3)]$, which is stable on its own and has been prepared from $(Ph_3P)_2(CO)Ir(O_2CCF_3)$ and $Ag(Me{-}\underline{N{-}N{-}N}{-}p\text{-tol})$, is subsequently decomposed by the trifluoroacetic acid formed in the reaction

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* A different type of structure was proposed for the nitrato compound $[(Ph_3P)_2(CO)IrAg(NO_3)_2]$ [7]. However, in the light of our results, reformulation of the structure as for the compounds reported here seems appropriate.

with triazenes. A gas was evolved, as is the case when methyl-*p*-tolyltriazenido complexes are treated with HO_2CCF_3.

In a subsequent publication it will be shown that the type of chemistry discussed in this and in previous publications [1,2] can also be observed for other metal atoms [11].

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