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METAL DIMERS AS CATALYSTS

VIII *. THE CATALYSED SYNTHESIS OF THE CARBONYL COMPLEXES $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)I]$ AND $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)_2]I$ (L = GROUP V DONOR LIGAND)

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Summary

The reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and Group V donor ligands in the presence of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ or $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ as catalyst yields $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)I]$ (L = PPh_3, PMe_2Ph, $PMePh_2$, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$, $0.5Ph_2PCH_2PPh_2$) and $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)_2]I$ (L = PMe_2Ph, $PMePh_2$, $0.5Ph_2P(CH_2)_nPPh_2$ where $n = 1$–4) in good yield. No evidence for $[(\eta^5\text{-}C_5H_5)Ru(L)_2I]$ formation was observed, even after long reaction times and in the presence of excess ligand.

Introduction

Complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(L)_2X]$ (I) and $[(\eta^5\text{-}C_5H_5)Ru(L)_3]X$ (II) (L = Group V donor ligand, X = halogen) have been the subject of extensive investigations [1]. However, only a limited amount of information is available on the properties and reactivity of the analogous carbonyl or mixed carbonyl derivatives, e.g. $[(\eta^5\text{-}C_5H_5Ru(CO)(L)X]$, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2(L)]X$, etc. The usual route to complexes I and II involves displacement of PPh_3 and/or X from $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2X]$ by a ligand L to yield the required product(s) [2–9]. For instance, diastereomeric diphosphine ligands, L–L, can replace PPh_3 in $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ to give $[(\eta^5\text{-}C_5H_5)Ru(L\text{-}L)Cl]$ in high yield [10,11]. In a similar procedure carbonylation of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with CO (or $Fe_2(CO)_9$) has been shown to lead to the CO complexes with displacement of at most one ligand and gives $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)Cl]$ [2] and $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)_2]X$ [2,8] as the final products.

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* For Part VII see ref. 18.

An alternative route to carbonyl substituted ruthenium complexes is via the reaction between [(η^5-C_5H_5)Ru(CO)$_2$X] and L [9,12–16] to give [(η^5-C_5H_5)Ru(CO)(L)X]. Kinetic studies have been carried out on the above reaction and data obtained are consistent with an S_N1 mechanism [12,15]. When X = I the reaction is slow, even in high boiling solvents such as xylene. The only other mixed carbonyl/Group V donor ligand ruthenium complexes of type I and II that have been reported, have been synthesized from [(η^5-C_5H_5)Ru(CO)$_2$X] and L is the presence of $AlCl_3$ (halogen abstraction agent) and has led to the synthesis of complexes of type II [16].

Recently we reported on the catalytic reaction between [(η^5-C_5H_5)Fe(CO)$_2$X] and isonitriles which produced [(η^5-C_5H_5)Fe(CO)$_{2-n}$(CNR)$_n$X] (n = 1,2) and [(η^5-C_5H_5)Fe(CNR)$_3$]X rapidly and in high yield [17]. In a continuation of our synthetic studies we have also extended the catalytic route to the synthesis of the analogous ruthenium complexes [18] (starting from [(η^5-C_5H_5)Ru(CO)$_2$I] and RNC). The facile nature of the above reaction suggested that the corresponding catalysed reaction between [(η^5-C_5H_5)Ru(CO)$_2$I] and Group V donor ligands should also be possible and herein we report on the results of this study.

Experimental

[(η^5-C_5H_5)Ru(CO)$_2$I] was synthesized via the literature procedures, either from $RuCl_3$ [19] or from $Ru_3(CO)_{12}$ [20]. The catalyst, [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$ was synthesized by a modification of the King procedure [21]. All the Group V ligands were purchased from Strem Chemicals. Solvents were dried and degassed before use and all reactions were routinely performed under nitrogen. Silica gel 60 (Merck) was used for column chromatographic procedures. Analytical data for the complexes are listed in Table 1, IR and ^{1}H NMR data in Table 2.

IR spectra were recorded on a Jasco IRA-1 or a Bruker IFS 85 FTIR spectrophotometer, mass spectra on a Varian Mat CH5 spectrometer (operating at 70 eV) and NMR spectra on a Bruker WP80 spectrometer. Microanalyses were performed by the Microanalytical Laboratories, C.S.I.R.

Reaction of [(η^5-C_5H_5)Ru(CO)$_2$I] and Group V donor ligands (1/1 ratio)

[(η^5-C_5H_5)Ru(CO)$_2$I] (100 mg, 0.29 mmol) and ligand (~ 0.31 mmol) were added to toluene (10 ml) contained in a 2 necked RB flask. The solution was heated in an oil bath pre-set at 105–110°C and catalyst (10 mg) added to the hot solution. The reaction was monitored by IR spectroscopy and on completion of the reaction (as detected by disappearance of starting material) the reaction solution was cooled and solvent removed. The product was then passed through a silica-gel column (washed with hexane) using benzene as eluant. A number of minor products (see text) as well as the major required complex [(η^5-C_5H_5)Ru(CO)(L)I] were collected. Recrystallization from toluene/hexane gave the required product (L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_3$, $P(O^iPr)_3$, $P(OPh)_3$.) The product with L = $P(OEt)_3$ was obtained as an oil.

Reaction of [(η^5-C_5H_5)Ru(CO)$_2$I] and $AsPh_3$ in the presence of NMe_3O

[(η^5-C_5H_5)Ru(CO)$_2$I] (100 mg, 0.29 mmol) and $AsPh_3$ (0.31 mmol) were added to benzene (10 ml) and the solvent brought to reflux. A methanol solution containing

NMe_3O (10 mg in 1 ml; 1.2 equiv.) was added to the benzene solution and the reaction monitored by IR spectroscopy. No reaction was observed, even after 3 h.

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and Group V donor ligands (1/2 ratio)

$[(\eta^5\text{-}C_5Me_5)Ru(CO)_2I]$ (100 mg, 0.29 mmol) and ligand (0.61 mmol or 0.31 mmol for the diphosphines) were added to toluene (10 ml) contained in a 2 necked RB flask. The solution was heated to reflux (oil bath pre-set at 110–115°C) and catalyst (10 mg) added to the hot solution. The reaction was monitored by both IR spectroscopy and TLC (toluene as eluant). Initially the reaction could be readily monitored by IR spectroscopy but as salt formation occurred, the reaction was monitored by the disappearance of the phosphine on TLC plates. On completion of the reaction (no change in the IR spectrum or TLC plates) the reaction solution was cooled and the precipitate filtered off. This was washed with toluene. Recrystallisation of the precipitate (CH_2Cl_2/hexane) gave the required product $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)_2]I$ (L = $PMePh_2$, PMe_2Ph, 0.5 $Ph_2P(CH_2)_nPPh_2$ where $n = 1\text{–}4$) as white or off-white solids. Elution of the filtrate through a silica-gel column (as described above) yielded varying amounts of the monosubstituted product $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)I]$.

TABLE 1

ANALYTICAL DATA FOR THE RUTHENIUM COMPLEXES

Complex	M.p. (°C)	Analyses (Found (calcd.) (%))		
		C	H	I
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(OMe)_3]I]$	105–110 [a]	24.50	3.28	26.70
		(24.28)	(3.17)	(28.51)
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(OEt)_3]I]$	Oil	29.31	4.11	26.72
		(29.58)	(4.14)	(26.05)
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(O^iPr)_3]I]$	–	34.41	4.89	24.22
		(34.04)	(4.95)	(23.98)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMe_2Ph)I]$	68–70	37.05	3.51	–
		(36.62)	(3.51)	
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMePh_2)I]$	149–150	43.15	3.35	27.93
		(43.77)	(3.48)	(24.34)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)I]$	215–218 [b]	50.46	3.72	20.25
		(49.41)	(3.46)	(21.75)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2PPh_2)I]$	70–75	52.83	3.94	–
		(52.78)	(3.86)	
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMe_2Ph)_2]I$	166–169	43.90	4.24	20.28
		(44.23)	(4.56)	(21.24)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMePh_2)_2]I$	155–158	54.49	4.70	16.48
		(53.26)	(4.33)	(17.59)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2PPh_2)]I$	~115	53.34	4.33	–
		(52.78)	(3.86)	
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2CH_2PPh_2)]I$	255–256	52.44	3.82	15.06
		(53.42)	(4.06)	(17.63)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2P(CH_2)_3PPh_2)]I$	~185	54.18	4.00	–
		(54.03)	(4.26)	
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2P(CH_2)_4PPh_2)]I$	> 90	55.00	4.83	–
		(54.63)	(4.45)	

[a] M.p. 77–78°C (ref. 14). [b] Decomposition 190–194°C (ref. 15).

TABLE 2

IR AND ^1H NMR DATA FOR THE RUTHENIUM COMPLEXES

Complex	IR ν(CO) (cm^{-1}) [a]	^1H NMR (δ, ppm; J in Hz) [b]		
		C_5H_5	C_6H_5	Other
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(OMe)_3]I]$	1985, 1974	4.66 (J 1.2)	–	CH_3: 3.39 (d,J 6.0)
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(O^iPr)_3]I]$	1985, 1968	4.75 (J 0.9)	–	CH_3: 1.19 (t,J 9.9) CH: 4.7(m)
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(OEt)_3]I]$	1985, 1973	4.72 (J 0.9)	–	CH_3: 1.08 (t,J 7.1) CH_2: 3.89 (q,J 7.2)
$[(\eta^5\text{-}C_5H_5)Ru(CO)[P(OPh)_3]I]$	1990	4.73	7.15	–
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMe_2Ph)I]$	1962	4.40	6.9–7.9(m)	CH_3: 1.77 (d,J 10.0) 1.61 (d,J 9.8)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMePh_2)I]$	1988, 1976	4.45	7.0–7.5(m)	CH_3: 2.15 (d,J 9.5)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)I]$	1950 [c]	4.49	7.0–7.8(m)	–
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2PPh_2)I]$	1965 [c]	4.45	~ 7.1	~ 1.0(m)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMe_2Ph)_2]I$	1975 [c]	5.54 [d]	7.54 [d]	CH_3 [d] 1.93 (d,J 5.3) 1.80 (d,J 5.3)
$[(\eta^5\text{-}C_5H_5)Ru(CO)(PMePh_2)_2]I$	1979 [c]	5.56 [d]	7.6–7.2(m) [d]	CH_3 [d]: 1.72 (d,J 9.5) [e]
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2PPh_2)]I$	1989 [c]	5.72 [d]	7.9–7.5(m) [d]	
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2CH_2PPh_2)]I$	1990 [c]	5.52 [d]	7.9–7.6(m) [d]	3.0–2.5(m) [d]
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2P(CH_2)_3PPh_2)]I$	1981 [c]	5.40 [d]	~ 7.4 [d]	3.5–2.5(m) [d]
$[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2P(CH_2)_4PPh_2)]I$	1981 [c]	5.12 [d]	7.6–7.5(m) [d]	3.5–2.5(m) [d]

[a] Recorded in hexane unless otherwise stated [b] Recorded in benzene-d_6 (relative to TMS) unless otherwise stated. [c] Recorded in CH_2Cl_2. [d] Recorded in acetone-d_6. [e] Complex spectrum.

Reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ *and* $PMePh_2$

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (100 mg, 0.2 mmol) and excess $PMePh_2$ (0.5 mmol) were added to toluene (10 ml) and the solution was brought to reflux. The reaction was monitored by IR spectroscopy but no reaction was observed to occur in 3 h.

Results and discussion

The reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and phosphines and phosphites occurs rapidly in toluene in the presence of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as catalyst. The reaction can be readily monitored by IR spectroscopy and the disappearance of starting material was found to take from 15–45 min under the reaction conditions (see Experimental). The final product $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)I]$ was typically obtained in yields of between 40–70% after purification by column chromatography.

In the absence of catalyst the above reaction is virtually non-existent (3 h) and this is consistent with kinetic data obtained for the reaction in the higher boiling solvent, xylene [14]. Variable reaction rates in the absence of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ were occasionally observed [22]. This arises from the presence of small amounts of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (which were obtained as a by-product in the formation of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ from $[(\eta^5\text{-}C_5H_5)Ru(CO)_2H]$ and MeI if air is not totally excluded from the reaction [20]), and this ruthenium dimer was shown in independent studies to catalyse the reaction. It can be removed by chromatographic procedures, as reported previously [18].

The reaction products were completely characterized by a combination of elemental analyses, IR and NMR spectroscopy and in some instances mass spectrometry. As had been reported previously, a number of the $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)I]$ complexes display two $\nu(CO)$ stretching frequencies in non-polar solvents (e.g. hexane). This phenomenon has been ascribed to restricted rotation around the P–R bond of the ligand [14].

From the limited data available in our study it is apparent that the size of the groups attached to the P atom plays some role in this effect. Thus the difference between the two $\nu(CO)$ bands increases for the series $P(OMe)_3 < P(OEt)_3 < P(O^iPr)_3$. Further only 1 $\nu(CO)$ band is observed for the smallest member of the phosphine series studied (i.e. the PMe_2Ph derivative) but two $\nu(CO)$ bands are observed for the $PMePh_2$ derivative. Unfortunately the insolubility of the PPh_3 derivative in hexane precluded measurement of its IR spectrum in this solvent but the analogous $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(PPh_3)I]$ derivative has also been reported to give 2 $\nu(CO)$ bands in heptane [14]. The NMR spectra of the $\eta^5\text{-}C_5H_5$ protons show the expected shifts as the basicity of the ligand varies, and the protons show coupling to the P ligand when the ligand is a phosphite. (No coupling is observed for L = phosphine). The iron atom in the mono-substituted derivatives is chiral and accounts for the four line spectrum observed for the methyl protons in the complex $[(\eta^5\text{-}C_5H_5)Ru(CO)(PMe_2Ph)I]$, as was observed for the analogous Fe complex [23]. The spectra (intensity, position, coupling constants) obtained for the coordinated L groups in the other complexes are not inconsistent with the product formulation.

Mass spectra of a number of the substituted complexes were recorded. For instance the mass spectrum of $[(\eta^5\text{-}C_5H_5)Ru(CO)(PMePh_2)I]$ shows a parent ion at $m/z = 522$ (^{102}Ru) and major fragment ions at $m/z = 494$ ($M^+ - CO$), 367 ($M^+ - CO - I$) and 352 ($M^+ - CO - I - Me$) with metastable peaks at $m/z = 467$, 338, 273, which are consistent with pathways involving the above fragment ions. No unusual features were observed in any of the mass spectra recorded.

Attempts to synthesize the $AsPh_3$ and $SbPh_3$ derivatives via the catalyst route were unsuccessful (no reaction as detected by IR spectroscopy, 6 h). An alternative approach using NMe_3O [24,25] as a reagent to induce CO dissociation was also unsuccessful.

Attempts to synthesize $[(\eta^5\text{-}C_5H_5)Ru(L)_2X]$ complexes were made, but extended heating of the reagents (excess L) was found to yield only $[(\eta^5\text{-}C_5H_5)Ru(CO)(L)_2]X$ ($L = PMePh_2$, PMe_2Ph). In these reactions I is displaced by PR_3 in preference to a CO group. The salts readily precipitate from solution and were characterized by elemental analyses and IR and NMR spectroscopy. No disubstituted products or salt formation was observed for $L = PPh_3$ and the phosphites, consistent with earlier studies [14].

The reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and the diphosphines L–L (L–L = $Ph_2P(CH_2)_nPPh_2$ where $n = 1\text{–}4$) were also carried out in toluene in the presence of catalysts. Salt formation to yield $[(\eta^5\text{-}C_5H_5)Ru(CO)L\text{–}L)]I$ was rapid for $n = 2\text{–}4$. A high yield of the mono-substituted derivative $[(\eta^5\text{-}C_5H_5)Ru(CO)(L\text{–}L)I]$ was observed and isolated when $n = 1$ and this complex only slowly converted through to the salt. For the other phosphines ($n = 2\text{–}4$) the intermediate products could also be detected and isolated (except for $n = 2$). The displacement of the second group from the starting material is clearly dependent on the size of the chelate ring to be formed and not unexpectedly this is maximized when $n = 2$. The complexes were all characterized by IR and NMR spectroscopy and elemental analyses. It is to be noted that the $\eta^5\text{-}C_5H_5$ resonance shows a near linear upfield shift as n increases from 1 to 4.

The reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and $PMePh_2$ was chosen as a standard reaction for catalyst testing. This reaction was found to be catalysed by numerous metal dimer complexes [24] e.g. $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, $[(\eta^5\text{-}C_5R'_5)Fe(CO)_2]_2$ ($R' = Me$, H). Due to its poor chemical reactivity (see later) and its ready availability, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ was ultimately chosen as the catalyst for further studies.

The qualitative reaction times observed for the reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and L suggest that the reaction rate is dependent on the nature of the incoming ligand (e.g. $PMe_2Ph > PMePh_2 > PPh_3 \gg AsPh_3$). However, it is possible that the reaction rate may be dependent on the nature of the catalyst which could be modified by the different ligands.

That the reaction is not simple is borne out by the following observations. Reaction between $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ and $PMePh_2$ (toluene, reflux) yields no substituted product as detected by IR spectroscopy (6 h). However, from the reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$, $PMePh_2$ and $[(\eta^2\text{-}C_5Me_5)Fe(CO)_2]_2$ (as catalyst) the required product $[(\eta^5\text{-}C_5H_5)Ru(CO)(PMePh_2)I]$ as well as $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ and trace amounts of $[(\eta^5\text{-}C_5Me_5)Fe(CO)(PMePh_2)I]$ were obtained after column chromatographic separation procedures. The $[(\eta^5\text{-}C_5Me_5)Fe(CO)(PMePh_2)I]$ was characterized by IR spectroscopy ($\nu(CO)$ 1920 cm^{-1}), and mass spectrometry (parent peak at $m/z = 484$ and major fragment ions at $m/z = 456$ ($M^+ - CO$) and 318 ($M^+ - CO - L$). It is thus apparent that I transfer from the ruthenium complex has occurred, presumably via a radical reaction [24]. Trace amounts of a green complex, also thought to be a derivative of

$[(\eta^5\text{-}C_5Me_5)Fe(CO)(L)I]$, was obtained from the catalysed reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ and L = $PMePh_2$, $P(OMe)_3$ and $P(OPh)_3$. It is to be noted that unreacted catalyst was isolated from all the substitution reactions.

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