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Decomposition of rhodium and iridium complexes of tripodal phosphine derivatives studied by thermal analysis

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Abstract

Thermal behaviour of five or six-coordinate rhodium and iridium complexes of two tripodal phosphines, $CH_3C(CH_2PPh_2)_3$ and $CH_3C\{CH_2P(m\text{-}CF_3C_6H_4)_2\}_3$, and their mixed-ligand complexes containing Cl, CO and MeCN was studied by TG, DTA and DTG in dynamic nitrogen atmosphere. The plain complexes exhibit very high thermal stability and degradation of the phosphine ligands follow a complicated process, while the first stage of the mixed-ligand complexes corresponds to removal of CO or MeCN and decomposition of the phosphine ligands occurs in the subsequent stages. All complexes undergo complete decomposition to form the respective metals as the final decomposition product. It was found that iridium complexes showed much higher thermal stability than their rhodium analogues. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tripodal phosphine complexes; Rhodium complexes; Iridium complexes; Thermal analysis

1. Introduction

Several rhodium complexes containing the triphenylphosphine ligand were found to act as catalytic precursors for the hydroformylation of terminal alkenes in 1960 [1]. Since then, the rhodium complexes have attracted considerable attention and in more recent years, the use of transition metal complexes with multidentate phosphines has become increasingly important, especially in organometallic chemistry and homogeneously catalysed processes such as hydrogenation [2–4], hydroformylation [5–7], and acetalisation [8,9].

The best known and most studied tripodal phosphine ligand is $CH_3C(CH_2PPh_2)_3$ (Htriphos) [10–13]. Synthesis and structural examination of the rhodium complexes of some derivatives of Htriphos were reported by Ott et al. [14] while Herolds et al. [15] studied the ruthenium and rhodium complexes of the tripodal phosphine ligands containing MeSi and *n*-BuSn groups. Thermal analysis and decomposition mechanisms of some triphenyl phosphine complexes of nickel, palladium and platinum complexes were studied in air by Barbieri et al. [16–18]. Thermal degradation of Pt(0)-triphenylphosphine complexes in toluene resulted in the formation of a dinuclear Pt(I) complex [19], however, no work on the thermal behaviour of metal complexes containing tripodal phosphines has appeared in the literature.

In this paper, we report on the thermal decomposition characteristics and non-isothermal kinetic

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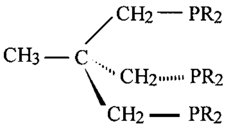
analysis of some rhodium and iridium complexes containing the tripodal Htriphos and CF_3triphos ligands which were synthesised and characterised by Sülü et al. [20,21], recently.

2. Experimental

2.1. Preparation of complexes

The rhodium and iridium complexes of Htriphos, its CF_3-substituted derivative and their mixed-ligand complexes were prepared by the method reported previously [8,14,20,21]. The molecular structure of tripodal phosphines studied is shown below:



R = Ph; Htriphos

R = CF_3Ph; CF_3triphos

These phosphines act as tridentate ligands and coordinate metal with a tripodal shape using their three P-atoms. In the presence of other ligands, they give five or six-coordinate metal complexes. The complexes reported include additional monodentate ligands such as Cl^-, CO and MeCN.

2.2. Thermal measurements

The simultaneous TG, DTG and DTA curves were obtained using a Rigaku TG8110 thermal analyser combined with TAS100 thermogravimetric analyser. The experiments were carried out in dynamic nitrogen atmosphere with a flow rate of 80 ml min^{-1} in the temperature range 20–1100°C, using platinum crucibles. Sample masses of 5–10 mg and a heating rate of 10 K min^{-1} were used. Sintered α-alumina was used as the reference material.

2.3. Kinetic analysis

Since thermal decomposition of the plain complexes such as $[MCl_3(Htriphos)]$ and $[MCl_3(CF_3triphos)]$ are complicated and usually take place in several steps, the elimination stages of CO and MeCN were chosen for a detailed kinetic study. The kinetic parameters such as energy of activation (E_a) and order of reaction (n) were evaluated graphically by employing the Freeman–Carroll method [22] with Jeres modification [23], using a computer program.

3. Results and discussion

3.1. Rhodium complexes

Thermoanalytical data for five or six-coordinate Rh(I) and Rh(III) complexes of Htriphos and CF_3triphos are given in Table 1, while thermal analysis curves of $[RhCl_3(Htriphos)]$ are shown in Fig. 1. Non-isothermal kinetic data are listed in Table 3.

3.1.1. $[RhCl_3(Htriphos)]$

The simultaneous TG–DTA–DTG curves (Fig. 1) of the complex show a three-step decomposition. The complex is stable up to 164°C and the decomposition of Htriphos takes place in the first and second stages with maxima at 260 and 378°C in DTA and DTG. The intermediate formed at about 600°C is $RhCl_3$and the experimental mass loss of 73.98% agrees well with the calculated value of 74.91%. In the third stage, the intermediate undergoes endothermic decomposition in the range 600–1100°C to form metallic Rh. Although $RhCl_3$ sublimes at temperatures higher than 800°C [24], under these experimental conditions, a metallic residue consisting of Rh was observed as the end product in the platinum crucible.

3.1.2. $[RhCl_3(CF_3triphos)]$

This complex undergoes complete endothermic decomposition in two stages. The first stage between 195 and 550°C is accompanied by a mass loss of 82.01% (calculated 83.15%) and corresponds to endothermic decomposition of the CF_3triphos ligand and subsequent formation of the solid $RhCl_3$. In the following stage, decomposition of $RhCl_3$ to metallic Rh occurs at 770°C.

3.1.3. $[RhCl(CO)(CF_3triphos)]$

The Rh(I) complex contains Cl, CO and CF_3triphos ligands and exhibits three distinct decomposition stages. Endothermic decarbonylation of the complex occurs in the temperature range 57–146°C accompanied by 2.50% mass loss. The decarbonylation is of 1.5-order and energy of activation is 14.17 kJ mol^{-1}. The second stage between 180 and 510°C, with a mass

Table 1
Thermoanalytical results (TG, DTG, DTA) for the Rh complexes

Complexes	Stage	Temperature range (°C)	DTG_{max} (°C)[a]	Removed group	Mass loss (%)		Total mass loss (%)		Solid residue	Colour
					Found	Calculated	Found	Calculated		
$[RhCl_3(Htriphos)]$	1	164–300	260 (+)							Yellow
	2	300–600	378 (+)	Htriphos	73.98	74.91			$RhCl_3$	
	3	600–1100	800 (+)	3Cl	12.97	12.75	86.95	87.66	Rh	Metallic
$[RhCl_3(CF_3triphos)]$	1	195–550	368 (+)	CF_3triphos	82.01	83.15			$RhCl_3$	Yellow
	2	550–955	770 (+)	3Cl	8.75	8.56	90.76	91.71	Rh	Metallic
$[RhCl(CO)(CF_3triphos)]$	1	57–146	103 (+)	CO	2.50	2.34			$RhCl(CF_3triphos)]$	Yellow
	2	180–500	362 (+)	CF_3triphos	88.88	89.08			RhCl	
	3	510–700	590 (+)	Cl	2.90	2.96	91.38	91.42	Rh	Metallic
$[Rh(CO)_2(CF_3triphos)]CF_3SO_3$	1	49–178	95 (+)	2CO	4.08	4.18				Yellow
	2	178–303	283 (+)		23.57					
	3	303–858	318 (+)	CF_3triphos	53.25				$RhCF_3SO_3$	
	4	858–985	955 (+)	CF_3SO_3	11.81	11.12	92.71	92.32	Rh	Metallic
$[RhCl(MeCN)_2(Htriphos)](CF_3SO_3)_2$	1	59–159	137 (+)	2MeCN	7.36	7.17				Yellow
	2	159–425	402 (+)	Htriphos	55.43	54.65			$RhCl(CF_3SO_3)_2$	
	3	425–905	825 (+)	$2CF_3SO_3$, Cl	28.65	29.18	91.44	91.00	Rh	Metallic
$[RhCl_2(MeCN)(Htriphos)]CF_3SO_3$	1	57–195	105 (+)	MeCN	3.87	4.15				Orange
	2	235–520	406 (+)	Htriphos	62.36	63.19			$RhCl_2CF_3SO_3$	
	3	520–730	670 (+)	CF_3SO_3	16.13	15.08	90.21	89.59		
	4	730–952	822 (+)	2Cl	7.85	7.17			Rh	Metallic

[a] (+) Endotherm.

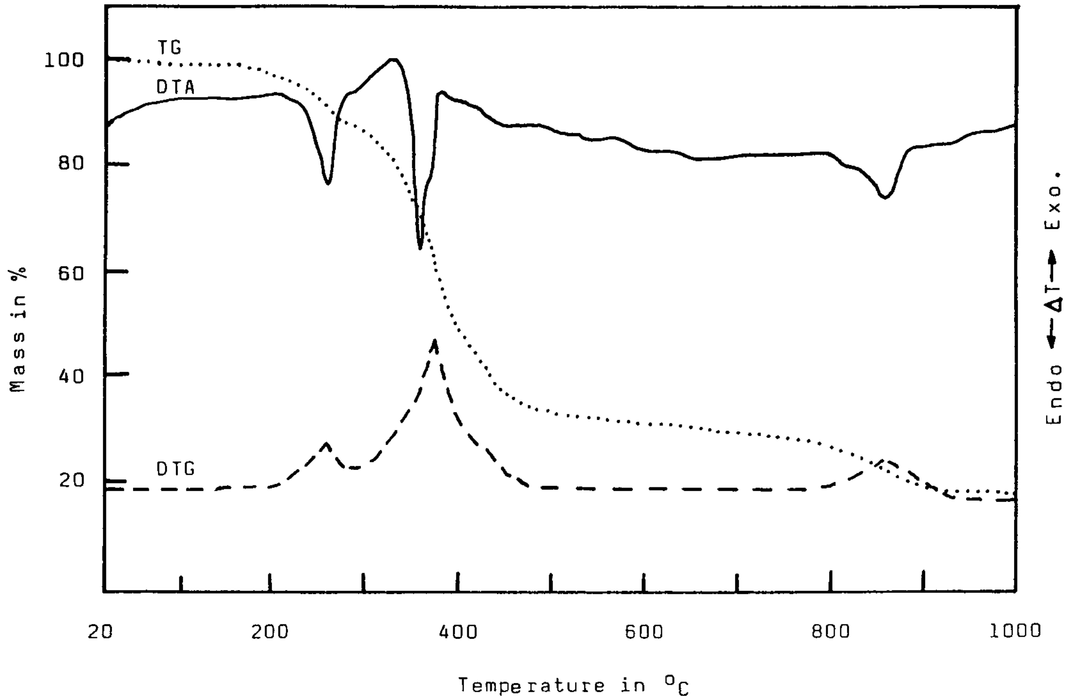


Fig. 1. Thermal analysis curves of [RhCl$_3$(Htriphos)].

loss 85.80% (calculated 86.13%) is attributed to the removal of the CF$_3$triphos ligands to produce RhCl which decomposes in the third stage at 590°C to give metallic Rh as the final decomposition product.

3.1.4. [Rh(CO)$_2$(CF$_3$triphos)]CF$_3$SO$_3$

This complex is also a mixed-ligand complex of Rh(I) containing CO and CF$_3$SO$_3$ as a ligand and complementary anion, respectively. The complex decomposes in four stages. In the first stage, endothermic removal of two CO molecules takes place at 95°C. The energy of activation and order of decarbonylation were found to be 15.26 kJ mol^{-1} and second order, respectively. The degradation of CF$_3$triphos occurs in the second and third stages in the temperature range 178–858°C to give the RhCF$_3$SO$_3$ intermediate. A 76.82% mass loss observed in these stages is in good agreement with the calculated mass loss of 77.03%. Over the 858–1100°C range, the DTA curve displays an endothermic peak at 955°C attributed to complete decomposition of the intermediate to metallic Rh.

3.1.5. [RhCl(MeCN)$_2$(Htriphos)](CF$_3$SO$_3$)$_2$

The complex undergoes three-step decomposition. The first step in the temperature range 59–159°C involves endothermic liberation of two MeCN molecules. The experimental mass loss of 7.36% is consistent with the calculated mass loss of 7.17%. This step is of 0.5-order and the E_a value was found to be 13.85 kJ mol^{-1}. In the second step, decomposition of the Htriphos ligand occurs between 160 and 420°C, with a mass loss of 55.43% (calculated 54.65%). The intermediate RhCl(CF$_3$SO$_3$)$_2$ formed at 425°C decomposes at 825°C to form metallic Rh.

3.1.6. [RhCl$_2$(MeCN)(Htriphos)]CF$_3$SO$_3$

This complex shows three stages of decomposition. The first endothermic peak at 105°C in the temperature range 57–195°C corresponds to loss of the MeCN molecule. The E_a and n values for this stage were found to be 15.11 kJ mol^{-1} and 1.5, respectively. A sharp DTA peak at 229°C is not due to the melting of the complex as checked by a melting point detection apparatus and may be attributed to some kind of phase changes occurred in the crystals of the complex. The second endothermic stage between 235 and 520°C is related to decomposition of Htriphos to produce the $RhCl_2CF_3SO_3$ intermediate. The CF_3SO_3 and chloride moieties of the intermediate decompose at the third and fourth stages in the temperature range 520–952°C to give metallic Rh.

3.2. Iridium complexes

Table 2 lists thermoanalytical data for five or six-coordinate Ir(I) and Ir(III) complexes of Htriphos and CF_3triphos and thermal analysis curves of [$IrCl_3$(Htriphos)] are shown in Fig. 2. Kinetic data are given in Table 3.

3.2.1. [$IrCl_3$(Htriphos)]

The complex has a very high thermal stability. Its decomposition begins at about 315°C and proceeds in four stages as shown in Fig. 2. This complex exhibits a very complicated decomposition process and mass loss calculations are not in agreement with an intermediate of definite composition. However, the total mass loss between 315 and 1100°C corresponds to the presence of metallic iridium as the final decomposition product as identified by chemical analysis and also from its lustrous appearance.

3.2.2. [$IrCl_3$(CF_3triphos)]

The complex is stable up to 215°C and then begins to decompose in five stages. The CF_3triphos ligand undergoes endothermic decomposition in four consecutive steps between 215 and 992°C to give $IrCl_3$. The experimental mass loss (76.49%) for these stages is in good agreement with the calculated mass loss (77.57%). The last stage is due to decomposition of $IrCl_3$ to produce metallic iridium.

3.2.3. [IrCl(CO)(CF_3triphos)]

The Ir(I) complex shows five stages of decomposition. The first stage is attributed to endothermic elimination of a CO molecule between 94 and 200°C, with a mass loss of 2.31% (calculated 2.17%). The decarbonylation process is of 1.5-order with an E_a value

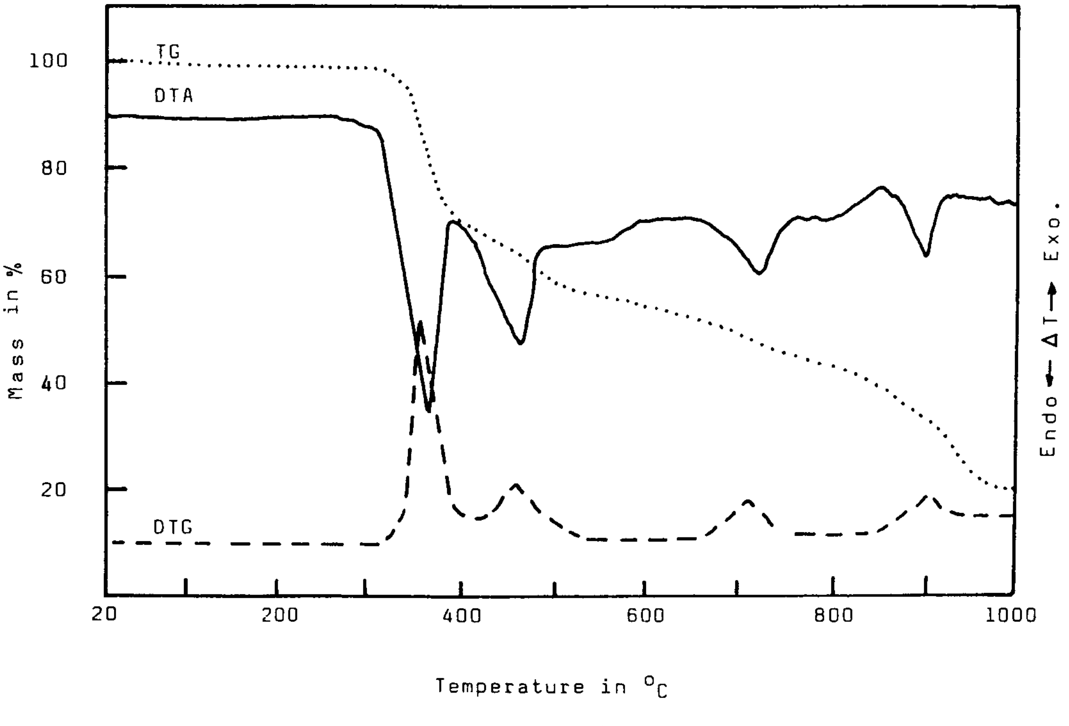


Fig. 2. Thermal analysis curves of [$IrCl_3$(Htriphos)].

Table 2
Thermoanalytical results (TG, DTG, DTA) for the Ir complexes

Complexes	Stage	Temperature range (°C)	DTG_{max} (°C)[a]	Removed group	Mass loss (%)		Total mass loss (%)		Solid residue	Colour
					Found	Calculated	Found	Calculated		
$[IrCl_3(Htriphos)]$	1	313–409	370 (+)		33.55					White
	2	409–539	480 (+)		12.16					
	3	539–800	720 (+)		10.28					
	4	800–1100	920 (+)	Htriphos, 3Cl	22.82		78.81	79.18	Ir	Metallic
$[IrCl_3(CF_3triphos)]$	1	215–325	292 (+)		12.34					Yellow
	2	325–410	352 (+)		20.37					
	3	410–570	470 (+)		21.74					
	4	570–992	932 (+)	CF_3triphos	22.04				$IrCl_3$	
	5	992–1100	1030 (+)	3Cl	8.31	7.99	84.80	85.56	Ir	
$[IrCl(CO)(CF_3triphos)]$	1	105–200	140 (+)	CO	2.31	2.17				Yellow
	2	200–373	330 (+)		25.10					
	3	373–436	400 (+)		14.97					
	4	436–546	470 (+)		17.17					
	5	546–1000	810 (+)		24.61		84.16	85.08	Ir	Metallic
$[Ir(CO)_2(CF_3triphos)]CF_3SO_3$	1	85–158	106 (+)	2CO	3.26	3.92				Yellow
	2	158–390	360 (+)		29.22					
	3	390–497	423 (+)		22.17					
	4	497–1000	880 (+)		34.12		88.77	86.56	Ir	Metallic
$[IrCl(MeCN)_2(Htriphos)](CF_3SO_3)_2$	1	35–84	52 (+)	MeCN	3.15	3.32				Yellow
	2	85–200	148 (+)	MeCN	3.08	3.32				
	3	250–388	322 (+)		17.27					
	4	388–460	425 (+)		20.71					
	5	460–535	480 (+)	Htriphos	12.29				$IrCl(CF_3SO_3)_2$	
	6	535–1100	930 (+)	$2CF_3SO_3$, Cl	28.08	27.07	84.33	84.41	Ir	Metallic
$[IrCl_2(MeCN)(Htriphos)]CF_3SO_3$	1	92–182	131 (+)	MeCN	4.20	3.80				White
	2	182–540	443 (+)		41.34					
	3	540–800	740 (+)	Htriphos	18.95				$IrCl_2CF_3SO_3$	
	4	800–926	875 (+)	CF_3SO_3	12.00	13.83				
	5	926–1100	880 (+)	2Cl	6.45	6.48	82.94	82.17	Ir	Metallic

[a] (+) Endotherm.

Table 3
Kinetic data for the thermal decomposition of Rh and Ir complexes

Reaction	E_a (kJ mol^{-1})	n	r[a]
$[RhCl(CO)(CF_3triphos)]\ (s) \xrightarrow[-CO]{57-146^\circ C} [RhCl(CF_3triphos)]\ (s)$	14.17	1.5	0.99
$[Rh(CO)_2(CF_3triphos)]CF_3SO_3\ (s) \xrightarrow[-2CO]{49-178^\circ C} [Rh(CF_3triphos)]CF_3SO_3\ (s)$	15.26	2	0.99
$[RhCl(MeCN)_2(Htriphos)]CF_3SO_3\ (s) \xrightarrow[-2MeCN]{59-159^\circ C} [RhCl(Htriphos)](CF_3SO_3)_2\ (s)$	13.85	0.5	0.97
$[RhCl_2(MeCN)(Htriphos)]CF_3SO_3\ (s) \xrightarrow[-MeCN]{59-159^\circ C} [RhCl_2(Htriphos)]CF_3SO_3\ (s)$	15.11	1.5	0.98
$[IrCl(CO)(CF_3triphos)]\ (s) \xrightarrow[-CO]{105-200^\circ C} [IrCl(CF_3triphos)]\ (s)$	20.22	1.5	0.99
$[Ir(CO)_2(CF_3triphos)]CF_3SO_3\ (s) \xrightarrow[-2CO]{85-158^\circ C} [Ir(CF_3triphos)]CF_3SO_3\ (s)$	18.90	1	0.99
$IrCl(MeCN)_2(Htriphos)](CF_3SO_3)_2\ (s) \xrightarrow[-MeCN]{35-84^\circ C} [IrCl(MeCN)(Htriphos)](CF_3SO_3)_2\ (s)$	14.98	2	0.99
$[IrCl(MeCN)(Htriphos)](CF_3SO_3)_2\ (s) \xrightarrow[-MeCN]{85-200^\circ C} [IrCl(Htriphos)](CF_3SO_3)_2\ (s)$	17.79	2	0.99
$[IrCl_2(MeCN)(Htriphos)]CF_3SO_3\ (s) \xrightarrow[-MeCN]{92-182^\circ C} [IrCl_2(Htriphos)]CF_3SO_3\ (s)$	19.60	2	0.99

[a] Correlation coefficient of the linear plot.

of 20.22 kJ mol^{-1}. The degradation of CF_3triphos together with Cl takes place in the subsequent stages in the range 200–1000°C. Mass loss calculations do not correspond to formation of a definite intermediate, but the total mass loss (experimental 84.80%, calculated 85.56%) agrees well with the presence of iridium as the end product.

3.2.4. *[Ir(CO)$_2$(CF$_3$triphos)]CF$_3$SO$_3$*

The first step in the decomposition sequence corresponds to the decarbonylation of the Ir(I) complex in the temperature range 85–158°C. The E_a and n values for this stage were found to be 18.90 kJ mol^{-1} and 1, respectively. The DTA curve shows a small endotherm at 168°C without a mass loss, associated with the melting point of the complex as also checked by a melting point detection apparatus. The decomposition of CF_3triphos and CF_3SO_3 proceeds in the following stages with a continuous mass loss process between 160 and 960°C. The final decomposition product is metallic iridium.

3.2.5. *[IrCl(MeCN)$_2$(Htriphos)](CF$_3$SO$_3$)$_2$*

This complex decomposes into six stages. The first two stages may be correlated with removal of two MeCN molecules at 52 and 148°C accompanied by 3.15 and 3.04% mass loss (calculated 3.32%), respectively. The elimination of the first MeCN molecule is of second order with an energy of activation 14.98 kJ mol^{-1}, while the removal of the second MeCN molecule is also second order and its E_a value is 17.79 kJ mol^{-1}. The solid residue is stable up to 250°C and then degradation of Htriphos occurs in the subsequent stages in the temperature range 250–535°C, with three DTG maxima at 322, 425 and 480°C. Mass loss calculations (experimental 50.27%, calculated 50.68%) indicate formation of $IrCl(CF_3SO_3)_2$ at 535°C which decomposes to metallic iridium at 930°C.

3.2.6. *[IrCl$_2$(MeCN)(Htriphos)]CF$_3$SO$_3$*

This complex exhibits five stages of decomposition. In the first stage, removal of the MeCN ligand takes place in the temperature range 92–182°C with a mass loss of 4.20% (calculated 3.80%). This process is of second order with an E_a value of 19.60 kJ mol^{-1}. The following two stages between 182 and 800°C are attributed to decomposition of the Htriphos ligand with two maxima at 443 and 740°C in DTG. Decomposition of CF_3SO_3 and Cl in the residue are observed in the subsequent stages between 800 and 1100°C to give metallic iridium.

4. Conclusions

Both the rhodium and iridium complexes except [Ir(CO)$_2$(CF$_3$triphos)]CF$_3$SO$_3$ have no melting points and decompose at temperatures given in Tables 1 and 2. All complexes yield the corresponding metal as the final decomposition products which are clearly detected from their lustrous shiny appearance. Elimination of potentially volatile ligands such as CO and MeCN occurs at temperatures up to 150°C and follows a low energetic process. The presence of these ligands decreases the thermal stability of both Rh and Ir complexes when compared with the plain complexes. The iridium complexes show more decomposition steps than the corresponding rhodium complexes and their energies of activation (E_a) are also significantly higher. These findings obviously indicate that thermal reactivity of the iridium complexes differs from that of their rhodium analogues. As the initial decomposition temperatures are taken as a measure of thermal stability, it is also shown that the iridium complexes usually exhibit much higher thermal stability than the corresponding rhodium complexes. For example, [RhCl$_3$(Htriphos)] begins to decompose at 164°C, while its Ir analogous decomposes at 315°C. This may be explained in terms of metal–ligand interactions. Ligand field stabilisation energy which is an indication of the metal–ligand strength increases on a descending group of transition metals due to expanding of the d-orbitals from 3d to 5d and therefore, the increase in thermal stability from rhodium to iridium may be due to the contribution of the ligand field stabilisation energy [25].

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