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NEW RHODIUM(III) AND IRIDIUM(III) CYCLOPENTADIENYL COMPOUNDS OBTAINED BY REACTION OF [CpM(CO)(PPh$_3$)CH$_2$CN]BPh$_4$ (M=Rh, Ir) COMPLEXES WITH NUCLEOPHILES

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SUMMARY

The new complexes [CpM(CO)(PPh$_3$)CH$_2$CN]BPh$_4$ where M is Rh or Ir, have been prepared, and their reactions with CH$_3$O$^-$, N$_3^-$, SCN$^-$, SeCN$^-$, halide ion, and C$_6$H$_5$SO$_2^-$ examined. The rhodium cationic complex reacts readily at room temperature to give cyclopentadienyl complexes of Rh^{III}; as expected, the CH$_3$O$^-$ and N$_3^-$ ions react at the carbonyl group. The reaction of [CpRh(CO)(PPh$_3$)-CH$_2$CN]$^+$ with C$_6$H$_5$SO$_2^-$ gives CpRh(PPh$_3$)(CH$_2$CN)(C$_6$H$_5$), formed by loss of SO$_2$ from the initially formed CpRh(PPh$_3$)(CH$_2$CN)(SO$_2$Ph).

[CpIr(CO)(PPh$_3$)(CH$_2$CN)]BPh$_4$ reacts at room temperature only with CH$_3$O$^-$ and N$_3^-$, and no reaction occurs during 12 h even in refluxing acetone with other anions. The lower reactivity of the iridium complex is interpreted in terms of the stability of the cationic complex and the strength of the M–CO bond.

INTRODUCTION

Neutral cyclopentadienyl complexes of rhodium(III) and iridium(III) have been described recently[1–6]. They were generally prepared by oxidative addition of halogens, alkyl and acyl halides, germanium and tin halides, or triphenyl- and tribenzylsilane to CpM(CO)L (L=CO or tertiary phosphine). We describe below a new series of cyclopentadienyl Rh^{III} complexes obtained from the reactions of nucleophiles such as CH$_3$O$^-$, N$_3^-$, SCN$^-$, SeCN$^-$, C$_6$H$_5$SO$_2^-$, Cl$^-$, Br$^-$, I$^-$ with the cationic complex [CpRh(CO)(PPh$_3$)(CH$_2$CN)]$^+$. The analogous complex [CpIr(CO)-(PPh$_3$)(CH$_2$CN)]$^+$ has been made, and this has allowed the effect of the metal to be examined in this type of reaction.

EXPERIMENTAL

CpRh(CO)PPh$_3$ and CpIr(CO)(PPh$_3$) were prepared as previously reported[7]. Other chemicals used were reagent grade. Basic alumina was used for chromatography. IR spectra were recorded with a Perkin–Elmer model 457 spectrometer, molecular weights were determined on a Knauer vapor pressure osmometer, and melting points were determined on a Fisher–Jones hot stage apparatus. Elemental analyses were by Alfred Bernhardt, Mikroanalytisches Laboratorium, Mülheim, Germany. All reactions were carried out under nitrogen. Analytical and physical data are listed in Table 1; IR data in Table 2.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compounds	*Colour*	*M.p. (°C)*	*Analysis found (calcd.) (%)*			
			C	*H*	*N*	*Hal*
$[CpRh(CO)(P(C_6H_5)_3)(CH_2CN)]B(C_6H_5)_4$	Yellow	120–124 dec.	73.21	5.10	1.86	
			(73.45)	(5.17)	(1.71)	
$[CpIr(CO)(P(C_6H_5)_3)(CH_2CN)]B(C_6H_5)_4$	Wine	111–118 dec.	66.12	4.66	1.73	
			(66.22)	(4.66)	(1.54)	
$CpRh[P(C_6H_5)_3](CH_2CN)(COOCH_3)$	Yellow	132–140 dec.	61.06	4.73	2.73	
			(61.25)	(4.76)	(2.64)	
$CpRh[P(C_6H_5)_3](CH_2CN)(NCO)$	Yellow	124–127	60.54	4.42	5.84	
			(60.90)	(4.32)	(5.46)	
$CpRh[P(C_6H_5)_3](CH_2CN)(SCN)$	Yellow	175–179	58.25	3.42	5.19	
			(58.14)	(3.20)	(5.42)	
$CpRh[P(C_6H_5)_3](CH_2CN)(SeCN)$	Brick	152–168 dec.	54.14	3.91	4.86	
			(54.29)	(3.85)	(4.86)	
$CpRh[P(C_6H_5)_3](CH_2CN)I$	Brick	94–98 dec.	50.41	3.56	2.51	21.44
			(50.27)	(3.71)	(2.34)	(21.24)
$CpRh[P(C_6H_5)_3](CH_2CN)Br$	Brick	119–125	54.75	3.91	2.42	15.03
			(54.57)	(4.03)	(2.54)	(14.62)
$CpRh[P(C_6H_5)_3](CH_2CN)Cl$	Orange	>125 dec.	58.98	4.57	2.94	7.34
			(59.37)	(4.38)	(2.76)	(7.01)
$CpRh[P(C_6H_5)_3](CH_2CN)(C_6H_5)$	Yellow-orange	76–80	68.01	4.92	2.43	
			(68.01)	(4.97)	(2.55)	
$CpIr[P(C_6H_5)_3](CH_2CN)(NCO)$	Ivory	90–95 dec.	52.14	3.78	4.35	
			(51.90)	(3.68)	(4.65)	
$CpIr[P(C_6H_5)_3](CH_2CN)(COOCH_3)$	Pale-yellow	138–145 dec.	52.12	4.21	2.14	
			(52.41)	(4.07)	(2.26)	

Preparation of $[CpRh(CO)(PPh_3)(CH_2CN)]BPh_4$

To a hexane solution of $CpRh(CO)PPh_3$ (100 mg; 0.22 mmoles) was added an excess of $ClCH_2CN$ (0.4 ml). The mixture was stirred, and a red oil was present after 5 h. After evaporation of the solvent, this oil was dissolved in CH_3OH; $NaBPh_4$ was added, and yellow needles were obtained.

Preparation of $[CpIr(CO)(PPh_3)(CH_2CN)]BPh_4$

Wine-coloured crystals of $[CpIr(CO)PPh_3(CH_2CN)]BPh_4$ were obtained analogously from $CpIr(CO)PPh_3$ and $ClCH_2CN$.

Preparation of $CpRh(PPh_3)(COOCH_3)(CH_2CN)$

CH_3OLi (1 ml of 0.15 *N*) in methanol was added to a suspension of $[CpRh(CO)(PPh_3)(CH_2CN)]BPh_4$ in the same solvent. After 2 h the solvent was evaporated and the yellow solid obtained was washed with water and dried. The product was crystallized from $CHCl_3$/pentane.

TABLE 2

IR DATA

Compound	$\nu(CN)^a$ (cm^{-1})	*Other bands*
$[CpRh(CO)(P(C_6H_5)_3)(CH_2CN)]B(C_6H_5)_4$	2204 m	2070 vs ν(CO)
$[CpIr(CO)(P(C_6H_5)_3)(CH_2CN)]B(C_6H_5)_4$	2223 m	2058 vs ν(CO)
$CpRh[P(C_6H_5)_3](CH_2CN)(COOCH_3)$	2200 m	1632 s ν(CO)
$CpRh[P(C_6H_5)_3](CH_2CN)(NCO)$	2200 s	2245 s ν(NCO)
$CpRh[P(C_6H_5)_3](CH_2CN)(SCN)$	2200 m	2108 s ν(CN)
$CpRh[P(C_6H_5)_3](CH_2CN)(SeCN)$	2200 m	2115 m ν(CN)
$CpRh[P(C_6H_5)_3](CH_2CN)I$	2200 m	
$CpRh[P(C_6H_5)_3](CH_2CN)Br$	2198 m	
$CpRh[P(C_6H_5)_3](CH_2CN)Cl$	2198 s	303 m ν(Rh-Cl)
$CpRh[P(C_6H_5)_3](CH_2CN)(C_6H_5)$	2201 m	
$CpIr[P(C_6H_5)_3](CH_2CN)(NCO)$	2205 s	2245 s ν(NCO)
$CpIr[P(C_6H_5)_3](CH_2CN)(COOCH_3)$	2200 m	1640 s ν(CO)

[a] Of the CH_2CN.

Preparation of $CpIr(PPh_3)(COOCH_3)(CH_2CN)$

In the same way, $[CpIr(CO)(PPh_3)CH_2CN]BPh_4$ (150 mg, 0.16 mmoles) was treated with CH_3OLi (1.3 ml of 0.15 *N*), and after about 5 h the solid obtained was washed with water, dried, and crystallized from $CHCl_3$/pentane.

Preparation of $CpRh(PPh_3)(NCO)(CH_2CN)$

NaN_3 (12 mg; 0.18 mmoles) in acetone was added to a suspension of $[CpRh(CO)(PPh_3)(CH_2CN)]BPh_4$ (150 mg; 0.183 mmoles) in the same solvent. The IR spectrum showed the reaction to be complete after about 20 min. The concentrated solution was passed through an alumina column with $CHCl_3$ as eluant, and the yellow solution obtained was diluted with pentane to give a yellow precipitate.

Preparation of $CpIr(PPh_3)(NCO)(CH_2CN)$

NaN_3 (9.4 mg; 0.145 mmoles) in acetone was added to a solution of $[CpIr(CO)(PPh_3)(CH_2CN)]BPh_4$ (130 mg; 0.143 mmoles) in the same solvent. The mixture was stirred for 3 h, then filtered, and the solvent was evaporated under vacuum. The solid residue was washed, dried, and crystallized from $CHCl_3$/pentane.

Preparation of $CpRh(PPh_3)(CH_2CN)Cl$

KCl (0.15 mg; 0.20 mmoles) in 1 ml of water was added to a solution of $[CpRh(CO)(PPh_3)(CH_2CN)]BPh_4$ (150 mg; 0.183 mmoles) in 60 ml of acetone. The colour of the solution changed from yellow to orange, and after 5 h the solution was concentrated and transferred to an alumina column. Acetone elution gave a yellow fraction, from which yellow crystals were obtained by addition of pentane at −78°.

Preparation of $CpRh(PPh_3)(CH_2CN)Br$ and $CpRh(PPh_3)(CH_2CN)I$

$N(CH_3)_4Br$ (31 mg; 0.2 mmoles) was added to a solution of $[CpRh(CO)(PPh_3)(CH_2CN)]BPh_4$ (160 mg; 0.195 mmoles) in 30 ml of acetone. The mixture was stirred for about 4 h and then evaporated. The residue was taken up in CCl_4, and the solution was filtered and concentrated. Addition of pentane gave a brick-coloured solid. $CpRh(PPh_3)(CH_2CN)I$ was prepared analogously.

Preparation of $CpRh(PPh_3)(CH_2CN)(SeCN)$ and $CpRh(PPh_3)(CH_2CN)(SCN)$

NaSeCN (25 mg; 0.19 mmoles) in acetone was added to $[CpRh(CO)(PPh_3)(CH_2CN)]BPh_4$ (150 mg; 0.183 mmoles) in the same solvent. The reaction mixture was stirred for 4 h, then filtered, concentrated, and passed through alumina. With acetone as eluant a yellow fraction was separated, and a solid was obtained by adding pentane. $CpRh(PPh_3)(SeCN)(CH_2CN)$ was prepared analogously.

Preparation of $CpRh(PPh_3)(CH_2CN)(C_6H_5)$

A slight excess of $NaSO_2C_6H_5$ was added to an acetone solution of $[CpRh(PPh_3)(CO)(CH_2CN)]BPh_4$ (160 mg; 0.195 mmoles). After 3 h the IR spectrum of the reaction mixture showed no ν(CO) band. The solvent was then evaporated and the solid residue dissolved in $CHCl_3$, filtered, and passed through alumina.

With $CHCl_3$ as eluant a yellow fraction was separated and a yellow solid obtained by adding pentane.

RESULTS AND DISCUSSION

The reaction of $ClCH_2CN$ with $CpRh(CO)(PPh_3)$ has been previously reported[8]. The cationic complex $[CpIr(CO)(PPh_3)(CH_2CN)]BPh_4$ has now been obtained as crystals by addition of $ClCH_2CN$ to $CpIr(CO)(PPh_3)$ in hexane. The IR spectrum is fairly similar to that of the analogous rhodium complex; it shows a ν(CN) band at 2223 cm^{-1} and a strong absorption due to the CO stretching frequency at 2058 cm^{-1}.

Reactions with CH_3O^- and N_3^-

The cationic complexes $[CpM(CO)(PPh_3)CH_2CN]^+$ (M=Rh, Ir) undergo nucleophilic attack at the carbon atom of the coordinated CO when treated with CH_3O^- or N_3^-. Many reactions reported in the literature show that metal carbonyls readily undergo such attack at the carbonyl carbon atom which is an electrophilic center and prefers hard nucleophiles such as CH_3O^- and N_3^-. It has also been shown[9-10] that if a complex contains groups which are more electrophilic than the CO entity, as in $[CpFe(CO)(CS)]^+$ or $[CpFe(CO)(C_2H_4)]^+$, the attack does not then occur at the carbonyl group[9,10]. Since we did not observe any attack at the CH_2CN ligand, this ligand must be less electrophilic than the CO group. Furthermore, the high value of the ν(CO) can be regarded, in accord with Darensbourg's suggestions[11], as being indicative of pronounced electrophilic character in the carbonyl group of the complexes under examination. This is probably enhanced by the positive charge on the complex and by the oxidation state of the metal.

The complex $CpRh(PPh_3)(CH_2CN)(COOCH_3)$ obtained from CH_3O^- and $[CpRh(CO)(PPh_3)CH_2CN]^+$ shows a band in the IR spectrum at 2200 cm^{-1} due to the ν(CN) and one at 1632 cm^{-1} due to the coordinated alkoxycarbonyl group. The reaction of $[CpIr(CO)(PPh_3)CH_2CN]^+$ with CH_3O^- is slower and requires several hours, but the spectrum of the product, $CpIr(PPh_3)(CH_2CN)(COOCH_3)$, shows a ν(CN) band at 2200 cm^{-1} and a ν(CO) band at 1640 cm^{-1}.

$[CpRh(CO)(PPh_3)CH_2CN]^+$ reacts with NaN_3 at a 1/1 molar ratio in acetone to give the isocyanate complex $CpRh(PPh_3)(CH_2CN)(NCO)$. In the light of kinetic results reported for related substrates[12], we suggest that the first step of the reaction is a N_3^- attack at the carbonyl carbon atom, with the formation of $CpRh(PPh_3)(CON_3)(CH_2CN)$, which subsequently loses N_2 to give the isocyanate derivative. The IR spectrum shows a band at 2245 cm^{-1} due to the asymmetric N=C=O stretching and a CN stretching frequency at 2205 cm^{-1}. A weak band at 2022 cm^{-1} is also present. The intensity of this increases if the reaction is carried out in methanol with an excess of azide, which suggests that another compound can be formed. We could not isolate this, but the stretching frequency of 2022 cm^{-1} indicates that an azide complex is probably involved.

The complex $[CpIr(CO)(PPh_3)(CH_2CN)]^+$ correspondingly reacts with N_3^- in acetone (molar ratio 1/1) to give $CpIr(PPh_3)(NCO)(CH_2CN)$. In accord with this formulation, the IR spectrum shows a ν(NCO) band at 2245 cm^{-1} and a ν(CN) band at 2205 cm^{-1}.

Reactions with halides, NCS^-, $NCSe^-$ and $PhSO_2^-$

The cationic complex $[CpRh(CO)(PPh_3)CH_2CN]^+$ reacts with these anions to give neutral complexes of Rh^{III} by loss of CO. The IR spectra of the $CpRh(PPh_3)(CH_2CN)X$ complexes, with X = Cl, Br or I, have a band at 2200 cm^{-1} due to the CN group. The complexes $CpRh(PPh_3)(SeCN)(CH_2CN)$ and $CpRh(PPh_3)(SCN)(CH_2CN)$ show, in addition to the band at 2200 cm^{-1} due to the CN group, bands at 2115 and 2108 cm^{-1}, respectively, due to the CN stretch of SeCN and SCN groups coordinated to the metal. As previously discussed[13-14], the value of the CN stretching frequency does not permit a firm decision to be made between Rh–NCY and Rh–YCN structures (Y = S or Se), but a value of ν(CSe) > 558 cm^{-1} is usually interpreted as indicative of an M–NCSe bond[13], while the ν(CS) frequency ranges between 720–690 cm^{-1} for an M–NCS bond and between 860–780 cm^{-1} for an M–SCN bond. We could not observe such bands for the complex $CpRh(PPh_3)(SCN)(CH_2CN)$ because several strong absorptions interfere in the relevant range. However, by comparing the IR spectrum of the selenocyanate derivative in the range 550–690 cm^{-1} with that of the corresponding halogen complex it is possible to infer that the ν(CSe) frequency is not in this range, and we conclude that an Rh–SeCN bond is involved. Since the same factors determine the type of bond formed in selenocyanate and thiocyanate complexes[13-16], we also infer that an Rh–SCN bond is present in the analogous thiocyanate complex. In accordance with previous results[17] for the reaction of cyclopentadienyliron tricarbonyl cation with cyanate ion, we regard the reaction with halides, SCN^- and $SeCN^-$ as simple nucleophilic displacements of CO from the cationic complex $[CpRh(CO)(PPh_3)(CH_2CN)]^+$.

$[CpRh(CO)(PPh_3)CH_2CN]^+$ reacts in acetone with $C_6H_5SO_2Na$ to give a neutral compound, which, on the basis of its analysis can be formulated as $CpRh(PPh_3)(CH_2CN)(C_6H_5)$. Probably the reaction first gives an *S*-sulfinate complex, which subsequently rearranges to a σ-aryl derivative*. This represents one of the few examples of a metal–aryl complex formed by loss of SO_2 at room temperature, though compounds such as $[Ir(PPh_3)_2(CO)(CH_3C_6H_4SO_2)Cl_2]$[18] and *trans*-$[PtL_2Cl$-

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* We confirmed that the loss of SO_2 was not due to purification of the complex on alumina.

$(CH_3C_6H_4SO_2)]^{19-20}$ (L = PPh_3 or PMe_2Ph) form σ-aryl derivatives by loss of SO_2 in boiling toluene. It is noteworthy that no carbene complex was isolated, as would be expected if the loss of SO_2 occurred before the breaking of the Rh–CO bond.

The cationic complex $[CpIr(CO)(PPh_3)(CH_2CN)]^+$ does not react in acetone with nucleophiles such as I^-, Cl^-, SCN^- and $SeCN^-$ even during 12 h under reflux, indicating that the reactivity of the complex $[CpM(CO)(PPh_3)(CH_2CN)]^+$ falls as the metal is changed from rhodium to iridium. Basolo and his colleagues[21–22] described a kinetic study of the reactions between *trans*-$[M(en)_2X_2]^+$ (M = Rh, Ir; X = Cl, Br, I) complexes and various nucleophiles, and found that the rate is independent of the nature and the concentration of the nucleophile and is faster with rhodium complexes. We believe that the iridium complex is more stable than the rhodium analog, and this can be related to the greater importance of back donation from the metal atom to the antibonding orbitals of the CO in the case of the iridium. In this connection it is relevant to note that the ν(CO) is higher in the cationic rhodium complex than in the iridium analog.

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