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REACTIONS OF THE CYCLOPENTADIENYLRUTHENIUM TRICARBONYL CATION WITH NUCLEOPHILES

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SUMMARY

A convenient preparation of $C_5H_5M(CO)_3^+$ (M=Ru or Fe) from $C_5H_5M(CO)_2Cl$ has been developed. Like $C_5H_5Fe(CO)_3^+$, the cation $C_5H_5Ru(CO)_3^+$ reacts with primary amines to form carbamoyl complexes $C_5H_5Ru(CO)_2(CONHR)$. With hydrazine it yields an unstable carbazoyl derivative $C_5H_5Ru(CO)_2(CONHNH_2)$ which rearranges with loss of NH_3 to form the isocyanate complex $C_5H_5Ru(CO)_2(NCO)$. Similar reactions take place with methyl substituted hydrazines. The isocyanate complex can also be prepared by the reaction of the cation with N_3^-. With I^- and Cl^- the cation yields $C_5H_5Ru(CO)_2X$; with OCH_3^-, $C_5H_5Ru(CO)_2COOCH_3$; and with NCS^-, $C_5H_5Ru(CO)_2(NCS)$. IR spectra of the new compounds and mechanisms of their reactions are discussed.

INTRODUCTION

Recently we have been investigating the preparations and reactions of different transition metal carbonyl cations, $[Mn(CO)_5NH_2R]^+$[1], $[Re(CO)_5NH_2R]^+$[2], and $[C_5H_5Fe(CO)_3]^+$[3,4]. It has been found that they react with amines to form carbamoyl complexes, *e.g.*[3]:

$$C_5H_5Fe(CO)_3^+ + 2\ NH_2CH_3 \rightarrow C_5H_5Fe(CO)_2(CONHCH_3) + CH_3NH_3^+$$

The latter two cations also react with hydrazine or N_3^- to produce an isocyanate complex[4]:

$$C_5H_5Fe(CO)_3^+ + 2\ NH_2NH_2 \rightarrow C_5H_5Fe(CO)_2(NCO) + NH_3 + NH_2NH_3^+$$
$$C_5H_5Fe(CO)_3^+ + N_3^- \rightarrow C_5H_5Fe(CO)_2(NCO) + N_2$$

In the present paper we wish to report a convenient synthesis of $C_5H_5Ru(CO)_3^+$ from $C_5H_5Ru(CO)_2Cl$ and the results of studies of the reactions of $C_5H_5Ru(CO)_3^+$ with amines, hydrazines, N_3^-, NCS^-, I^-, Cl^-, and OCH_3^-.

RESULTS AND DISCUSSION

Preparations of $C_5H_5Fe(CO)_3^+$ and $C_5H_5Ru(CO)_3^+$

The previous syntheses[5-8] of $C_5H_5M(CO)_3^+$ (M=Fe or Ru) from C_5H_5M-

$(CO)_2Cl$ have all used high pressures of carbon monoxide, *i.e.*, from 90 to 360 atm. We have found that these high pressures are unnecessary, and one needs only to bubble carbon monoxide through a mixture of $C_5H_5M(CO)_2Cl$ and anhydrous $AlCl_3$ in benzene at an elevated temperature (40–80°). Besides the advantage of atmospheric pressure, the time of the reaction is shortened from 48 h to 20 min for the ruthenium cation and from 16 h to 3 h for the iron cation.

Another route to $C_5H_5Ru(CO)_3^+$ is through the anion[9] $C_5H_5Ru(CO)_2^-$. This anion can be reacted with methyl chloroformate, $ClCOOCH_3$, to yield the methoxycarbonyl complex $C_5H_5Ru(CO)_2COOCH_3$ which with HCl gives the cation $C_5H_5Ru(CO)_3^+$. This synthesis is similar to that recently reported for the analogous iron complex[3]. The methoxycarbonyl complex can also be prepared by reacting $C_5H_5Ru(CO)_3^+$ with $NaOCH_3$ in CH_3OH.

Reactions of $C_5H_5Ru(CO)_3^+$

Upon bubbling CH_3NH_2 into a mixture of $C_5H_5Ru(CO)_3^+$ in diethyl ether, rapid formation of the carbamoyl complex $C_5H_5Ru(CO)_2(CONHCH_3)$ occurs:

$$C_5H_5Ru(CO)_3^+ + 2\,CH_3NH_2 \rightarrow C_5H_5Ru(CO)_2(CONHCH_3) + CH_3NH_3^+ \quad (1)$$

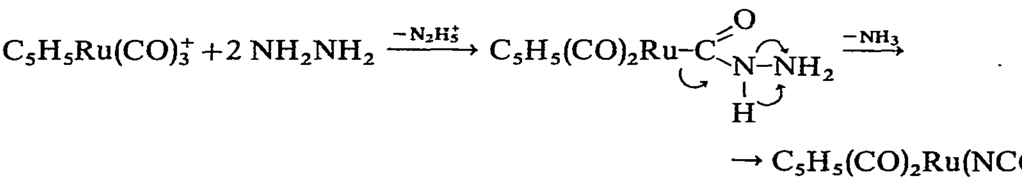
As in previous cases with other cations $C_5H_5Fe(CO)_3^+$[3], $[Mn(CO)_5(NH_2CH_3)]^+$[1], and $[Re(CO)_5(NH_2CH_3)]^+$[2], the reaction is presumed to proceed by nucleophilic attack of the amine on a terminal carbonyl ligand with loss of a proton to another amine molecule to give the two products, $C_5H_5Ru(CO)_2(CONHCH_3)$ and $CH_3NH_3^+$. Similar attack by stronger nucleophiles such as C_6H_5Li and C_6F_5Li on $C_5H_5Fe(CO)_3^+$ has also been observed[10].

Other primary aliphatic amines also react with $C_5H_5Ru(CO)_3^+$ to give carbamoyl derivatives (see Table). Aniline, however, does not react under the same conditions.

If gaseous HCl is bubbled into an ether solution of the carbamoyl complex, the cation is regenerated.

$$C_5H_5Ru(CO)_2(CONHCH_3) + 2\,HCl \rightarrow [C_5H_5Ru(CO)_3]^+Cl^- + CH_3NH_3^+Cl^- \quad (2)$$

Previous work[4] showed that $C_5H_5Fe(CO)_3^+$ reacts with hydrazine, NH_2NH_2, to initially form a carbazoyl intermediate $C_5H_5Fe(CO)_2(CONHNH_2)$ which then goes on to give the final isocyanate product $C_5H_5Fe(CO)_2(NCO)$. An analogous reaction occurs with the ruthenium cation; a carbazoyl intermediate is presumably formed by nucleophilic attack of the hydrazine on a carbonyl carbon atom:



$$C_5H_5Ru(CO)_3^+ + 2\,NH_2NH_2 \xrightarrow{-N_2H_5^+} C_5H_5(CO)_2Ru{-}C(=O){-}N(H){-}NH_2 \xrightarrow{-NH_3} C_5H_5(CO)_2Ru(NCO) \quad (3)$$

The carbazoyl derivative is not stable and is converted to the final $C_5H_5Ru(CO)_2$-(NCO) product presumably by migration of a proton on the nitrogen atom bound to the carbon to the other nitrogen and release of NH_3. Migration of Ru from C to N completes the formation of the isocyanate complex.

The characterization of the carbazoyl intermediate is based on the similarity of its IR spectrum at 2030 s, 1961 s, and 1575 m cm^{-1} to that of the analogous iron compound (2023 s, 1967 s and 1588 m cm^{-1}) and also to that of the carbamoyl complex $C_5H_5Ru(CO)_2(CONHCH_3)$(2030 s, 1969 s and 1631 m cm^{-1}).

The mass spectrum of the carbazoyl intermediate shows substantial amounts of the isocyanate complex which is expected since the carbazoyl complex is thermally unstable and rearranges even in the solid state to the isocyanate product. Although a parent ion peak for $C_5H_5Ru(CO)_2(CONHNH_2)$ was not observed, the spectrum (70 eV) showed peaks for $C_5H_5Ru(CO)_3^+$ and $C_5H_5Ru(CO)_2^+$ which may be attributed to the intermediate since these ions are not present in the 70 eV spectrum of the isocyanate complex. That these two peaks may be attributed to the $C_5H_5Ru(CO)_2$-$(CONHNH_2)$ complex is supported by the observation of the same peaks in the 70 eV spectrum of $C_5H_5Ru(CO)_2(CONHCH_3)$. In both cases cleavage of the $-NHNH_2$ or $-NHCH_3$ groups presumably occurs.

Similar reactions occur with methyl substituted hydrazines. Carbazoyl complexes are initially formed and rearrangement occurs to give the isocyanate:

$$\begin{aligned} &C_5H_5Ru(CO)_3^+ + 2\,(CH_3)_2NNH_2 \rightarrow \\ &\qquad C_5H_5Ru(CO)_2[CONHN(CH_3)_2] + (CH_3)_2NNH_3^+ \\ &\qquad \downarrow \\ &\qquad C_5H_5Ru(CO)_2(NCO) + (CH_3)_2NH \end{aligned} \tag{4}$$

Based on the results[4] of the reactions of the iron cation with these two hydrazines and 1,2-dimethylhydrazine, $CH_3NHNHCH_3$, it is proposed that the nitrogen atom that attacks the carbonyl is that one which is not methyl substituted. Thus the carbazoyl intermediates for CH_3NHNH_2 and $NH_2N(CH_3)_2$ are $C_5H_5Ru(CO)_2$-$(CONHNHCH_3)$ and $C_5H_5Ru(CO)_2[CONHN(CH_3)_2]$.

The formation of the carbazoyl intermediate is rapid for all hydrazines; the reaction of the intermediate to give the isocyanate product is much slower, and the rate qualitatively decreases with the hydrazine in the following order: NH_2N-$(CH_3)_2 > NH_2NHCH_3 > NH_2NH_2$. This is the same order of reactivity noted in the reaction of the hydrazines with $C_5H_5Fe(CO)_3^+$ (ref. 4) and $Re(CO)_5(NH_2CH_3)^+$ (ref. 2).

The isocyanate can also be prepared by the rapid reaction of N_3^- with $C_5H_5Ru(CO)_3^+$:

$$C_5H_5Ru(CO)_3^+ + N_3^- \rightarrow [C_5H_5Ru(CO)_2(CON_3)] \rightarrow C_5H_5Ru(CO)_2NCO + N_2 \tag{5}$$

This reaction presumably proceeds in a similar manner to that of the hydrazines. Although there is no evidence for its presence, an intermediate of structure $C_5H_5Ru(CO)_2(CON_3)$ is postulated as being initially formed[11]. This then loses a molecule of nitrogen and upon rearrangement, the isocyanate is formed. This latter reaction is analogous to the Curtius reaction in organic chemistry. The 70 eV mass spectrum of the isocyanate complex shows the successive loss of three CO groups with the $C_5H_5RuN^+$ ion giving the most intense peak in the spectrum. This peak supports the assignment of N-bonding of the NCO^- ligand to the metal.

The cation reacts with KNCS to form $C_5H_5Ru(CO)_2(NCS)$ in a similar manner to that of the iron. The presence of a very weak band at 826 cm^{-1} and the absence of one around 700 cm^{-1} in the IR spectrum indicates that the NCS^- ligand is N-bonded to the ruthenium[12]. The mass spectrum unfortunately does not provide a peak for either $C_5H_5RuN^+$ or $C_5H_5RuS^+$. Since at 16 eV the only peaks are $C_5H_5Ru(CO)_2(NCS)^+$, $C_5H_5Ru(CO)(NCS)^+$, and $C_5H_5Ru(NCS)^+$, it appears that the $-NCS$ ligand is held more tightly to the metal than the carbonyls.

The reactions of the cation with the halides Cl^- and I^- to give $C_5H_5Ru(CO)_2X$ are very much slower than observed for the analogous iron preparations. The product isolated from the I^- reaction had a melting point of 121–122°. This is higher than the value of 103–105° reported by Wilkinson *et al.*[13]. The mass spectrum run at 70 eV supported the structure $C_5H_5Ru(CO)_2I$ and also indicated that the I^- ligand is held more strongly than the carbonyl groups.

IR spectra and Ru–CONHR and Ru–COOCH₃ bonding

The unusually low terminal C≡O stretching frequencies of the carbamoyl, $C_5H_5Ru(CO)_2(CONHCH_3)$, 2030 and 1969 cm^{-1}, and of the methoxycarbonyl, $C_5H_5Ru(CO)_2(COOCH_3)$, 2047 and 1988 cm^{-1}, complexes as compared to $C_5H_5Ru(CO)_2Cl$, 2056 and 2008 cm^{-1}, suggests that these groups place a higher electron density on the ruthenium than does the chlorine. This could presumably result from these groups being either better σ- or π-donors than Cl. One treatment[14] suggests that Cl is a rather good π-donor in $Mn(CO)_5Cl$. Since it seems unlikely that either the carbamoyl or the methoxycarbonyl group is a better π-donor than Cl the decrease

TABLE 1

CARBONYL STRETCHING FREQUENCIES OF Ru AND Fe DERIVATIVES OF THE TYPE $C_5H_5M(CO)_2X$

Complex	$\nu(CO)$ (cm^{-1})		
	M=Ru	M=Fe	Ref. for M=Fe
$[C_5H_5M(CO)_2]_2$	2021 m, 2011 m, 1972 vs, 1964 s, 1943 vs, 1794 $s^{c,f}$	2005 s, 1961 vs, 1794 vs^{f}	20
$[C_5H_5M(CO)_3][B(C_6H_5)_4]$	2125 vs, 2075 vs, 2066 $vs^{d,g}$	2120 vs, 2070 vs^{g}	6
$C_5H_5M(CO)_2Cl$	2056 vs, 2008 $vs^{d,h}$	2050 vs, 2010 vs^{j}	21
$C_5H_5M(CO)_2I$	2055 vs, 2007 vs, 1976 $w^{e,k}$	2044 vs, 2000 vs^{k}	22
$C_5H_5M(CO)_2(NCO)^a$	2058 vs, 2008 vs^{j}	2066 vs, 2020 vs^{j}	4
$C_5H_5M(CO)_2(NCS)^b$	2053 vs, 2008 vs^{l}	2075 s, 2033 s^{h}	4
$C_5H_5M(CO)_2(COOCH_3)$	2047 s, 1988 m, 1660 m^{h}	2046 s, 1995 s, 1665 s^{h}	23
$C_5H_5M(CO)_2(CONHCH_3)$	2030 s, 1969 s, 1631 m^{l}	2015 s, 1972 s, 1625 m^{l}	3
$C_5H_5M(CO)_2[CONHCH(CH_3)_2]$	2026 s, 1965 s, 1628 m^{h}	2015 s, 1965 s, 1620 m^{l}	3
$C_5H_5M(CO)_2[CONH(CH_2)_3CH_3]$	2026 s, 1965 s, 1626 m^{h}	2019 s, 1968 s, 1622 m^{l}	3
$C_5H_5M(CO)_2(CONHC_6H_{11})$	2024 s, 1964 s, 1621 m^{l}		
$C_5H_5M(CO)_2(CONHNH_2)$	2030 s, 1961 s, 1575 m^{m}	2023 s, 1967 s, 1588 m^{m}	4
$C_5H_5M(CO)_2(CONHNHCH_3)$	2033 s, 1969 s, 1595 m^{m}	2025 s, 1969 s, 1592 m^{m}	4
$C_5H_5M(CO)_2[CONHN(CH_3)_2]$	2033 s, 1969 $s^{m,n}$		

[a] Asymmetric N=C=O stretching frequencies at 2232 cm^{-1} m and 2252 cm^{-1} m in $CHCl_3$ for Ru and Fe, respectively. [b] Asymmetric N=C=S stretching frequencies at 2123 cm^{-1} m (methylcyclohexane) and 2123 cm^{-1} m ($CHCl_3$) and symmetric stretching frequencies at 826 cm^{-1} vw (CS_2) and 826 cm^{-1} w (KBr) for Ru and Fe, respectively. [c] Ref. 20. [d] Ref. 8. [e] Ref. 13. [f] Octane. [g] Nujol mull. [h] Cyclohexane. [j] $CHCl_3$. [k] CS_2. [l] Methylcyclohexane. [m] CH_2Cl_2. [n] Solution not concentrated enough to unequivocally identify carbazoyl carbonyl.

in the terminal C≡O stretching frequencies is most likely due to the stronger σ-donor strength of $-CONHCH_3$ or $-COOCH_3$ as compared to Cl.

The $\rangle$C=O stretching frequency in the carbamoyl group of $C_5H_5Ru(CO)_2(CONHCH_3)$, 1631 cm^{-1}, is lower than that of the methoxycarbonyl carbonyl in $C_5H_5Ru(CO)_2(COOCH_3)$, 1660 cm^{-1}. This is also observed[15] in simple organic amides and esters as, for example, $CH_3CONHCH_3$ (1700 cm^{-1}) and CH_3COOCH_3 (1751 cm^{-1}). The lower amide frequency is usually attributed to π-bonding from the lone electron pair on nitrogen to the π^* orbital of the carbonyl group; this decreases the strength and stretching frequency of the $\rangle$C=O bond. This type of π-bonding presumably also accounts for the lower carbonyl stretching frequency observed in the carbamoyl metal complexes as compared to the methoxycarbonyl derivatives.

Sigma bonding probably dominates the interaction between Ru and the $-CONHCH_3$ group. In the one known crystal structure[16] of a complex *cis*-$Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ containing a carbamoyl ligand, the Mn–$CONHCH_3$ bond length is unusually long (2.07 Å). This compares with manganese–terminal carbonyl bond lengths of 1.85 Å in the same molecule. The Mn–$CONHCH_3$ bond is also longer than the few other known Mn–C bonds. In $Mn(CF{=}CFH)(CO)_5$, the Mn–C bond[17] to the olefinic carbon is only 1.95 Å, and in $[C_5H_5Mn(COC_6H_5)(CO)_2]^-$ the Mn–C bond[18] to the benzoyl carbon is also 1.95 Å. Thus it appears that there is relatively little π-bonding between Mn and the carbamoyl group. Unfortunately there are no Mn–C bond lengths available in the literature which can be assigned unequivocally as a single bond distance.

EXPERIMENTAL

The $RuCl_3 \cdot xH_2O$ was purchased from Engelhard Industries. The hydrazines, 97% N_2H_4, NH_2NHCH_3, and $NH_2N(CH_3)_2$ were used as obtained from commercial sources. Tetrahydrofuran (THF) was dried over CaH_2 and saturated with nitrogen before use. All other solvents and materials were reagent grade with the exception of pentane which was practical grade.

IR spectra were recorded on a Beckman IR-8 spectrophotometer using a polystyrene standard. Mass spectra were obtained on an Atlas CH-4 mass spectrometer. Melting points are uncorrected. All the reactions described were run in a nitrogen atmosphere, and solvents were deaerated with nitrogen before use as routine precautionary measures.

Preparation of $[C_5H_5Ru(CO)_2]_2$ *and* $C_5H_5Ru(CO)_2Cl$

$[C_5H_5Ru(CO)_2]_2$[9] and $C_5H_5Ru(CO)_2Cl$[8] were prepared from $RuCl_3 \cdot xH_2O$ by Stone's method. However the syntheses were not found to be straightforward. In the preparation of $[Ru(CO)_3Cl_2]_2$ the product frequently not only contained the desired bands at 2143, 2079, and 2062 cm^{-1} but also a strong broad band at 2018 cm^{-1}. We found that yields of $[C_5H_5Ru(CO)_2]_2$ formed from $[Ru(CO)_3Cl_2]_2$ were at a maximum when the intensity of the band at 2018 cm^{-1} was at a minimum. This occurred with reaction times of about 40 h, CO pressures of ~300 p.s.i., temperatures in the range 65–70°, and by using reagent grade CH_3OH that was not dried further. Still it was very infrequent when orange crystals were isolated in the preparation of $[C_5H_5Ru(CO)_2]_2$. Usually a brown solid was used as starting material in the next step, the preparation[8] of $C_5H_5Ru(CO)_2Cl$.

Preparation of $C_5H_5Ru(CO)_3^+$

Method 1. Reaction of $C_5H_5Ru(CO)_2Cl$ with CO. To a mixture of 0.45 g (1.8 mmoles) of $C_5H_5Ru(CO)_2Cl$ in 40 ml of carbon monoxide-saturated benzene at 40° was added 0.94 g (7 mmoles) of $AlCl_3$ (anhydrous) under a CO atmosphere. A stream of CO (1 atm) was bubbled through the solution for the length of the reaction which was terminated when the solution became very light yellow or colorless (~1 h). The benzene was pipetted off, and the precipitate dried by a stream of CO. Approximately 10 ml of ice-cold water was added, the mixture quickly filtered, and an aqueous solution of 0.29 g (1.8 mmoles) of NH_4PF_6 added to the filtrate. The precipitate which formed was filtered off, washed with 5 ml of ice-cold water, and reprecipitated from an acetone solution by the dropwise addition of diethyl ether giving a 60% yield of white $[C_5H_5Ru(CO)_3]PF_6$. It was identified by its IR spectrum (see Table 1). The preparation of the analogous iron cation $[C_5H_5Fe(CO)_3]PF_6$ was done in the same way except the initial solution was refluxed, and the time was approximately 3 h. The yield was 42%, and it also was identified by its IR spectrum (see Table 1).

Method 2. Reaction of $[C_5H_5Ru(CO)_2]^-$ with $ClCOOCH_3$. To 12 ml of a 1% sodium amalgam was added 0.44 g (1 mmole) of $[C_5H_5Ru(CO)_2]_2$ in 50 ml of THF in a reaction vessel described by King[19]. After 5 h the amalgam was removed through the stopcock at the bottom of the flask, the mixture washed with 5 ml more of mercury which was also removed, and 0.15 ml (2 mmoles) of $ClCOOCH_3$ in 10 ml of THF added dropwise. After stirring for 20 h, the mixture was filtered through Celite Filter Aid, the solvent removed from the filtrate under vacuum, and the residue extracted with dry benzene. An IR spectrum of the solid after evaporating the benzene indicated that both the desired compound $C_5H_5Ru(CO)_2(COOCH_3)$, identified by the similarity of its spectrum to that of the analogous iron compound (see Table 1), and $[C_5H_5Ru(CO)_2]_2$ were present. Gaseous HCl was bubbled through the benzene solution for 10 min giving a brown oil. An acetone solution of $NaB(C_6H_5)_4$ was added to the benzene-oil mixture. Upon partial evaporation of the acetone, the desired product precipitated. It was identified by its IR spectrum (see Table 1).

Preparation of $C_5H_5Ru(CO)_2(CONHR)$

Monomethyl amine was bubbled into a mixture of 0.4 g (1 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 50 ml of diethyl ether. After 20 min an IR spectrum indicated that no starting material was left. The solvent was removed, and the resulting oil was extracted with $CHCl_3$. After filtering and reducing the volume of the filtrate, pentane was slowly added, and during the next 15 min white crystals slowly precipitated giving an 18% yield of $C_5H_5Ru(CO)_2(CONHCH_3)$ m.p. 105–107° (decompn.). The product slowly decomposes under vacuum in the dark over a period of weeks. (Found: C, 38.47; H, 3.52; N, 5.38. $C_9H_9NO_3Ru$ calcd.: C, 38.51; H, 3.24; N, 5.00%)

A mass spectrum run at 70 eV showed the following major ions and their intensities: $C_5H_5Ru(CO)_2(CONHCH_3)^+$, 17; $C_5H_5Ru(CO)(CONHCH_3)^+$, 17; $C_5H_5Ru(CO)_3^+$, 33; $C_5H_5Ru(CONHCH_3)^+$, 15; $C_5H_5Ru(CO)_2^+$, 15; $C_5H_5Ru(CO)^+$, 89; $C_5H_5Ru^+$, 100; and Ru^+, 9. The mass spectrum at 16 eV gives only the following major ions together with their relative intensities: $C_5H_5Ru(CO)_2(CONHCH_3)^+$, 60; $C_5H_5Ru(CO)(CONHCH_3)^+$, 100; and $C_5H_5Ru(CONHCH_3)^+$, 30.

Other amines that give similar products are $(CH_3)_2CHNH_2$, $CH_3(CH_2)_3NH_2$, and $C_6H_{11}NH_2$. These reactions were run using a ten-fold excess of amine. The products were identified by their IR spectra (see Table 1). Aniline was also tried using the same conditions as above but no reaction took place. Upon refluxing in acetone for periods longer than 10 h, a reaction occurred, but no attempt was made to isolate and characterize the products.

Secondary amines such as $(C_2H_5)_2NH$, $(CH_3)_2NH$, piperidine, and pyrrolidine were also tried. In all cases, two products were formed, one probably being $C_5H_5Ru(CO)_2(CONR_2)$. However, none of the products was isolated or characterized.

Reaction of $C_5H_5Ru(CO)_2(CONHCH_3)$ with HCl(g)

Gaseous HCl was bubbled into a solution of $C_5H_5Ru(CO)_2(CONHCH_3)$ in 20 ml of diethyl ether; after 5 min an off-white precipitate appeared. After 10 min, the ether was decanted off; an IR spectrum of the product indicated that it was $[C_5H_5Ru(CO)_3]^+$.

Preparation of $C_5H_5Ru(CO)_2(CONHNH_2)$

To a mixture of 0.395 g (1 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 30 ml of CH_2Cl_2 was added 72 μl (2.25 mmoles) of NH_2NH_2. After 10 min the $[NH_2NH_3]^+PF_6^-$ was filtered off, the volume of the filtrate reduced to ~5 ml, and hexane added to leave a white precipitate of $C_5H_5Ru(CO)_2(CONHNH_2)$ which was washed with pentane and dried under high vacuum. A melting point was attempted but the product was thermally unstable and rearranged to the isocyanate complex $C_5H_5Ru(CO)_2(NCO)$ at ~45°. In fact this same rearrangement occurred under vacuum at room temperature over a period of days. A mass spectrum of the complex was run at 70 eV. The major ions and their relative intensities follow: $C_5H_5Ru(CO)_3^+$, 21; $C_5H_5Ru(CO)_2^+$, 10; $C_5H_5Ru(CO)^+$, 21; $C_5H_5Ru(CO)_2(NCO)^+$, 51; $C_5H_5Ru(CO)(NCO)^+$, 42; $C_5H_5Ru(NCO)^+$, 37; $C_5H_5RuN^+$, 100; $C_5H_5Ru^+$, 42; and Ru^+, 20.

Preparation of $C_5H_5Ru(CO)_2(NCO)$

Method 1. Reaction of N_3^- with $C_5H_5Ru(CO)_3^+$. A solution of 0.041 g (0.63 mmole) of NaN_3 in 2 ml of H_2O was added to a solution of 0.23 g (0.58 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 40 ml of acetone. The solution turned immediately yellow, and a gas (N_2) was evolved. After 15 min the acetone was removed on a water aspirator. Twenty ml of water was added, and this solution was extracted with two 10 ml portions of $CHCl_3$. The volume was reduced to 2 ml, and the green $C_5H_5Ru(CO)_2(NCO)$ was precipitated with pentane giving a 65% yield. It can be recrystallized from $CHCl_3$ by the dropwise addition of diethyl ether, m.p. 145–150° (decompn.). (Found: C, 36.29; H, 2.50; N, 5.70. $C_8H_5NO_3Ru$ calcd.: C, 36.36; H, 1.91; N, 5.30%).

The mass spectrum run at 70 eV showed the following peaks and their relative intensities: $C_5H_5Ru(CO)_2(NCO)^+$, 33; $C_5H_5Ru(CO)(NCO)^+$, 29; $C_5H_5Ru(NCO)^+$, 21; $C_5H_5RuN^+$, 100; $C_5H_5Ru^+$, 14; and Ru^+, 6.

Method 2. Reaction of NH_2NH_2 with $C_5H_5Ru(CO)_3^+$. To a mixture of 0.02 g (0.05 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 15 ml of CH_2Cl_2 was added 3.6 μl (0.55 mmole) of NH_2NH_2 at room temperature. The solution slowly turned yellow.

After 20 h an IR spectrum indicated that $C_5H_5Ru(CO)_2(NCO)$ had formed but that a substantial amount of the intermediate $C_5H_5Ru(CO)_2(CONHNH_2)$ was also still present.

Method 3. Reaction of NH_2NHCH_3 with $C_5H_5Ru(CO)_3^+$. To a mixture of 0.0017 g (0.003 mmole) of $[C_5H_5Ru(CO)_3][B(C_6H_5)_4]$ in 15 ml of CH_2Cl_2 was added 3 μl (~0.07 mmole) of NH_2NHCH_3. After 4 h an IR spectrum indicated that $C_5H_5Ru(CO)_2(NCO)$ had formed but that also a very small amount of the intermediate $C_5H_5Ru(CO)_2(CONHNHCH_3)$ identified by the similarity of its IR spectrum to that of the analogous iron compound (see Table 1) was still present. Phenylhydrazine was also tried but no reaction took place at room temperature. At 40° over a period of days, $NH_2NH(C_6H_5)$ did react with the cation, but the product was neither isolated nor characterized.

Method 4. Reaction of $NH_2N(CH_3)_2$ with $C_5H_5Ru(CO)_3^+$. To a mixture of 0.02 g (0.05 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 15 ml of CH_2Cl_2 was added 4.1 μl (0.055 mmole) of $NH_2N(CH_3)_2$. An IR spectrum after 5 min showed that the intermediate $C_5H_5Ru(CO)_2[CONHN(CH_3)_2]$, identified by the similarity of its spectrum to that of the other carbazoyl compounds (see Table 1) was present along with the isocyanate complex. After 45 min the only carbonyl product present was $C_5H_5Ru(CO)_2(NCO)$.

Preparation of $C_5H_5Ru(CO)_2(COOCH_3)$

To a solution of 0.02 g (0.05 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 20 ml of CH_3OH (dried over $MgSO_4$) was added 0.027 g (0.5 mmole) of $NaOCH_3$. After 1 h the solvent was removed and an IR spectrum indicated that $C_5H_5Ru(CO)_2(COOCH_3)$ and $[C_5H_5Ru(CO)_2]_2$ were present. The former was identified by the similarity of its IR spectrum to that of the analogous iron complex and by the identity of its spectrum to that of the analogous iron complex and by the identity of its spectrum with that of the product prepared from $C_5H_5Ru(CO)_2^-$ and $ClCOOCH_3$ (see Table). The methoxycarbonyl complex is very air-sensitive.

Preparation of $C_5H_5Ru(CO)_2(NCS)$

A solution of 0.7 g (7 mmole) of KNCS in 2 ml of H_2O was added to 0.4 g (1 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 50 ml of acetone. The solution immediately turned yellow, and after 4 h the solvent was removed. The residue was extracted with 25 ml of $CHCl_3$, the volume reduced to ~5 ml, hexane added, and the temperature lowered to −78° precipitating the product $C_5H_5Ru(CO)_2(NCS)$ m.p. 54–56°. (Found: C, 34.68; H, 1.80; N, 4.95. $C_8H_5NO_2RuS$ calcd.: C, 34.16; H, 1.79; N, 4.98%.)

The mass spectrum at 70 eV gave the following peaks with their relative intensities: $C_5H_5Ru(CO)_2(NCS)^+$, 27; $C_5H_5Ru(CO)NCS^+$, 19; $C_5H_5RuNCS^+$, 42; $C_5H_5Ru^+$, 100 and Ru^+, 22.

Preparation of $C_5H_5Ru(CO)_2X$

A solution of 0.41 g (2.5 mmoles) of KI in 1 ml of H_2O was added to a solution of 0.1 g (0.25 mmole) of $[C_5H_5Ru(CO)_3]PF_6$ in 20 ml of acetone. After refluxing for 18 h, the solution had turned yellow-orange. The solvent was removed and an orange product was sublimed at ~100° (~1 mm) to give a 60% yield of $C_5H_5Ru(CO)_2I$, m.p. 121–122° (see Text). (Found: C, 23.71; H, 1.43; I, 35.19. $C_7H_5IO_2Ru$

calcd.: C, 24.04; H, 1.44; I, 36.35%.)

The mass spectrum supported this structure with peaks and relative intensities for $C_5H_5Ru(CO)_2I^+$, 83; $C_5H_5Ru(CO)I^+$, 54; $C_5H_5RuI^+$, 33; $C_5H_5Ru^+$, 100; and Ru^+, 8.

The chloride derivative can be prepared in the same manner using KCl, but the reaction time is longer. Both halide complexes can also be prepared by refluxing the cation $C_5H_5Ru(CO)_3^+$ with $R_4N^+X^-$ [$R=-(CH_2)_3CH_3$ for X=I and $R=-CH_2CH_3$ for X=Cl] in CH_2Cl_2. In CH_2Cl_2 the iodide reaction is slower than the chloride, and both are slower under these less vigorous conditions than in acetone/water solvent.

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