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FORMATION OF (η-R_5C_5)Ru(NO)X_2 BY THE NITROSYLATION OF (η-R_5C_5)Ru$(CO)_2$X UNDER UV IRRADIATION

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Summary

The ruthenium(II) complexes (η-R_5C_5)Ru$(CO)_2$X with R = H, CH_3 and X = Cl, Br, I undergo a facile reaction with nitric oxide under UV irradiation to afford ruthenium(IV) nitrosyl derivatives of the general type (η-R_5C_5)Ru(NO)X_2.

Introduction

Some attention has been given in the past to the study of cyclopentadienylnitrosyliron complexes. For instance, Brunner reported [1] the preparation of $[(\eta\text{-}C_5H_5)Fe(NO)]_2$ by the reaction of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ with NO in alkanes at 120°C. The oxidative cleavage of the cyclopentadienylnitrosyliron with iodine gives [2] $(\eta\text{-}C_5H_5)Fe(NO)I_2$, a product containing a four-valent iron atom. The preparation of $[(\eta\text{-}C_5H_5)Fe(CO)(NO)]_2$ and $(\eta\text{-}C_5H_5)Fe(CO)(NO)I$ by the nitrosylation (NO) of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ and $(\eta\text{-}C_5H_5)Fe(CO)_2I$, respectively, was claimed more recently by Pandey [3] to take place in benzene under mild conditions (25°C). The current study examines similar aspects of the chemistry of organoruthenium complexes.

Discussion

Attempts to prepare $[(\eta\text{-}C_5H_5)Ru(NO)]_2$ and $[(\eta\text{-}C_5H_5)Ru(CO)(NO)]_2$ by utilizing the above-mentioned procedures used for the preparation of the iron analogues failed to yield the desired products. Nevertheless, a general procedure for the preparation of four-valent ruthenium complexes of the type $(\eta\text{-}R_5C_5)Ru(NO)X_2$, which circumvents the need for $[(\eta\text{-}R_5C_5)Ru(NO)]_2$, was discovered. This procedure involves the reaction of $(\eta\text{-}R_5C_5)Ru(CO)_2X$, dissolved in benzene, with NO under UV irradiation at 35°C. Complexes of the type $(\eta\text{-}R_5C_5)Ru(NO)X_2$ with R = H, CH_3 and X = Cl, Br, I are formed by this procedure in yields of 30–45%. Selected data pertaining to the characterization of the new complexes are furnished in Tables 1 and 2.

TABLE 1

SELECTED DATA FOR THE NEW (η-R_5C_5)Ru(NO)X_2 DERIVATIVES

(η-R_5C_5)Ru(NO)X_2		Color	m.p. decomp (°C)	Yield (%)	Infrared (cm^{-1}) ν(NO)	^{1}H NMR C_5H_5(δ,ppm)
R	X					
H	Cl	Green	230–235	31	1809	6.31,s
H	Br	Green	180–185	35	1818	6.30,s
H	I	Black	230–240	32	1797	6.17,s
CH_3	Cl	Green	215–220	45	1768	
CH_3	Br	Green	205–210	35	1782	
CH_3	I	Black	255–260	30	1764	

[a] Range of extensive decomposition. [b] Taken in KBr pellet. [c] Obtained in acetone-d_6 solution, using TMS as calibrant.

The infrared spectra of the new ruthenium(IV) complexes show (Table 1) a very strong absorption in the region 1818–1764 cm^{-1} which is characteristic of a stretching frequency of a terminal nitrosyl group. A similar band at 1835 cm^{-1} was reported [2] for the related iron complex (η-C_5H_5)Fe(NO)I_2. The ^{1}H NMR spectra of the parent cyclopentadienyl complexes (η-C_5H_5)Ru(NO)X_2 consist of singlets at δ 6.31 (X = Cl), 6.30 (X = Br) and 6.17 (X = I) ppm. The spectroscopic and elemental composition data provided in Tables 1 and 2 are fully consistent with the formulation of the new complexes as (η-R_5C_5)Ru(NO)X_2 derivatives.

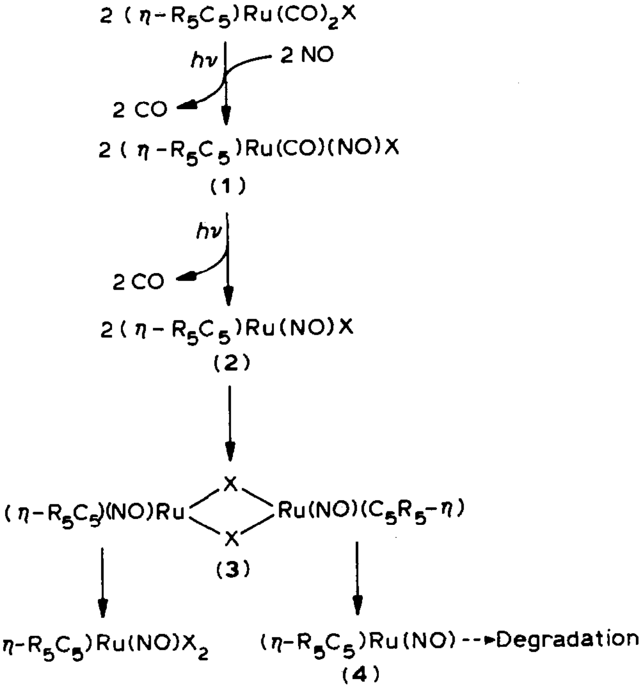
While the exact mechanistic details of the reaction under review are not known, the formation of the product must involve a multi-step process. A plausible sequence must include an initial step of an oxidative replacement of a carbonyl by nitrosyl to afford (η-R_5C_5)Ru(CO)(NO)X (**1**), by analogy with the formation of (η-C_5H_5)Fe(CO)(NO)I [3]. The decarbonylation of **1** to **2**, followed by a dimerization process would account for the formation of **3**, which then disproportionates to (η-R_5C_5)Ru(NO)X_2. A by-product of the type [(η-R_5C_5)Ru(NO)]$_2$, expected from the presumed disproportionation product **4**, was neither isolated nor detected. The absence of the dimer may be due to the degradation of its precursor **4**. The failure to

TABLE 2

ANALYTICAL DATA FOR THE NEW (η-R_5C_5)Ru(NO)X_2 DERIVATIVES[a]

(η-R_5C_5)Ru(NO)X_2		Analysis (Found(calcd.)(%))		
R	X	H	C	N
H	Cl	22.15 (22.48)	1.78 (1.87)	5.45 (5.24)
H	Br	16.95 (16.86)	1.63 (1.40)	4.05 (3.93)
H	I	13.65 (13.34)	1.14 (1.11)	3.31 (3.11)
CH_3	Cl	35.76 (35.60)	4.36 (4.45)	4.05 (4.15)
CH_3	Br	27.79 (28.18)	3.47 (3.52)	3.29 (3.28)
CH_3	I	23.52 (23.08)	2.65 (2.88)	2.53 (2.69)

obtain $[(\eta\text{-}R_5C_5)Ru(NO)]_2$ by the direct nitrosylation of $[(\eta\text{-}R_5C_5)Ru(CO)_2]_2$, suggests that its formation during the disproportionation proces is not significant. The disproportionation step in this process dictates a maximum yield of 50% for $(\eta\text{-}R_5C_5)Ru(NO)X_2$, and this requirement is consistent with the experimental yields (Table 1). The essential role of UV light in this reaction is believed to involve the decarbonylation steps. The labilizing effect of the light appears to require the presence of NO, since the irradiation of a benzene solution of $(\eta\text{-}R_5C_5)Ru(CO)_2X$ in the absence of NO does not result in any apparent reaction, such as the formation of a bridged complex of the type $[(\eta\text{-}R_5C_5)Ru(CO)X]_2$.



The reaction studied represents a facile synthetic route to ruthenium(IV) complexes of the type $(\eta\text{-}R_5C_5)Ru(NO)X_2$. The starting complexes $(\eta\text{-}R_5C_5)Ru(CO)_2X$ ($X = Cl$, Br, I) for this reaction are readily available in high yields by a simple recently reported experimental procedure [4]. The combination of readily available reactants and a fairly simple experimental procedure makes this an attractive route to a series of novel four-valent ruthenium complexes.

Experimental

The halides $(\eta\text{-}R_5C_5)Ru(CO)_2X$ ($X = Cl$, Br, I) were prepared from $[(\eta\text{-}R_5C_5)Ru(CO)_2]_2$ by the procedure described by Eisenstadt et al. [4]. Solvents were redistilled before use.

Melting-decomposition points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra, recorded on a Perkin–Elmer 467 grating IR spectrometer, were taken in KBr pellets. ^{1}H NMR spectra were obtained in acetone-d_6 on a Varian FT-80A spectrometer.

Synthesis of (η-C_5H_5)Ru(NO)Cl_2. A benzene solution (70 ml) of (η-C_5H_5)Ru(CO)$_2$Cl (0.1 g; 0.39 mmol) was degassed by reflux under nitrogen for 10 min. After being cooled to ambient temperature (25°C), the magnetically stirred solution was irradiated with an external UV lamp (Hanovia, 125W) while nitric oxide was passed through the mixture. The UV lamp was placed approximately 10 cm from the reaction flask and the heat generated during the irradiation caused the reaction mixture to warm to 35°C. After a period of 30 min, the reaction was stopped and the solvent removed under vacuum on a rotary evaporator. The dry product was dissolved in an acetone/hexane mixture and chromatographed on a silica gel column to afford some of the yellow starting material (η-C_5H_5)Ru(CO)$_2$Cl (0.005 g) and a green product, which was characterized as (η-C_5H_5)Ru(NO)Cl_2 (0.032 g), in 31% yield. The yield was based on the amount of the starting material consumed during the course of the reaction.

Synthesis of (η-R_5C_5)Ru(NO)X_2 (R = H; X = Br, I and R = CH_3; X = Cl, Br, I). These compounds were prepared by essentially the same procedure described for (η-C_5H_5)Ru(NO)Cl_2. Data for the new complexes are listed in Tables 1 and 2.

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