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Reactions of Alkali-Metal Derivatives of Metal Carbonyls. IX. Preparation and Properties of Allyl Derivatives of Cyclopentadienylruthenium Carbonyl*

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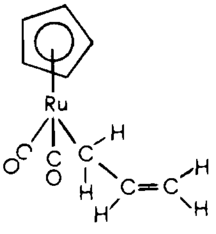
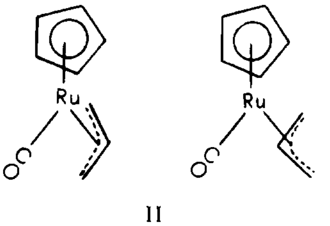
Reaction of $NaRu(CO)_2C_5H_5$ with excess allyl chloride gives the yellow liquid σ-allyl derivative (σ–C_3H_5)-$Ru(CO)_2C_5H_5$. Ultraviolet irradiation of this σ-allyl derivative in hexane solution results in decarbonylation to give the pale yellow crystalline π-allyl derivative (π–C_3H_5)$RuCOC_5H_5$. The proton n.m.r. and infrared spectra of solutions of this π-allyl derivative at 29° both indicate the presence of two stereoisomers in a $\sim$4:1 ratio. The mass spectra of various allyl derivatives of cyclopentadienylmetal carbonyls of molybdenum, ruthenium, and tungsten, are compared. The σ-allyl derivatives undergo decarbonylation in the mass spectrometer at $\sim$210° to give the corresponding π-allyl derivatives.

Introduction

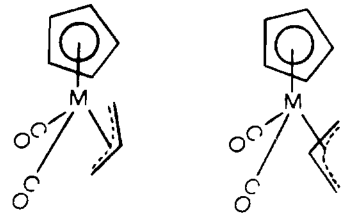
The discovery of the 16-electron[2] π-allyl rhodium complex[3] (π–C_3H_5)Rh(π–C_8H_{12}) analogous to the 18-electron π-cyclopentadienylrhodium complex[4] (π–C_5H_5)Rh(π–C_8H_{12}) suggested the possibility of preparing other 16-electron π-allyl derivatives of the *4d* transition metals analogous to stable 18-electron π-cyclopentadienyl derivatives. In this connection the stability of ruthenocene[5] $(C_5H_5)_2Ru$ suggested the possible existence of a stable π-cyclopentadienyl-π-allylruthenium $C_3H_5RuC_5H_5$. This paper describes attempts to prepare this compound by decarbonylation of the σ-allyl derivative (σ–C_3H_5)$Ru(CO)_2C_5H_5$ (I). However, none of these decarbonylation attempts yielded the carbonyl-free derivative $C_3H_5RuC_5H_5$; instead the monocarbonyl (π–C_3H_5)$RuCOC_5H_5$ (II) analogous to a known[6] iron complex was always obtained. Nevertheless, the monocarbonyl derivative II was of interest for exhibiting in solution both infrared and proton n.m.r. spectra indicating the presence of two geometrical isomers which were not interconverting at room temperature. This contrasts with the situation in the molybdenum derivative (π–C_3H_5)-$Mo(CO)_2C_5H_5$ (III: M = Mo) which likewise exhibits two geometrical isomers in solution which can be shown by a temperature dependence of the n.m.r. spectrum to be interconverting at temperatures above 0°.[7]



I



II



III

Experimental Section

Microanalyses were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken on a Perkin-Elmer Model 621 spectrometer in the indicated media. The proton n.m.r. spectra were taken in $CDCl_3$ solution on Varian A–60 and HA–100 spectrometers. The $[C_5H_5Ru(CO)_2]_2$ starting material was prepared by reaction of ruthenium carbonyl chloride[8] with sodium cyclopentadienide in boiling tetrahydrofuran similar to the published procedure.[9] A nitrogen atmosphere was routinely provided for the following three operations: (a) Carrying out reactions; (b) Handling filtered solutions of organometallic compounds; (c) Admitting to evacuated vessels.

(*) For part VIII of this series see reference 1.

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Preparation of $(\sigma{-}C_3H_5)Ru(CO)_2C_5H_5$. A solution of 1.0 g (2.25 mmoles) of $[C_5H_5Ru(CO)_2]_2$ in 50 ml of redistilled tetrahydrofuran was reduced to $NaRu(CO)_2C_5H_5$ by stirring with excess 1% sodium amalgam for several hours.[9] After removing excess amalgam, the sodium salt solution was stirred for 2 hr with excess (~4 ml) of allyl chloride. Solvent was then removed at ~25°/40 mm. A filtered solution of the residue in 30-60° petroleum ether was chromatographed on a 2×40 cm alumina column (70 g of alumina). The first pale yellow band was eluted with petroleum ether. Evaporation of the filtered eluate gave 0.35 g (30% yield) of yellow liquid $(\sigma{-}C_3H_5)Ru(CO)_2C_5H_5$. Further development and elution of the chromatogram with petroleum ether gave a second yellow band from which $[C_5H_5Ru(CO)_2]_2$ was isolated. *Anal.* Calcd. for $C_{10}H_{10}O_2Ru$: C, 45.6; H, 3.8; O, 12.2. Found: C, 46.7; H, 4.0; O, 11.4. Finally a small amount of the mercury derivative $Hg[Ru(CO)_2C_5H_5]_2$ was eluted from the column with diethyl ether. The products $[C_5H_5Ru(CO)_2]_2$ and $Hg[Ru(CO)_2C_5H_5]_2$ were identified by comparison of their infrared spectra with those of authentic samples.

Infrared Spectrum (neat liquid unless otherwise indicated). ν(CH) frequencies at 3105 (w), 3065 (m), 3015 (w), 2975 (sh), 2951 (m), 2905 (m), 2850 (w), and 2815 (sh) cm^{-1}; ν(CO) frequencies (cyclohexane solution) at 2015 (vs) and 1970 (vs) cm^{-1}; ν(C=C) frequency at 1610 (m) cm^{-1}; other bands at 1435 (m), 1425 (m), 1411 (m), 1395 (w), 1348 (w), 1287 (w), 1255 (w), 1190 (m), 1085 (m), 1050 (m), 1030 (m), 1004 (m), 990 (m), 909 (w), 867 (m), 801 (s), 717 (m), and 664 (m) cm^{-1}.

Preparation of $(\pi{-}C_3H_5)RuCOC_5H_5$. A solution of 0.4 g (1.52 mmoles) of $(\sigma{-}C_3H_5)Ru(CO)_2C_5H_5$ in 40 ml of hexane was irradiated for 8 hr in a glass flask with a General Electric GBL-100C ultraviolet lamp placed 20 cm from the flask. Solvent was then removed from the reaction mixture at ~25°/40 mm. A petroleum ether solution of the residue was chromatographed on a alumina column. The chromatogram was developed with petroleum ether. The first yellow band was eluted with petroleum ether. Evaporation of the filtered eluate gave a solid which was purified by low temperature crystallization from pentane to give 0.11 g (31% yield) of pale yellow $(\pi{-}C_3H_5)RuCOC_5H_5$, m.p. 44-45°. *Anal.* Calcd. for $C_9H_{10}ORu$: C, 45.9; H, 4.2; O, 6.8. Found: C, 46.0; H, 4.2; O, 7.1. Petroleum ether elution of the weak yellow band remaining on the column after removal of the π–allyl derivative followed by evaporation of the filtered eluate gave 0.03 g (9% yield) of $[C_5H_5Ru(CO)_2]_2$ identified by its infrared spectrum.

Infrared Spectrum (neat liquid unless otherwise indicate). ν(CH) frequencies at 3064 (w), 3000 (w), 2928 (w), and 2850 (vw) cm^{-1}; ν(CO) frequencies (cyclohexane solution) at 1958 (vs) and 1936 (s) cm^{-1}; other bands at 1470 (vw), 1461 (w), 1419 (w), 1408 (w), 1208 (vw), 1195 (vw), 1102 (w), 1055 (vw), 1005 (m), 995 (w), 958 (vw), 940 (vw), 910 (w), 850 (vw), and 808 (s) cm^{-1}.

Preparation of $(\sigma{-}C_3H_5)Re(CO)_5$. A tetrahydrofuran solution containing 2.0 g (3.07 mmoles) of $Re_2(CO)_{10}$ was reduced to $NaRe(CO)_5$ by stirring with excess ~1% sodium amalgam for 5 hr. After removing the excess amalgam the $NaRe(CO)_5$ was stirred with excess allyl chloride for 3 hr. Solvent was then removed at ~25°/40 mm. A pentane solution of the residue was chromatographed on a 2×35 cm alumina column (60 g of alumina). Elution of the pale yellow band with pentane followed by evaporation of the filtered eluate gave a pale yellow liquid shown by its n.m.r. spectrum (Table I) to be mainly $(\sigma{-}C_3H_5)Re(CO)_5$. The low yield (~10%) of this product prevented attempts at further purification or decarbonylation to a π-allyl derivative.

Discussion

The proton n.m.r. and infrared spectra both indicate the presence of two stereoisomers of $(\pi{-}C_3H_5)RuCOC_5H_5$ in a ~20:80 ratio in solution at room temperature. Thus the proton n.m.r. spectrum of $(\pi{-}C_3H_5)RuCOC_5H_5$ shows clearly distinct $\pi{-}C_5H_5$ and CH_2 resonances for the two different isomers; the complex multiplet resonances for the CH protons of the two isomers apparently overlap and hence cannot be distinguished. N.m.r. spectra of two independent samples were identical. The infrared spectrum exhibits ν(CO) frequencies at 1958 and 1936 cm^{-1} with approximate area ratio 4:1 corresponding to the abundant (A) and rare (B) isomers, respectively. This doubling of the ν(CO) frequency in $(\pi{-}C_3H_5)RuCOC_5H_5$ is thus similar to the doubling of the two ν(CO) frequencies in $(\pi{-}C_3H_5)Mo(CO)_2C_5H_5$[10] which has been shown[7] to be a consequence of stereoisomerism.

Davison and Rode[7] have demonstrated by a temperature-dependence n.m.r. study on $\pi{-}C_3H_5Mo(CO)_2C_5H_5$ that the two stereoisomers of this complex interconvert at significant rates at temperatures above about 0°. The proton n.m.r. spectrum of $(\pi{-}C_3H_5)RuCOC_5H_5$ at ambient temperature (~30°) resembled that of $(\pi{-}C_3H_5)Mo(CO)_2C_5H_5$ at –5°. Similarly the proton n.m.r. spectrum of $(\pi{-}C_3H_5)W(CO)_2C_5H_5$ at ambient temperature resembled that of $(\pi{-}C_3H_5)Mo(CO)_2C_5H_5$ at +50°. On this basis the relative rates of interconversion of the stereoisomers of the three complexes decrease in the following sequence:

$$(\pi{-}C_3H_5)W(CO)_2C_5H_5(\text{fastest}) >$$
$$(\pi{-}C_3H_5)Mo(CO)_2C_5H_5 > (\pi{-}C_3H_5)RuCOC_5H_5(\text{slowest})$$

The faster rate of interconversion of the tungsten compound than of the molybdenum compound is somewhat surprising in view of the generally higher stability of tungsten-carbon bonds than corresponding molybdenum-carbon bonds.[11] The relatively slow rate of interconversion of the ruthenium compound may arise from increased metal-π-allyl retrodative

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[10] R. B. King, *Inorg. Chem.*, 5, 2242 (1967).
[11] R. B. King, *Inorg. Nucl. Chem. Letters*, 5, 905 (1969).

Table I. Proton N.M.R. Spectra of new Compounds prepared in this work

	Chemical Shifts, τ [a]			
Compound	π—C_5H_5	CH	CH_2	
π–$C_3H_5Ru(CO)C_5H_5$ (29°)				
Isomer A	5.01 s	~6.0 m	7.11d (7)	8.75d (11)
Isomer B	4.86 s	~6.0 m	6.97d (7)	8.23d (11)
σ–$C_3H_5Ru(CO)_2C_5H_5$	4.86 s	3.84 m	5.04 m 5.50 m	7.59dd(8, 2)
σ–$C_3H_5Re(CO)_5$	—	3.76 m	5.41dd (16, 2) 5.72dd (10, 2)	8.19d (8)

[a] The fine structures of the observed resonances are indicated by the following abbreviations: s = singlet, d = doublet, dd = double doublet, m = complex multiplet. The coupling constants in c.p.s. are given in parentheses.

Table II. Principal ions in the Mass Spectra of various Allyl derivatives of Cyclopentadienylmetal Carbonyls [a]

	Relative Abundance [b]				
Ion	$C_5H_5Ru(CO)_2(\sigma\text{—}C_3H_5)$	$C_5H_5Ru(CO)(\pi\text{—}C_3H_5)$	$C_5H_5Mo(CO)_2(\pi\text{—}C_3H_5)$[c]	$C_5H_5W(CO)_3(\sigma\text{—}C_3H_5)$	$C_5H_5W(CO)_2(\pi\text{—}C_3H_5)$
$C_5H_5M(CO)_3C_3H_5^+$	—	—	—	<0.5	—
$C_5H_5M(CO)_2C_3H_5^+$	<0.3	—	28 (23)	26	20
$C_5H_5MCOC_3H_5^+$	33	31	31 (28)	30	25
$C_5H_5MC_3H_5^+$	46	49	28	18	20
$C_5H_5MC_3H_3^+$	100	100	100 (100)	100	10
$C_6H_6M^+$	3	8	16 (18)	4	4
$C_6H_4M^+$	8	9	6	18	20
$C_5H_5M^+$	55	52	14 (14)	10	10
$C_3H_3M^+$	18	18	16 (18)	9	6
M^+	10	~11	17 (17)	<4	<2

[a] These data were obtained on a Perkin-Elmer Hitachi RMU—6 mass spectrometer at 70 e.v. electron energies and a chamber temperature of ~210°. [b] The abundances of the ions $C_5H_5MC_3H_3^+$ were given the arbitrary values of 100. [c] The numbers in parentheses indicate relative abundances obtained from previous work using the Mellon Institute MS—9 mass spectrometer and reported in reference 12.

bonding in the ruthenium compound relative to the molybdenum and tungsten compounds owing to competition with only one rather than two strongly π-accepting carbonyl groups.

A recent investigation of the mass spectrum of (π—C_3H_5)Mo(CO)$_2C_5H_5$ [12] suggested that the loss of its last carbonyl group was accompanied by the loss of two hydrogen atoms to give the $C_3H_3MoC_5H_5^+$ ion rather than the $C_3H_5MoC_5H_5^+$ ion. We have now investigated further the mass spectra of other allyl derivatives of the π—cyclopentadienylmetal carbonyls (Table II). Careful evaluation of the metal isotope patterns indicates the presence of some $C_3H_5MC_5H_5^+$ ion as well as the more abundant $C_3H_3MC_5H_5^+$ ion in all cases, even the previously studied molybednum compound. The relatively common eliminations of neutral CO, H_2, and C_2H_2 fragments[12] are sufficient to account for the observed ions in the mass spectra of the π-allyl derivatives of the cyclopentadienyl metal carbonyls. In all cases successive decarbonylation of the molecular ion occurs until the $C_3H_5MC_5H_5^+$ ion is reached. This ion then undergoes facile dehydrogenation giving the $C_3H_3MC_5H_5^+$ ion. This latter ion can lose C_2H_2 giving $C_6H_6M^+$ which can then undergo dehydrogenation giving $C_6H_4M^+$. The ion $C_5H_5M^+$ and its fragmentation products can arise from cleavage of the allyl group.

Some pyrolysis effects are also noted in the mass spectra listed in Table II. The mass spectra of the σ-allyl derivatives (σ—C_3H_5)Ru(CO)$_2C_5H_5$ and (σ—C_3H_5)W(CO)$_3C_5H_5$ are identical within experimental error to the mass spectra of the corresponding π-allyl derivatives indicating that decarbonylation occurs within the mass spectrometer. Furthermore, attempts to obtain the mass spectrum of (π—C_3H_5)FeCOC$_5H_5$ were unsuccessful: the mass spectrum of ferrocene was obtained when a sample of this π-allyl derivative was introduced into the mass spectrometer.

In a further attempt to extend the range of known allylmetal carbonyl derivatives the rhenium carbonyl system was briefly investigated. Reaction of NaRe(CO)$_5$ with excess allyl chloride gave a relatively low yield of impure (σ—C_3H_5)Re(CO)$_5$ identified by its n.m.r. spectrum. Limited attempts to decarbonylate this material were unpromising; however, the small quantities of (σ—C_3H_5)Re(CO)$_5$ available from this work prevented detailed decarbonylation studies from being carried out.[13]

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(12) R. B. King, *J. Am. Chem. Soc.*, *90*, 1417 (1968).

(13) Note added in proof: In a lecture at the 1970 Organosilicon Symposium in Albany, New York, May, 1970, Dr. E. W. Abel described the preparation of the π-allylrhenium derivative (π—C_3H_5)Re(CO) from allyltrimethyltin and rhenium carbonyl halides!