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DYNAMICS AND STRUCTURE OF SOME RHODIUM-ACETYLENE DERIVATIVES

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Summary

The acetylene ligand of $(C_5H_5)_3Rh_3(CO)(Ph^{13}C{\equiv}CPh)$ is fluxional in solution at room-temperature but static at —87°C. The acetylene ligand of $(C_5H_5)_3$-$Rh_3(Ph^{13}C{\equiv}CPh)$ is fluxional even at —127°C. The acetylene carbon signal is very deshielded suggesting the possibility of carbenoid-type bonding for this ligand.

According to C NMR evidence the derivative $[(C_5H_5)Rh(PhC_2Ph)]_2$ does not have a metallocyclopentadiene structure but an unsymmetrical four-carbon ligand. The complex $[(C_5H_5)Rh(CO)]_2CF_3C_2CF_3$ possesses a static bridging acetylene ligand. However the carbonyl groups appear to be scrambling at room temperature and in a static terminal position at —60°C.

Introduction

Recently we presented NMR data which demonstrated that $(\pi\text{-}C_5H_5)_3Rh_3$-$(CO)PhC_2Ph$ (I) was fluxional in solution at room temperature but static at —87°C [1]. In addition, we showed that $(\pi\text{-}C_5H_5)_3Rh_3(CO)C_6F_5C_2C_6F_5$ was static at room temperature but fluxional at +85°C [1]. In these fluxional processes the carbonyl group is migrating from rhodium to rhodium. Since the cylopentadienyl groups appeared to be equivalent in the fluxional state, it seemed likely that the acetylene ligand was also mobile. We have therefore prepared I incorporating ^{13}C-enriched diphenylacetylene and studied its variable temperature C NMR spectrum. In addition this paper includes NMR studies of

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(π-$C_5H_5)_3Rh_3(PhC_2Ph)$ (II), [(π-$C_5H_5)Rh(PhC_2Ph)]_2$ (III) and [(π-$C_5H_5)Rh(CO)]_2$-$CF_3C_2CF_3$ (IV), which add useful information concerning the dynamics and/or solution structures of these compounds.

Experimental

Instrumentation and ^{13}C NMR procedures

The ^{13}C NMR spectra were obtained at 25.2 MHz with a Varian XL-100-15 instrument. The ^{13}C chemical shifts were measured relative to an internal solvent reference and then reported relative to a tetramethylsilane (TMS) standard. The chemical shifts conversion factors used in this study are $\delta(TMS) = \delta(CH_2Cl_2) + 53.89$ ppm and $\delta(TMS) = \delta(CD_3)_2CO + 29.22$ ppm. Tris(acetylacetonato)chromium(III) (approximately 0.07 *M*) was added to C NMR samples to reduce T_1 relaxation times [2]. An internal deuterium lock was used with all samples run in $(CD_3)_2CO$ solvent and an external ^{19}F lock was used with samples measured in CH_2Cl_2 solvent.

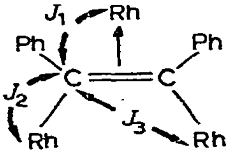
Materials

The compounds (π-$C_5H_5)_3Rh_3(CO)Ph^{13}C{\equiv}CPh$ (I) [3], (π-$C_5H_5)_3$-Rh_3-(PhC_2Ph) (II) [3], [(π-$C_5H_5)RhPhC_2Ph]_2$ (III) [3] and (π-$C_5H_5)_2Rh_2(CO)_2$-$(CF_3C_2CF_3)$ (IV) [4] were prepared by literature procedures. Twenty percent ^{13}C-enriched $^{13}CO_2$ was treated with phenyllithium to form $(C_6H_5)_2{}^{13}CO$ [5]. Benzophenone was converted to $(C_6H_5)^{13}C{\equiv}C(C_6H_5)$ by the method of Reimlinger [6].

Results and discussion

(π-$C_5H_5)_3Rh_3(CO)(Ph^{13}C{\equiv}CPh)$ (I)

The room temperature C NMR spectrum of this compound contained a quartet signal at 150.8 ppm, *J*(Rh—C) 11 Hz, which is due to the ^{13}C-enriched acetylene carbon. At a lower temperature (—87°C), where I is known to be static [1], this signal becomes an unsymmetrical eight-line multiplet. A careful measurement of the single frequency-off resonance C NMR spectrum of I containing no ^{13}C enrichment showed that the resonance of the substituted phenyl carbons was also at 150 ppm and was the cause of the unsymmetrical shape of the acetylene carbon eight line multiplet. It therefore appears that the acetylene carbon signal in the static structure experiences first order coupling to each of the three nonequivalent rhodium nuclei as indicated below. The C_5H_5 and CO groups are omitted from the structure for clarity.

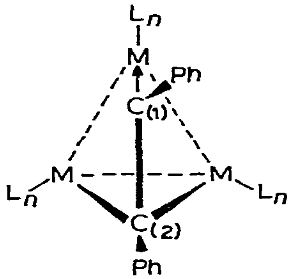


(I)

The fluxional process appears to involve migration of the carbonyl group around a quasi-threefold axis on one side of the Rh_3 plane and concurrent migration of the diphenylacetylene ligand about the threefold axis on the opposite side of the plane.

(π-C_5H_5)$_3$$Rh_3$(PhC≡CPh) (II)

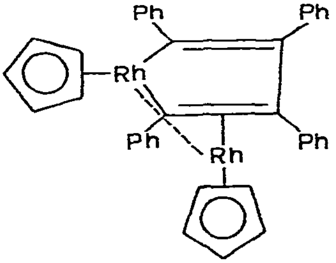
Previously a single crystal X-ray structure of $Fe_3(CO)_9(PhC{\equiv}CPh)$ was determined [7]. Compound II has the same number of valence electrons and presumably the same structure as the iron derivative. The acetylene ligand was located above the trinuclear plane as indicated below.



(II)

ML_n = $(C_5H_5)Rh$ or $(OC)_3Fe$

The acetylene ligand of II prepared from ^{13}C-enriched diphenylacetylene appeared to be moving fairly rapidly in the temperature range +30 to −127°C since the acetylene carbon signal remained as a sharp quartet within this temperature range. The acetylene carbon signal is highly deshielded and the rhodium—carbon coupling constant is relatively large. This information prompts us to propose the bonding scheme for the acetylene ligand indicated in the structure for II. In this scheme C(1) has the bonding characteristics of a terminal carbenoid carbon and C(2) the bonding properties of a bridging carbenoid carbon. The former type of carbon resonance is very deshielded (see $Ph_2C{=}W(CO)_5$ [8]) and the bridging type carbenoid signal is found in the 156-188 ppm region [9]. Therefore the fluxional molecule has about the averaged carbenoid signal expected for equal contributions from the two carbenoid types. In addition this type of bonding scheme is consistent with the geometry of the coordinated acetylene ligand as found in the solid state structure of $Fe_3(CO)_9(PhC{\equiv}CPh)$ [7].

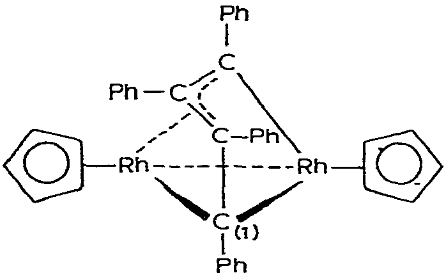


(A)

$[(\pi\text{-}C_5H_5)Rh(PhC_2Ph)]_2$ (III)

This dinuclear compound is an analog of the well known iron derivative $Fe_2(CO)_6(PhC_2Ph)_2$ [10]. The ^1H NMR spectrum of III has two cyclopentadienyl group resonances of equal area. On this basis structure A has been proposed for this molecule [3].

The C NMR spectrum of III prepared from ^{13}C-enriched diphenylacetylene contained four acetylene carbon-derived signals of equal area spread over an 86 ppm range. The two different cyclopentadienyl groups were pinpointed in the C NMR spectrum as the signals at 89.8 and 86.4 ppm by a single frequency off resonance measurement. Based on the C NMR information given in Table 1 we propose the unsymmetrical structure for III which is given below:



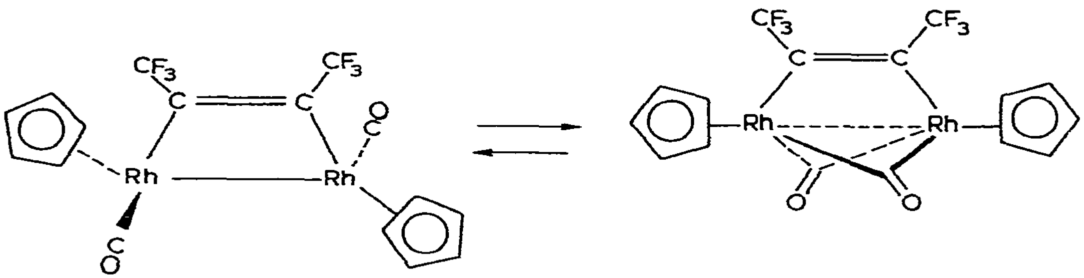
(III)

For the molecules $(C_5H_5)Rh(\mu\text{-}C_7H_8)Rh(C_5H_5)$ and (C_5H_5) Rh $(\mu\text{-}C_8H_{10})$-$Rh(C_5H_5)$ the π-allyl carbon signals were found in the 48 to72 ppm region, J(Rh—C) 6-10 Hz [11]. Phenyl group substitution on the allyl carbons will deshield these signals so that resonances in the 75-101 region appear reasonable for the π-allyl carbons. We suggest that the low field signal at 161.5 ppm is due to C(1) in III. The presence of a doublet of doublets signal suggests that bridging carbon is not equally bonded to both rhodium atoms. However the large size of both J(Rh—C) values suggests that there is considerable single bond character to both of these bonds. The shielding and J(Rh—C) values of C(1) are consistent with the NMR values found previously for the CPh_2 groups of $[(C_5H_5)$-$Rh(CPh_2)]_2CO$ which are known to be bridging units between two rhodium atoms [9].

High temperature ^1H NMR spectra (up to 125°C at which point extensive decomposition occurs) indicate that the two cyclopentadienyl ligands in the complex remain distinct with no hint of coalescence. Thus there does not seem to be a facile fluxional process available which effectively generates a mirror plane perpendicular to the Rh—Rh axis in structure III. Lack of sufficient ^{13}C-enriched sample precluded in high temperature C NMR study which might indicate a fluxional process which generates a mirror plane along the Rh—Rh axis.

$[(C_5H_5)Rh(CO)]_2CF_3C_2CF_3$ (IV)

Treatment of $(C_5H_5)Rh(CO)_2$ with excess $CF_3C{\equiv}CCF_3$ in hexane at 100-106°C in a sealed tube formed IV in moderate yield [4]. A recent single crystal X-ray structure determination of IV gave the structure shown below [12]:



(IV)

The room temperature C NMR spectrum of the dimer contained a triplet (J(Rh—C) 39.3 Hz) signal at 189.8 ppm assigned to the terminal carbonyl carbons. The CF_3 signal was a quartet (J(F—C) 271 Hz) centered at 121.2 ppm and the acetylene carbon resonance was a broad bump at 118 ppm which was diffi-

TABLE 1

^{13}C NMR DATA OF RHODIUM-ACETYLENE DERIVATIVES

Compound	Temp. (°C)	δ(C) (ppm)	Assignment and remarks
$(C_5H_5)_3Rh_3(CO)PhC_2Ph$ (I)	30^a	150.8	Acetylene carbons: quartet, J(Rh—C) 11 Hz
		150.4	Substituted phenyl carbons
		128.6-125.1	Phenyl carbons
		89.7	Cyclopentadienyl carbons
	—87^a	149.8	Acetylene carbons: eight line multiplet, J(Rh—C) 7.0; J(Rh—C) 15.4; J(Rh—C) 25.2 Hz
$(C_5H_5)_3Rh_3(PhC_2Ph)$ (II)	30^b	301.6	Acetylene carbons: quartet, J(Rh—C) 36.6 Hz
		139.9	Substituted phenyl carbons
		127.4, 126.4, 125.3	Phenyl carbons
		86.5	Cyclopentadienyl carbons
$[(C_5H_5)RhPhC_2Ph]_2$ (III)	30^a	161.5	Rhodacycle carbon: J(Rh—C) 31.5; J(Rh—C) 21.5 Hz
		131.5-124.3	Phenyl carbons
		101.5	Rhodacycle carbon: J(Rh—C) 6.3 Hz
		96.9	Rhodacycle carbon: J(Rh—C) 5.8 Hz
		89.8	Cyclopentadienyl carbons: J(Rh—C) 5 Hz
		86.4	Cyclopentadienyl carbons: J(Rh—C) 5.3 Hz
		75.4	Rhodacycle carbon: J(Rh—C) 11.8 Hz
$[(C_5H_5)Rh(CO)]_2CF_3C_2CF_3$ (IV)	30^a	189.8	Carbonyl carbons: triplet, J(Rh—C) 39.3 Hz
		121.2	CF_3 carbons: quartet, J(F—C) 271 Hz
		115.1	Acetylene carbons: broad singlet
		89.6	Cyclopentadienyl carbons
	—66^a	189	Carbonyl carbons: doublet, J(Rh—C) 80 Hz

[a] CH_2Cl_2 solvent. [b] $(CD_3)_2CO$ solvent.

cult to see. Application of ^{19}F decoupling to the C NMR at room temperature clarified the acetylene carbon signal as a doublet of doublets (^1J(Rh—C) 26.8 Hz, ^2J(Rh—C) 9 Hz). It appears that the $CF_3C_2CF_3$ group is static at room temperature and bridging the two rhodium atoms as has been determined in the solid state structure. However the carbonyl groups appear to be scrambling at room temperature. A C NMR spectrum measured at —60°C showed that the carbonyl signal is a doublet (J(Rh—C) 80 Hz). The pairwise bridge opening and closing mechanism proposed previously for $(C_5H_5)_2Mo_2(CO)_5CNCH_3$ [13] and $(C_5H_5)_2$-$Fe_2(CO)_4$ [14] is the most plausable process to explain the carbonyl scrambling observed in the C NMR spectrum of this compound and this is illustrated in the equation above. This process has some similarity to that observed previously for $(C_5H_5)_2Rh_2(CO)_3$ [15].

Acknowledgement

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