

## REACTIONS OF ACETYLENES WITH NOBLE-METAL HALIDES VII\*. THE REACTIONS OF 3-HEXYNE AND DIPHENYLACETYLENE WITH CHLORODICARBONYLRHODIUM DIMER

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(Received April 18th, 1969)

### SUMMARY

At 80° diethylacetylene reacted with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (I) to give chloro(tetraethylcyclopentadienone)rhodium (III), duroquinone, and a novel blue complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})(\text{EtC}_2\text{Et})_2]_2$  (IV). The structure and reactions of (IV) are discussed; with two moles of triphenylphosphine a bis-adduct (V) was obtained whereas an excess gave the  $\text{Ph}_3\text{P}$  adduct of (III) among other products. At low temperatures diethylacetylene reacted with (I) to give a material (A) presumed to contain a diethylmaleoylrhodium moiety from its further reactions. Diphenylacetylene also gave a complex analogous to (IV).

### INTRODUCTION

We recently described the reaction of 2-butyne (dimethylacetylene) with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (I) in benzene at 80° and 25°<sup>1</sup>. At the higher temperature the products comprised duroquinone and its RhCl complex, the RhCl complex of tetramethylcyclopentadienone, and hexamethylbenzene. At 25° reaction also occurred with the formation of a brown amorphous solid which was probably non-stoichiometric, and which still contained the elements of  $[\text{Rh}(\text{CO})_2\text{Cl}]$ . This solid was shown, from its further reactions, to contain (dimethylmaleoyl)rhodium units and evidence was presented that an intermediate of this type was involved in the formation of *p*-benzoquinones in the high temperature reaction.

We have also extended this work to the reactions of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with 3-hexyne (diethylacetylene) and diphenylacetylene, as has already been briefly reported<sup>2</sup>. This work is now presented in detail.

### RESULTS

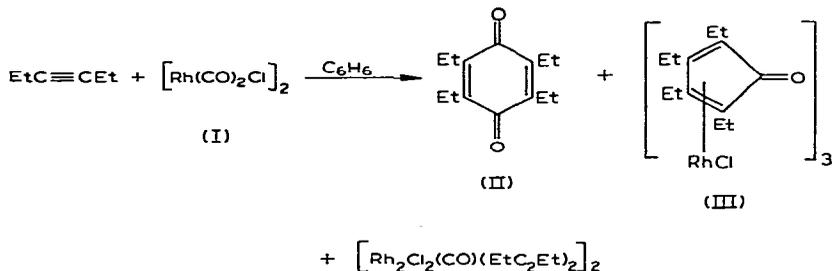
#### *The reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with 3-hexyne*

When a large excess of 3-hexyne was refluxed with (I) in benzene, the products

\* For Part VI see ref. 1.

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isolated were tetraethyl-*p*-benzoquinone (II), chloro(tetraethylcyclopentadienone)-rhodium (III) (trimeric in chloroform) and a crystalline blue complex. The latter and (III) were the major products, only a small amount (8%) of (II) was obtained; in one experiment a trace of hexaethylbenzene was also confirmed.



The blue complex (IV) was shown to have the formula (IV)  $[\text{Rh}_2\text{Cl}_2(\text{CO})(\text{EtC}_2\text{Et})_2]_2$  by analysis and molecular weight determinations. The IR spectrum showed the presence of a terminal metal carbonyl  $[\nu(\text{CO}) 2035 \text{ cm}^{-1}]$  and the absence of uncoordinated double bonds. The PMR spectrum indicated the presence of two different ethyl groups in the molecule.

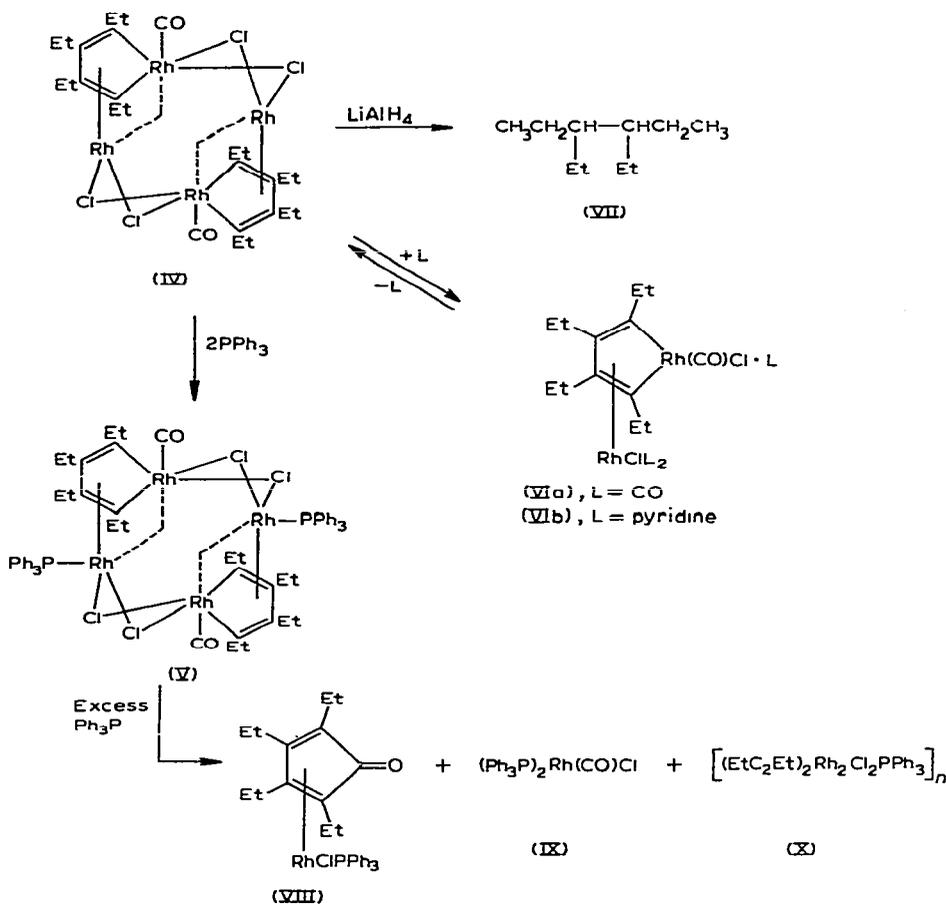
A particularly significant experiment was the reduction of the complex with  $\text{LiAlH}_4$  which gave a 66% yield of a saturated hydrocarbon, identified from its mass-spectral cracking pattern as 4,5-diethyloctane (VII). This was strong evidence for the existence of a unit in the complex in which two diethylacetylenes were linked. We are indebted to Professor Dahl and Miss Bateman for the X-ray structural determination of the complex, which now shows it to have the structure represented as (IV) and is in complete agreement with our chemical and spectroscopic data. This work, and a discussion of the details of the structure is being published separately<sup>3</sup>.

The complex (IV) is thermally very stable, and reacts with a variety of ligands, L, to give adducts. These, however, are not very stable and either revert to (IV) in the cases of L = pyridine, CO or decompose further, when L =  $\text{PPh}_3$ . The molecular sizes of the pyridine and CO adducts [(VIa) and (VIb)] could not be determined owing to their lability. Elemental analyses indicated that 6 molecules of ligand were needed to form these adducts from (IV), and we suggest that the chlorine bridges in (IV) are broken to give the monomers (VI).

With two moles of triphenylphosphine per mole of (IV), a red adduct (V) was obtained. Although the observed molecular weight of (V) was very low by comparison with the expected value, it still favours a structure for (V) in which the dimer is intact. In view of the lability of this adduct, a low molecular weight is not unexpected. The complex (V) again shows a terminal  $\nu(\text{CO})$  at  $2020 \text{ cm}^{-1}$ , very close to that for (IV). By contrast, the pyridine adduct (VIb) shows  $\nu(\text{CO})$  at  $1984 \text{ cm}^{-1}$ . This suggests that in (V) the phosphines are not attached to the rhodium atoms which already bear the carbonyls, whereas pyridine is very probably attached to both rhodiums in (VIb). The good  $\sigma$ -donor and poor  $\pi$ -acceptor capacity of pyridine account for the observed large decrease in  $\nu(\text{CO})$ . Models of (IV) show that the  $\pi$ -bonded rhodiums [which are formally  $\text{Rh}^I$ ] each have a vacant coordination site and attack by ligand can occur there. We therefore favour the structure (V) for the adduct.

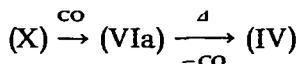
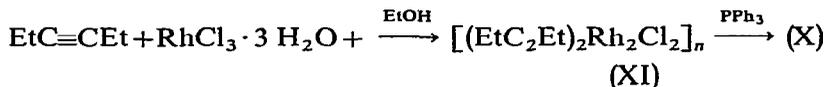
Treatment of either (IV) or (V) with an excess of triphenylphosphine gave three new products: (a) a totally insoluble blue solid which, from its IR spectrum contained triphenylphosphine, an organic ligand, and no carbonyl, and from its analysis is formulated as (X) (48%); (b) chlorocarbonylbis(triphenylphosphine)rhodium (IX) (26%); and (c) chloro(triphenylphosphine)(tetraethylcyclopentadienone)rhodium (VIII), (20%).

SCHEME 1

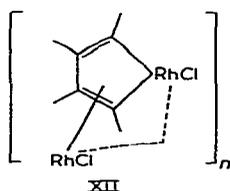


Very little is known about the blue solid (X), but the isolation of this material appears to provide link between the reactions described here and some other studies we have carried out on the reactions of 3-hexyne with rhodium trichloride under a variety of conditions. Although the latter reactions (and those of other acetylenes) proceeded readily, the products obtained were unfortunately non-crystalline and generally indeterminate. In aqueous ethanol a green-black solid (XI) was isolated which was non-stoichiometric but which analysed fairly closely to that expected for

"EtC<sub>2</sub>EtRhCl". On reaction with triphenylphosphine, (XI) gave a blue solid, apparently identical to (X). Furthermore, on carbonylation, (X) gave an orange crystalline complex, identical to (VIa) which on brief heating in light petroleum gave (IV).

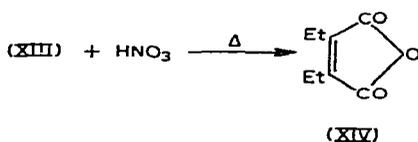
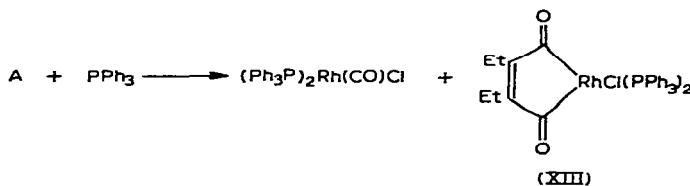
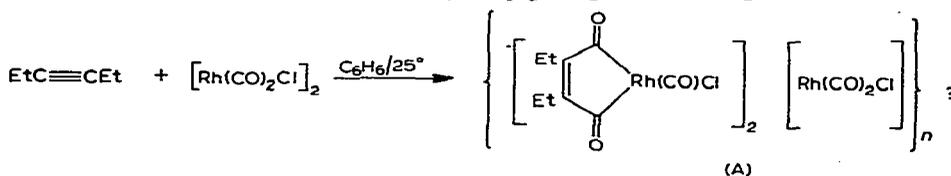


If it is presumed that no gross structural changes have occurred in these reactions, then it appears reasonable that (X) and (XI) both contain a rhodacyclopentadiene moiety such as (XII).



A considerable degree of chlorine-bridging and probably also further metal-metal bonding must also be present in (X) and (XI) to satisfy the expected coordination numbers of the rhodium atoms. The stability of the unit (XII) must be very considerable.

The reaction of 3-hexyne and (I) in benzene was also performed at 25°, as in the case of the 2-butyne reactions<sup>11</sup>. Again, a brown complex (A) was obtained, though in lower yield than with the 2-butyne. Purification of this complex was not possible here either and analytical data indicated that (A) was probably non-stoichiometric. Two possible formulations of one sample are EtC<sub>2</sub>Et(CO)<sub>2</sub>RhCl · Rh(CO)<sub>2</sub>Cl<sub>0.33</sub> · 0.66 H<sub>2</sub>O and [EtC<sub>2</sub>Et(CO)<sub>2</sub>Rh(CO)Cl]<sub>2</sub>[Rh(CO)<sub>2</sub>Cl]. The latter appears the more reasonable since, on reaction of (A) with triphenylphosphine it was possible to isolate



approximately equal amounts of  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$  (IX), and chloro(diethylmaleoyl)-bis(triphenylphosphine)rhodium (XIII). The latter product is similar to that obtained in the analogous reaction sequence starting from 2-butyne and is formulated as such on the basis of analysis and molecular weight determinations and its IR and PMR spectra. It was oxidized to diethylmaleic anhydride (XIV) by boiling 14 *N* nitric acid.

*The reaction of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with diphenylacetylene*

The reactions of diphenylacetylene and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in benzene at 80° have already been described<sup>4</sup>. The products obtained were hexaphenylbenzene, chloro-(tetraphenylcyclopentadienone)rhodium and a 12% yield of an insoluble brown material, (B). The latter compound, which is very hard to purify was originally formulated as  $[\text{PhC}_2\text{PhRh}(\text{CO})\text{Cl}]_n$ . In view of our results on the 3-hexyne reaction and the presence of a terminal  $\nu(\text{CO})$  in (B) at 2025  $\text{cm}^{-1}$ , it now appears that (B) is probably the phenyl analogue of the ethyl complex (IV). The analytical data is in good agreement with a formulation  $[\text{Rh}_2\text{Cl}_2(\text{CO})(\text{PhC}_2\text{Ph})_2]_n$  but a molecular weight determination was not possible.

#### DISCUSSION

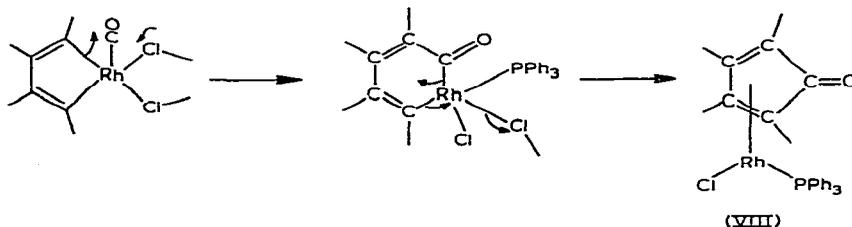
Disubstituted acetylenes react with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  to give a variety of products in which the acetylene has been dimerised either with, or without, incorporation of CO. The benzenoid trimers are also usually obtained in these reactions. The three main products containing two acetylenes obtained are the cyclopentadienones, *p*-benzoquinones (and/or their RhCl complexes) and the complexes  $[\text{Rh}_2\text{Cl}_2(\text{CO})(\text{RC}_2\text{R})_2]_2$  of type (IV). These results are summarized below; the reaction of  $\text{RC}_2\text{R}$  when  $\text{R} = \text{CF}_3$  was reported by Dickson and Wilkinson<sup>5</sup>.

- (a). The free cyclopentadienone is obtained only when  $\text{R} = \text{CF}_3$ .
- (b). Cyclopentadienone-RhCl complexes are obtained for  $\text{R} = \text{Me}$ , Et and Ph but not for  $\text{R} = \text{CF}_3$ .
- (c). Quinones are only obtained for  $\text{R} = \text{Me}$  and Et and to a much smaller extent for the latter. Duroquinone-RhCl was the only complex of this type isolated.
- (d). Complexes of type (IV) are only formed when  $\text{R} = \text{Et}$  and Ph and to a lesser extent for the latter.
- (e). The benzenoid trimers are only very significant when  $\text{R} = \text{Me}$ ; a low yield is obtained when  $\text{R} = \text{Ph}$  and only traces for  $\text{R} = \text{Et}$ .

It appears that formation of the cyclopentadienone (or its complex) is favoured for all cases, but that where R is sufficiently small (methyl and to a lesser extent, ethyl) quinone formation competes strongly. In this work, as in our study of the 2-butyne reactions, we feel that the quinones probably arise via intermediates which contain maleoylrhodium moieties [for example, (A)]. The fact that we isolated smaller quantities of (A) in the 3-hexyne than in the 2-butyne reactions, is paralleled by the lower yields of quinone here in the high temperature reaction.

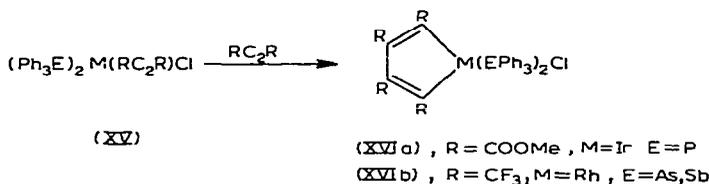
At first sight the complexes of type (IV) look promising as intermediates in the formation of the cyclopentadienones, in particular since (IV) is converted to (VIII) by triphenylphosphine. This is probably an example of a phosphine-catalysed insertion of carbonyl into a metal-carbon  $\sigma$ -bond (many examples of which are now known)

followed by an isomerisation which also effectively reduces the Rh from the III to the I state. However, no other reactions which we have tried on (IV) have led to a cyclopentadienone complex; in particular, we find (IV) to be exceptionally stable thermally on its own.



It is possible that (IV) is closely related to the true intermediate for the above reaction and that under the conditions in which (IV) is isolable it is an artifact, not a true intermediate. An alternative possibility is that (IV) is not an intermediate in the formation of the cyclopentadienone but rather of the intermediate on the formation of the cyclopentadienone but rather of the benzenoid trimer. This is an attractive possibility since when  $R = \text{Me}$ , much trimer and no type (IV) complex is isolated whereas the opposite is found for  $R = \text{Et}$ , while when  $R = \text{Ph}$ , small amounts of both complex and trimer are produced.

Furthermore Collman *et al.*<sup>6</sup> have prepared an iridium complex for which they propose structure (XVIa), which they have shown is probably an intermediate in the trimerisation of dimethyl acetylenedicarboxylate to hexamethyl mellitate.



The complex, formulated as (XVIb), has been reported by Mague and Wilkinson<sup>7</sup>, though it is not clear whether this is involved in the trimerisation. Similar results have been reported for the reactions of cyclopentadienylcobalt/diphenylacetylene systems by Yamazaki and Hagihara<sup>8</sup>. These complexes are derived from mono-acetylene complexes such as (XV). It is possible that complexes of type (IV) also arise from analogous mono-acetylene complexes but it has not been possible to isolate them yet.

Experiments to determine the role which complexes of type (IV) play as intermediates are proceeding and will be reported in due course.

## EXPERIMENTAL

3-Hexyne was purchased from Columbia Organic Chemicals. Light petroleum refers to the fraction of b.p. 30–60°.  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  was prepared by the method of McCleverty and Wilkinson. PMR spectra were measured in deuteriochloroform on a Varian A60 spectrometer; hexamethyldisiloxane was used as an internal standard. IR spectra, except where mentioned were run as KBr discs, in the region 625–5000

$\text{cm}^{-1}$ ; only the significant bands in the region  $1600\text{--}2100\text{ cm}^{-1}$  are usually quoted, but the remainder of the spectra was always in agreement with the proposed structures. Molecular weights were determined osmometrically in chloroform. All reactions were carried out under dry nitrogen.

*Reaction of 3-hexyne with chlorodicarbonylrhodium in benzene at  $80^\circ$*

3-Hexyne (1.4 g, 17 mmoles) was added to a solution of 1.0 g (2.6 mmoles) of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (I) in 80 ml of benzene and the solution refluxed for 24 h. The solution was then cooled and filtered to give 0.45 g (35%) of a crystalline blue solid (IV). The filtrate was reduced to dryness and left a red gummy solid. This was then chromatographed on Florisil; elution with benzene gave a yellow solution from which 0.40 g (35%) of a yellow crystalline solid was obtained. This was shown to be tetraethyl-*p*-benzoquinone, (II), m.p., after recrystallization from methanol,  $57\text{--}59^\circ$ . [Found: C, 76.34; H, 9.02; mol.wt., 220 (mass-spectroscopic).  $\text{C}_{14}\text{H}_{20}\text{O}_2$  calcd.: C, 76.32; H, 9.15%; mol.wt., 220.]

The IR spectra showed two strong ketonic carbonyl stretching frequencies at  $1620$  and  $1650\text{ cm}^{-1}$ . The PMR spectrum only consisted of a quartet at  $\tau$  7.56 and a triplet at  $\tau$  8.97 due to the equivalent ethyl protons as expected [ $J(\text{H}\text{--}\text{H}) = 7.5\text{ Hz}$ ].

On elution of the column with methylene chloride/ethanol (9/1) a red solution was obtained which, after removal of the solvent and recrystallization gave 0.50 g (30%) of red crystals which were identified as chloro- $\pi$ -(tetraethylcyclopentadienone)-rhodium (III) m.p.  $318^\circ$  (decompn.). In chloroform solution this exists as a trimer. [Found: C, 47.23; H, 6.10; Cl, 10.72; Rh, 31.13; mol.wt., 1050, 960, 1010, 1000.  $(\text{C}_{13}\text{H}_{20}\text{ClORh})_3$  calcd.: C, 47.45; H, 6.37; Cl, 10.60; Rh, 30.0%; mol.wt., 993.]

The complex (III) showed a strong ketonic carbonyl band at  $1645\text{ cm}^{-1}$  in the IR spectrum. The PMR spectrum was not clearly resolvable; the methylene protons appeared as a broad multiplet centred at about  $\tau$  7.7 while the methyl protons gave rise to two overlapping triplets, centred at  $\tau$  8.59 and 8.69 ( $J = 7.5\text{ Hz}$ ).

In one experiment a trace of hexaethylbenzene was also found among the products of this reaction.

$[\text{Rh}_2\text{Cl}_2(\text{CO})(\text{EtC}_2\text{Et})_2]_2$  [complex (IV)]. The blue complex (IV), the X-ray crystal structure of which has been reported, gave the analysis expected; the complex was also of the same molecular size in chloroform solution. (Found: C, 33.53; H, 4.20; Cl, 14.67; O, 3.72; Rh, 41.5; mol.wt., 946.  $\text{C}_{26}\text{H}_{40}\text{Cl}_4\text{O}_2\text{Rh}_4$  calcd.: C, 33.30; H, 4.30; Cl, 15.12; O, 3.41; Rh, 43.88%; mol.wt., 938.)

The complex was very thermally stable and did not appear to decompose below  $400^\circ$ . The IR spectrum was chiefly notable for the presence of a strong terminal metal carbonyl band, at  $2025\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  solution. There was no absorption in the region where an uncoordinated  $\text{C}=\text{C}$  bond usually appears. The PMR spectrum in deuteriochloroform (in which the complex was not very soluble) showed a broad band centred at *ca.*  $\tau$  7.7 due to the methylene protons and six peaks at  $\tau$  8.43, 8.58, 8.61, 8.80, 8.92 and 9.07. These appeared to be due to two partially overlapping triplets. Addition of a small amount of pyridine to the deuteriochloroform markedly increased the solubility of the complex and also increased the resolution so that the methylene protons now appeared as a quintet, and the methyl protons were clearly resolved into two triplets, with  $J(\text{HH}) = 7.5\text{ Hz}$ , in each case.

*Lithium aluminum hydride reduction of  $[Rh_2Cl_2(CO)(EtC_2Et)_2]_2$  (IV)*

The complex (IV) (0.50 g, 0.53 mmole) was slowly added to a suspension of 1 g lithium aluminum hydride in dry ether and the mixture stirred for 12 h. The excess lithium aluminum hydride was destroyed with moist ether, the mixture filtered to leave behind a black gummy solid and the ethereal solution dried and the solvent removed. The oil which was left (0.12 g, 66%) could not be crystallized; it was shown to be homogeneous by vapor phase chromatography, and the IR spectrum agreed with that of a saturated hydrocarbon and showed no evidence of  $\nu(C=C)$  bands. It was identified unambiguously as 4,5-diethyloctane (VII) by its mass-spectral cracking pattern which in addition to the molecular ion peak at  $m/e$  170 showed strong peaks at  $m/e$  141, 127 and 99, corresponding to the loss of ethyl, propyl and pentyl from the parent ion. The base peak at  $m/e$  85 clearly arose by cleavage of the 4-5 bond, which is particularly easily cleaved since the carbons on each side of it are tertiary. No significant peaks corresponding to the loss of methyl or butyl were observed.

*Reaction of  $[Rh_2Cl_2(CO)(EtC_2Et)_2]_2$  with pyridine*

Pyridine (2 ml) was added to a suspension of 0.10 g of the complex (IV) in 25 ml of methylene chloride. The solid dissolved rapidly and the solution turned orange; after being stirred at 25° for 10 min, the solution was filtered and concentrated to a volume of 5 ml. On the addition of light petroleum (0.115 g, 77%) an orange crystalline solid (VIb) was obtained. On dissolution in methylene chloride or benzene, the complex readily dissociated and reverted back to the original complex (IV). The analysis appeared to indicate that six molecules of pyridine had coordinated to one molecule of (IV). (Found: C, 45.84; H, 4.83; N, 5.84; O, 2.03.  $C_{28}H_{35}Cl_2N_3ORh_2$  calcd.: C, 47.61; H, 5.0; N, 5.94; O, 2.27%.)

The complex showed one  $\nu(CO)$  at  $1984\text{ cm}^{-1}$  corresponding to a terminal metal carbonyl.

*Reaction of  $[Rh_2Cl_2(CO)(EtC_2Et)_2]_2$  with carbon monoxide*

Carbon monoxide was bubbled through a suspension of 80 mg of complex (IV) in 20 ml methylene chloride at 20° for 15 min. The solid dissolved to give an orange solution; this was taken to dryness to leave 79 mg of an orange crystalline solid (VIa), m.p. 186-193° (slow decompn. from 100°). Since this solid was very labile and reverted rapidly back to the complex (IV) on standing in solution, recrystallization could not be affected. The analysis was carried out on the unrecrystallized material. Solution molecular weight, and PMR measurements were also not meaningful. (Found: C, 34.96; H, 3.71.  $C_{16}H_{20}Cl_2O_4Rh$  calcd.: C, 34.78; H, 3.62%.)

The IR spectrum of this complex showed carbonyl bands at 1923 m, 1965 (sh), and 2028 vs  $\text{cm}^{-1}$ .

*Reaction of  $[Rh_2Cl_2(CO)(EtC_2Et)_2]_2$  with triphenylphosphine*

(a). A solution of 100 mg (0.38 mmole) of triphenylphosphine in 10 ml of methylene chloride was added to a suspension of 100 mg (0.11 mmole) complex (IV) in 10 ml of the same solvent and the reaction mixture stirred for one h at 25°. The solution was then filtered, the methylene chloride evaporated off and 10 ml of benzene, added to the residue. This yielded 86 mg (0.06 mmole) of the bis(triphenylphosphine) adduct (V). This material decomposed on attempted recrystallization. It exhibited one strong

terminal metal carbonyl stretching vibration at  $2028\text{ cm}^{-1}$ . (Found: C, 51.83; H, 4.85; mol. wt., 940.  $\text{C}_{62}\text{H}_{70}\text{Cl}_4\text{O}_2\text{P}_2\text{Rh}_4$  calcd.: C, 50.90; H, 4.83%; mol. wt., 1462.)

(b). A solution of 0.44 g of (1.7 mmoles) of triphenylphosphine in 5 ml of benzene was added to a suspension of 0.20 g (0.21 mmole) of complex (IV) in 20 ml of benzene and the mixture stirred for 18 h at  $25^\circ$ . The solution was then filtered to give a 0.12 g of blue-black solid, (X), m.p.  $303\text{--}305^\circ$  (decompn.). This solid was totally insoluble in all solvents. The IR spectrum showed no bands which could be assigned to a carbonyl group. [Found: C, 51.40; H, 4.85.  $(\text{C}_{30}\text{H}_{35}\text{Cl}_2\text{PRh}_2)_n$  calcd.: C, 51.22; H, 5.02%.]

On removal of the benzene from the filtrate, and addition of light petroleum to the residue 0.15 g, (0.22 mmole) of yellow crystals, identified as chlorocarbonylbis(triphenylphosphine)rhodium (IX) by its IR spectrum and m.p., were obtained.

Careful crystallization of the red light petroleum solution afforded 0.10 g (0.17 mmole) of orange crystals of chloro(triphenylphosphine)- $\pi$ -(tetraethylcyclopentadienone)rhodium. (VIII), m.p.  $201\text{--}203^\circ$ . (Found: C, 63.00; H, 6.06; mol. wt., 550.  $\text{C}_{31}\text{H}_{35}\text{ClOPRh}$  calcd.: C, 62.78; H, 5.95%; mol. wt., 593.)

The IR spectrum showed the presence of a carbonyl band at  $1625\text{ cm}^{-1}$ . The complex was identical with a sample obtained by reaction of chloro- $\pi$ -(tetraethylcyclopentadienone)rhodium trimer with triphenylphosphine.

(c). A solution of 70 mg of the bis(triphenylphosphine) adduct (V) and 0.22 g of triphenylphosphine in 10 ml of benzene was stirred at  $25^\circ$  for 15 h. The products were worked up as described above to yield 32 mg of the blue-black solid (X) 40 mg of chlorocarbonylbis(triphenylphosphine)rhodium (IX) and a small amount of orange crystals of chloro(triphenylphosphine)- $\pi$ -(tetraethylcyclopentadienone)rhodium (VIII).

#### *The reaction of 3-hexyne with rhodium trichloride*

Rhodium trichloride hydrate (0.5 g) in 5 ml of water was added to a solution of 0.82 g (10 mmoles) of 3-hexyne in 15 ml of ethanol and the solution refluxed for 30 min. The solution was cooled and filtered, to give 0.15 g of a green-black crystalline solid. This material had variable analyses but appeared to be best represented as  $[(\text{C}_6\text{H}_{10})_2\text{Rh}_2\text{Cl}_2]_n$  (XI) in view of its further reactions. [Found: C, 34.14; H, 5.00; Cl, 15.86; mol. wt., 2870.  $(\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{Rh}_2)_n$  calcd.: C, 32.69; H, 5.54; Cl, 16.09%; mol. wt. ( $n=2$ ), 220.]

The above product was dissolved in 20 ml of benzene and carbon monoxide bubbled through the solution for 3 h at  $25^\circ$ . The solution was filtered and the solvent removed from the filtrate to leave an orange-brown solid of identical IR spectrum to that of the carbonylation product (VIa). On heating this orange-brown solid briefly in light petroleum an insoluble dark blue solid was formed which was shown to be identical with (IV).

#### *The reaction of 3-hexyne with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ at $25^\circ$*

3-Hexyne (1.0 g, 12.2 mmoles) and 0.5 g (1.3 mmoles) of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in 20 ml of benzene were stirred for 3 h at  $25^\circ$ . Filtration gave 0.25 g of a yellow solid (A); this complex was non-stoichiometric as is the analogous material from 2-butyne. The analysis of one sample of this material agreed well with the formulation  $[\text{Et}_2\text{C}_2\text{--C}_2\text{O}_2\text{Rh}(\text{CO})\text{Cl}]_2[\text{Rh}(\text{CO})_2\text{Cl}]$  (Found: C, 29.52; H, 3.23; Cl, 13.23; Rh, 39.06.

$C_{20}H_{20}Cl_3O_8Rh_3$  calcd.: C, 29.82; H, 2.50; Cl, 13.45; Rh, 38.33%.) This was reasonably compatible with the stoichiometry of the following reaction with triphenylphosphine.

The IR spectra of (A) was very complex in the region  $1600\text{--}2100\text{ cm}^{-1}$  and bands were observed at  $1620\text{ s (b)}$ ,  $1695\text{ s (b)}$ ,  $1885\text{ s}$ ,  $1940\text{ w (sh)}$ ,  $2030\text{ (sh)}$  and  $2085\text{ vs cm}^{-1}$ . All attempts to purify this material failed.

*Chloro(diethylmaleoyl)bis(triphenylphosphine)rhodium (XIII)*

The complex (A) (0.20 g) was added to a solution of 0.50 g triphenylphosphine in 10 ml of benzene and the mixture stirred for 1 h at  $25^\circ$ . The solution was then filtered, and the benzene removed on a rotary evaporator. The residue crystallized on addition of methylene chloride to give 0.21 g of a yellow crystalline solid which was identified as chlorocarbonylbis(triphenylphosphine)rhodium (IX). Addition of light petroleum to the concentrated methylene chloride mother liquors gave 0.24 g of another yellow crystalline solid which, after recrystallization from methylene chloride/light petroleum, was shown to be chloro(diethylmaleoyl)bis(triphenylphosphine)rhodium, (XIII) m.p.  $258^\circ$ . (Found: C, 65.61; H, 4.90; Cl 3.77; P, 8.80; mol. wt., 761, 765.  $C_{44}H_{40}ClO_2P_2Rh$  calcd.: C, 65.97; H, 5.03; Cl, 4.43; P, 7.73%; mol. wt., 801.)

The IR spectrum showed a strong ketonic  $\nu(\text{CO})$  at  $1625\text{ cm}^{-1}$ . The PMR spectrum showed the presence of phenyl protons as multiplets centered at  $\tau$  2.55, a quartet at 8.39, due to the methylenic protons and a triplet at 9.27 due to the methyl protons. The intensity ratios were those expected, 15/2/3.

Chloro(diethylmaleoyl)bis(triphenylphosphine)rhodium (XIII) (275 mg) was refluxed in 20 ml of 14 N nitric acid for 30 min, then poured into ice/water, and the mixture extracted with ether. After drying the solution and removal of the ether a small amount of an oil remained. This was distilled at  $75^\circ/0.2\text{ mm}$  and was shown to be diethylmaleic anhydride by its IR spectrum which very closely resembled that of dimethylmaleic anhydride and showed bands at  $1550\text{ m}$ ,  $1635\text{ m}$ ,  $1770\text{ vs}$  and  $1855\text{ m-w cm}^{-1}$ . The mass-spectrum showed the molecular ion peak at  $m/e$  154.

*Reaction of diphenylacetylene with chlorodicarbonylrhodium dimer*

The details of the reaction of diphenylacetylene with chlorodicarbonylrhodium dimer have already been given. However, in view of the structure which has now been found for (A), we feel it appropriate to revise the structure previously suggested for the brown insoluble polymeric product (B). This is most probably, from the analysis and the  $\nu(\text{CO})$  the phenyl analogue of (IV). (Found: C, 51.79; H, 2.95; Rh, 31.4.  $C_{58}H_{40}Cl_4O_2Rh_4$  calcd.: C, 52.68; H, 3.05; Rh, 31.1%.)

ACKNOWLEDGEMENT

We thank the National Research Council of Canada for supporting this work and for the award of a Post-doctoral Fellowship (to S.M.) and Johnson, Matthey and Mallory for the loan of rhodium trichloride.

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