Journal of Organometallic Chemistry, 105 (1976) 271—279

REACTION OF DIBENZOSEMIBULLVALENES WITH $Rh(CO)_2Cl_2$. ISOLATION OF 4-MEMBERED RHODIUM(III)-CONTAINING HETEROCYCLES

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(Received August 7th, 1975)

Summary

Dibenzosemibullvalene and its dicarbomethoxy derivative react with dicarbonylchlororhodium(I) dimers to yield complexes consisting of a novel Rh(III)-containing 4-membered heterocyclic ring system as the initial products. Upon reaction with carbon monoxide or at higher reaction temperature, CO-insertion occurs to give thermodynamically more stable metal acyl derivatives. The presence of the two strongly electron withdrawing substituents in the dicarbomethoxy derivatives (i) greatly reduces the reaction rate in complex formation, and (ii) readily regenerates the free organic ligand from the metal acyl complexes.

Introduction

Cyclopropanes are known to undergo insertion of transition metals, notably Pt(II), Fe(0), and Rh(I), to form 4-membered heterocycles and/or their metal acyl derivatives. For example: Cyclopropane and substituted cyclopropanes react with H_2PtCl_6 or $[C_2H_4PtCl_2]_2$ to yield Pt(IV)-complexes of I [1,2] and dibenzosemibullvalene (VIII), which reacts with $Fe_2(CO)_9$ as an isolated cyclopropane system, to give ferretane (II) [3] and its metal acyl derivative III [4]; cyclopropanes as well as other compounds incorporating in the molecules cyclopropane system, such as quadricyclene, react readily with $Rh_2(CO)_4Cl_2$ to give only the metal acyl complexes, e.g. IV [5], V [6] and VI [7].

Although a common reaction pathway, as illustrated in Scheme 1, which involves intermediates of (VII) has been proposed [6,8], the isolation of such complexes of the type VII * has still not been hitherto achieved.

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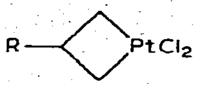
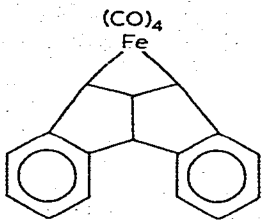
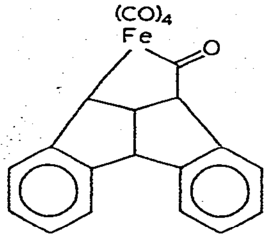
* The product VI isolated from the reaction of phenylcyclopropane with $Rh_2(CO)_4Cl_2$ showed IR bands at 1600 and 1640 cm^{-1} which were anomalously low for acyl carbonyls. In addition, its low solubility and readiness to precipitate from the reaction mixture suggest some similarities between this product and our compound IX. It might be possible that this product was, in fact, the intermediate of type VII.



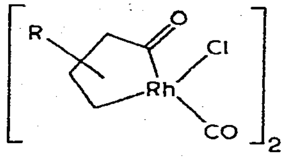
(I)



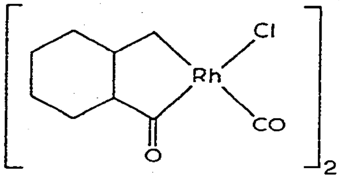
(II)



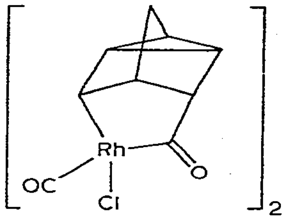
(III)



(IV)



(V)



(VI)

Results and discussion

When a mixture of dibenzosemibullvalene (VIII) and $Rh_2(CO)_4Cl_2$ in 2.2/1 molar ratio in cyclohexane was stirred at room temperature yellow crystalline solid began to separate out after about 25 min and after 5 h the reaction was complete (85% yield). The yellow product was virtually insoluble in any organic solvent. On the basis of its elemental analysis, which favoured a 2/1 adduct, its spectral data, and with reference to ferretane (II), where the iron was inserted into the weakest bond of the cyclopropane ring [9], structure IX was assigned.

Comparison of its IR absorptions with those of X and XI in the 2100—1500 cm^{-1} region are summarized in Table 1.

The IR spectrum of IX was free from any absorption in the 1750—1700 cm^{-1} region, which suggests the absence of acyl carbonyl in IX, and the moderate but slightly broad band at 1605 cm^{-1} may be attributed to the ν(C=C) of the aromatic rings which were also observed in compounds X and XI.

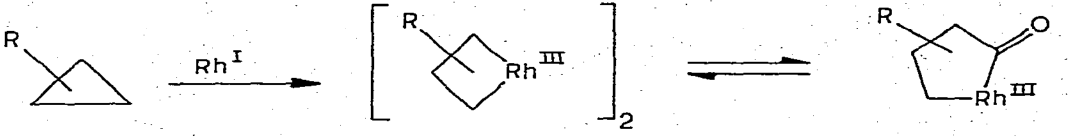
The highest observable peak in the mass spectrum of IX (*m/e* 511), corresponds to the fragment ion $[(C_{18}H_{12})_2Rh]^{+}$. The next group of peaks appeared

TABLE 1

IR ABSORPTION IN THE REGION 2100-1500 cm^{-1} FOR IX—XI

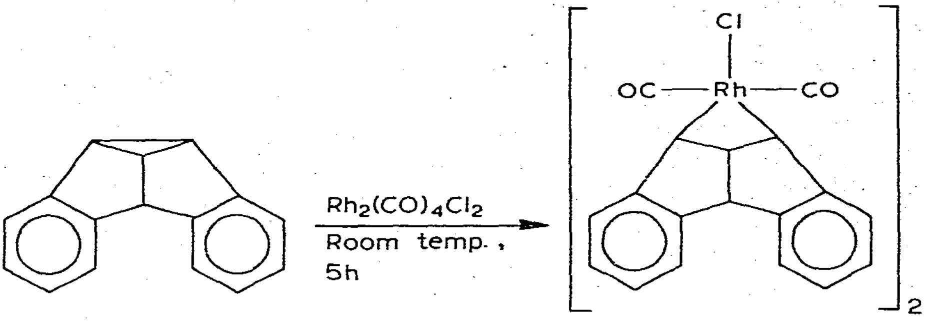
Compound	Terminal ν (—C=O)	Acyl ν (C=O)	Aromatic ν (C=C)
IX (nujol)	2080, 2040	—	1605 (moderate)
X (CH_2Cl_2)	2070	1730-1700 (broad)	1590 (moderate)
XI (nujol)	2080, 2060	1725 (sharp)	1680 (strong)

SCHEME 1



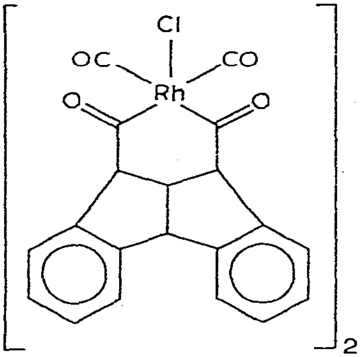
(IV, V or VI)

(VII)

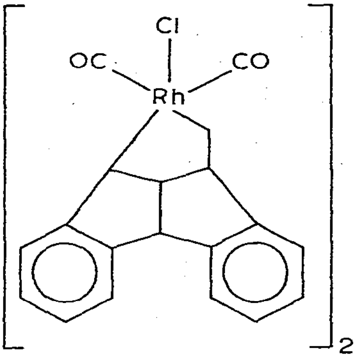


(VIII)

(IX)



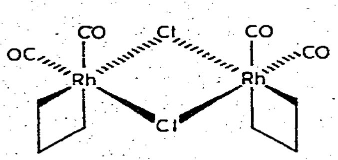
(X)



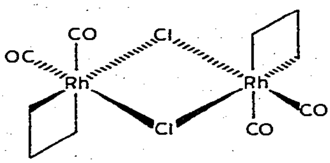
(XI)

to be two sets of Cl containing ions at *m/e* 443, 445 and *m/e* 442, 444 representing ions of $[(C_{16}H_{12})Cl]^+$ and $[(C_{16}H_{12})_2Cl{-}H]^+$, and another prominent peak in the higher mass region at *m/e* 408 indicates the presence of an ion, $(C_{16}H_{12})_2^+$. Although there is no direct evidence that this product is dimeric in nature, the observation of the peaks in the mass spectrum as shown above, together with the preference of rhodium(III) for 6-coordination, suggested a Cl-bridged dimeric complex [5]. The exact geometry around the metal is not known since the two CO-groups can be *cis* or *trans* to each other and the organic ligand can be *syn* or *anti* to one another.

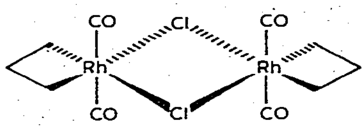
When carbon monoxide gas was bubbled into a suspension of IX in CH_2Cl_2 for 1 h, a clear yellow solution was obtained. Its NMR spectrum showed three



(IXa)
cis-syn



(IXb)
cis-anti



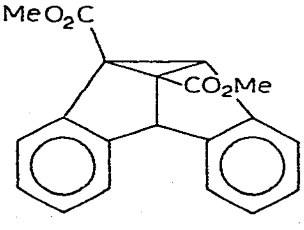
(IXc)
trans

broad envelops at τ 2.3—3.0 (aromatic H); τ 4.9—5.4 and τ 6.0—6.5. The terminal carbonyl absorption was very strong but slightly broader than those for IX and XI. The broad acyl carbonyl absorption at 1730—1700 cm^{-1} could be the result of two or more overlapping bands. Elemental analysis was not possible since this compound could only be obtained in solution. Taking into account the analogy of the quadricyclene derivative [7], structure X was tentatively proposed.

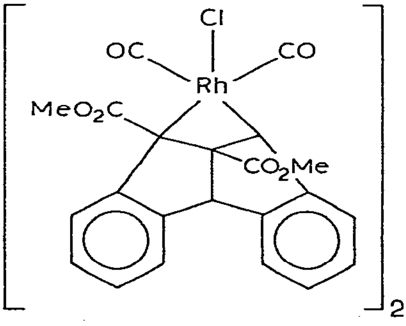
Evaporation of the solution to dryness or prolonged passage of carbon monoxide until the sample became dry, gave a yellow crystalline solid which could no longer be redissolved in CH_2Cl_2 or $CHCl_3$. On the basis of its elemental analysis and the strong and sharp acyl carbonyl band at 1725 cm^{-1}, which suggests one acyl group, structure XI was assigned.

Unlike the ready interconversion between II and III [4], no appreciable change was observed when carbon monoxide was bubbled into a suspension of XI in CH_2Cl_2 at atmospheric pressure and room temperature for 15 h or on prolonged heating of XI at 100°C under vacuum for 15 h. There was no sign of reconversion of XI into IX or X.

In order to examine the general application to form 4-membered heterocycles with $Rh_2(CO)_4Cl_2$, we treated 1,2-dicarbomethoxydibenzosemibullvalene (XII) with $Rh_2(CO)_4Cl_2$ under similar conditions, but no product was obtained after the mixture was stirred at temperatures up to 55°C for 3 days.



(XII)



(XIII)

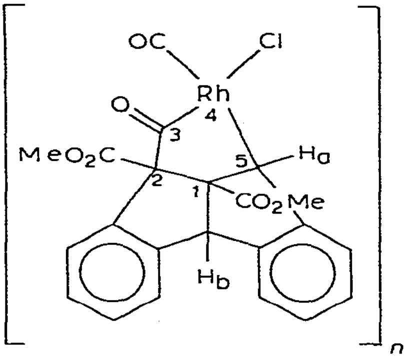
When the mixture was stirred at a bath temperature of 60—65°C for 36 h, subsequent cooling gave a small quantity of yellow crystalline solid (5% yield). Its IR spectrum showed one fairly sharp band at 1730 cm^{-1} (similar in shape to the ester ν(C=O) of XII at 1740 cm^{-1}). On the basis of its elemental analysis and by comparison of its IR and NMR data with that of the parent ligand XII and its derivatives XIV and XV, which were summarized in Tables 2 and 3, structure XIII was proposed.

TABLE 2

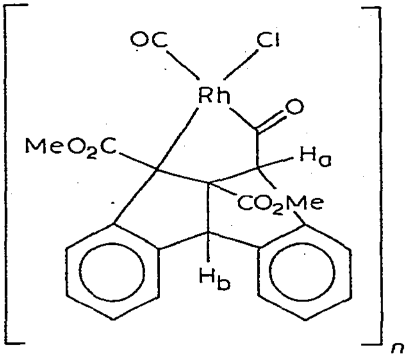
IR ABSORPTION IN THE REGION 2100-1500 cm^{-1} FOR XII-XVI

Compounds	terminal ν(—C=O)	acyl ν (C=O)	ester ν (C=O)	aromatic ν(C=O)
XII (CCl_4)	—	—	1740 (sharp)	
XIII (CH_2Cl_2)	2095, 2025	—	1730 (sharp)	1600 (weak)
XIV, XV (CH_2Cl_2)	2070	1740-1700	(overlapping)	1640 (weak)
XVI (CH_2Cl_2)	2060	1730-1700	(overlapping)	1635, 1600 (weak)

The conditions for the formation of XIII were found to be critical. At a slightly higher temperature (around 70°C), the first crop of a mixture of at least two (possibly three) products, as indicated by the IR and NMR spectra, were obtained (44% yield). When the temperature was further raised to 80—83°C, a further crop of two yellow crystalline products were derived, as indicated by the NMR spectrum (43% yield). The IR spectrum of the mixture showed bands at 2070 (terminal ν(—C=O)) and 1740—1700 cm^{-1} (very broad; overlapping ester and acyl ν(C=O)). Elemental analysis favoured a mixture of two isomers whose empirical formulae were identical with that of XIII. On the basis of the above evidence, coupled with the interpretation of the NMR spectrum (see Table 3) structures of XIV and XV were proposed.



(XIV)



(XV)

TABLE 3

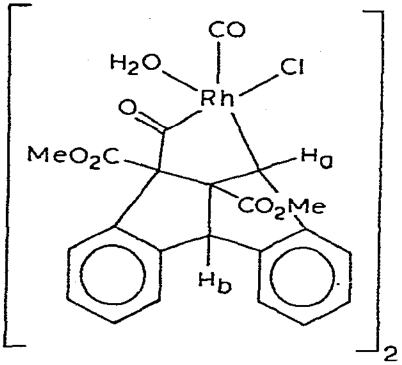
CHEMICAL SHIFTS (τ, ppm) OF PROTONS [a] IN COMPOUNDS XII-XVI

Compounds	ester	OCH_3	H_a	H_b
XII	6.34	6.22	5.67	5.09
XIII	6.30	6.15	5.70	4.96
XIV	6.36	5.93	5.28 (d) J 3.5 Hz	4.91
XV	6.36	6.05	5.24	4.91
XVI	6.40	6.08	5.52 (d) J 3.5 Hz	4.73

[a] Unless otherwise specified, all signals appeared as singlets.

The chemical shifts of the protons of one carbomethoxy group (possibly on C_1) and of the methine proton H_b in both XIV and XV were identical. The signals of the second carbomethoxy groups in these two isomers were approximately 0.1 ppm apart and the ratio of their intensities gave an indication of the composition of the mixture (roughly 2/1). The signal for H_a of at least one of the isomers was broad, possibly with the adjacent rhodium metal.

Attempts to separate the mixture of both crops by TLC were unsuccessful. Because of the high polarity of the complexes (probably because of the presence of two ester groups), mixed solvents of methanol and methylene dichloride were employed as eluent (15/85) as well as for extraction.(50/50) from the silica gel. Only one product was obtained from each of the TLC operations on the two crops, and it was the same in both cases. Its elemental analysis and spectroscopic data were consistent with structure XVI. Some spectroscopie data are given in Tables 2 and 3, and in addition its IR spectrum showed a band at 3680 cm^{-1} (H_2O) and its NMR spectrum broad envelopes around τ 6.2—6.4 and 7.55—7.75 (H_2O).



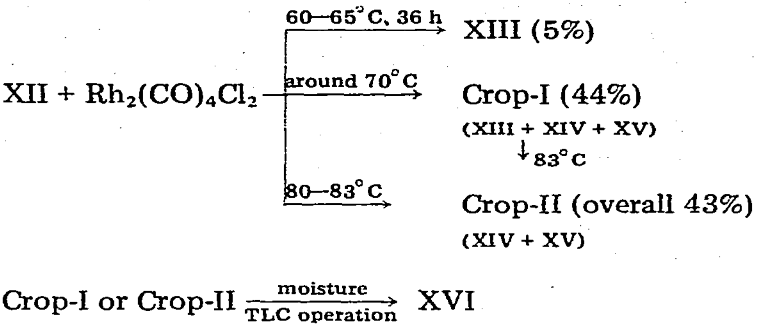
(XVI)

Since H_a appears as a doublet (J = 3.5 Hz), it is most likely that this small coupling is effected by the rhodium metal adjacent to H_a; i.e. the acyl carbonyl is α to one of the ester groups.

These observations, as summarized in Scheme 2 below, suggested that Crop-I could be a mixture of XIII, XIV, and XV and Crop-II was simply a mixture of XIV and XV. Stirring a suspension of Crop-I in cyclohexane at 83°C for 15 h gave a yellow crystalline solid which was identical in all respects with the Crop-II mixture. The moisture present in the $MeOH/CH_2Cl_2$ solvent system and/or absorbed during the TLC operation was sufficient to react with the complexes to generate one single product XVI (see Scheme 2).

When carbon monoxide was bubbled into the solution of the Crop-II mixture in $CDCl_3$, with the reaction monitored by NMR, interesting results were obtained. After 21 h, when the reaction was complete, two compounds, the free organic ligand XII and $Rh_2(CO)_4Cl_2$, were obtained from the resulting mixture as sole products. If the resulting mixture was heated in cyclohexane at

SCHEME 2



83°C for 15 h, a yellow crystalline solid was obtained whose IR and NMR spectra were identical with Crop-II mixture in all respects. This established the direct reversibility of the reaction between the organic ligand XII together with $Rh_2(CO)_4Cl_2$ and the two metal acyl complexes XIV and XV.

$$\mathrm{XII} + \mathrm{Rh(CO)_4\,Cl_2} \overset{\Delta}{\rightleftharpoons} \mathrm{XIV} + \mathrm{XV} + \mathrm{CO}$$

The ability to regenerate the organic ligand XII through the cleavage of the metal portion of complexes XIV and XV simply by bubbling carbon monoxide into their $CHCl_3$ or CH_2Cl_2 solutions is in distinct contrast to the behaviour of the corresponding complex of the parent hydrocarbon XI or the quadricyclene derivative VI [7]. The presence of two strong electron withdrawing substituents and their steric effects may play an important role in controlling the direction of the reaction. Indeed, in the complex formation as illustrated above, the parent hydrocarbon VIII reacted with $Rh_2(CO)_4Cl_2$ under much milder conditions and at a faster rate than its di-ester substituted derivative XII. This is in complete agreement with the observations that electron withdrawing substituents reduced the rate of complex formation [2] with $PtCl_2$ and the rate of isomerization of cubanes by transition metals [10].

The interaction of cyclopropane ring systems with metal ions may be related to the interaction of olefins with metals; as the resultant product also formally involves the formation of metal—carbon σ-bonded systems, it is of interest to contrast to the two alternative bonding modes of metal-carbon systems. As has been discussed [1], the stability of metal—olefin bonds is enhanced by low oxidation states of a metal whilst metal—carbon σ-bonding is favoured by high metal oxidation states. The facility for complex formation does not appear to follow the defined pattern for the cyclopropane ring systems. It is therefore of interest to consider the effects of substituents in the cyclopropane ring system. In general the inclusion of electron withdrawing groups should enhance the reactivity of the ring system to nucleophilic rather than electrophilic attack and favour interaction with metals in low oxidation states. This correlates with the decreasing reactivity of substituted cyclopropane—Pt(II) systems observed by McQuillin et al. on substituting electron withdrawing group in the cyclopropane ring, but contrasts with the lower reactivity of iron(0) complexes towards dibenzosemibullvalene compared with rhodium(I). The variation in general reactivity of substituted olefins towards metal ions, on substitution by electron withdrawing groups decrease with decreasing oxidation states. The presence of electron-withdrawing group also radically affects the stability of metal—carbon σ-bonded system and in general increase the stability of the carbon—metal σ-bond. In addition the ease of CO insertion is normally reduced by the presence of such a group. The marked decrease in stability of the rhodium complexes towards carbon monoxide may therefore be related to the overall decrease in stability relative to the parent hydrocarbon brough about by the substituent effects.

The success in obtaining the stable Rh(III)-containing 4-membered heterocycle IX confirmed our initial belief that milder reaction conditions and shorter reaction time are the prime governing factors. The thermodynamically more stable Rh(III)-complexes are the metal acyl derivatives which is exactly opposite to the Fe(II)-complexes, cf. II and III [4]. Our observations provide evidence to support the proposed reaction pathways for rhodium complex formation illustrated in Scheme 1.

Experimental

Microanalyses were performed by the microanalytical department of the Laboratory. Melting points were measured in open capillary tubes on a Gallenkamp melting point apparatus. IR spectra were recorded using a Perkin—Elmer 257 spectrometer. ^{1}H NMR spectra were measured on a Varian HA 100 spectrometer and tetramethylsilane was used as internal reference. Mass spectra were recorded on an A.E.I. MS-9 spectrometer.

Dicarbonylchloro-3-rhodia(III)-dibenzotricyclo[3.2.2.0]nonadiene (IX)

A mixture of dibenzosemibullvalene (VIII) [12] (112.2 mg, 0.55 mmol) and dicarbonylchlororhodium dimer (97.5 mg, 0.5 mmol) in cyclohexane (20 ml) was stirred at room temperature and very fine yellow crystalline solid began to deposit after 25 min. The mixture was stirred for 5 h and the solid collected gave the complex IX (169.6 mg, 85%) m.p. 214—215°C (dec.) (Found: C 56.16, 56.36; H, 3.84, 3.85; Cl, 8.44. $C_{18}H_{12}ClO_2Rh_2 \cdot \frac{2}{3}\ C_6H_{12}$ calcd.: C, 56.29; H, 3.78; Cl, 8.31%). A sample after drying over P_2O_5 at 100°C/1 mmHg for 2 days gave the complex, m.p. 220.0—220.5°C (dec.) (Found: C, 53.98; H, 3.10; Cl, 8.55. $C_{18}H_{12}ClO_2Rh$ calcd.: C, 54.23; H, 3.03; Cl, 8.89%).

Dicarbonylchloro-3-rhodia(III)-dibenzotricyclo[4.2.2.0] decadiene-4-one (XI)

Carbon monoxide was bubbled for 1 h through a suspension of IX (ca. 10 mg) in CH_2Cl_2 (4 ml) to give a clear yellow solution. Evaporation of the solvent gave the complex XI as a yellow crystalline solid which was no longer soluble in CH_2Cl_2 or $CHCl_3$ (quantitative) m.p. 225—226°C (dec.) (Found: C, 52.66; H, 3.11. $C_{19}H_{12}ClO_3Rh_2 \cdot H_2O$ calcd.: C, 52.37; H, 3.01%).

Dicarbonylchloro-3-rhodia(III)-1,2-dicarbomethoxydibenzotricyclo[3.2.2.0]-nonadiene (XIII)

A mixture of 1,2-di-carbomethoxy-dibenzosemibullvalene (XII) [12] (35.2 mg, 0.11 mmol) and dicarbonylchlororhodium dimer (19.5 mg, 0.1 mmol) in cyclohexane (7 ml) was stirred at room temperature, 40°C, and 55°C for 24 h each, but no reaction had been observed. Further heating at 65°C for 36 h gave, upon cooling, fine yellow crystals of the complex XIII (2.5 mg, 5%) m.p. 160—162°C (dec.) (Found: C, 51.09; H, 3.38. $C_{22}H_{16}ClO_6Rh$ calcd.: C, 51.33; H, 3.13%). After separation of complex XIII, the mother liquor was again stirred at 70°C for 15 h to give yellow crystalline solid of Crop-I (18.5 mg, 36%). IR showed terminal —C=O bands at 2095, 2070 and 2025 cm^{-1}. Further heating of the mother liquor at 83°C yielded yet for 60 h another batch of yellow crystalline solid of Crop-II (20.3 mg, 39%) m.p. 243°C (dec.).

Carbonylchloro-4-rhodia(III)-1,2-dicarbomethoxy-dibenzotricyclo[4.2.2.0]decadiene-3-one (XIV) and carbonylchloro-3-rhodia(III)-1,2-dicarbomethoxy-dibenzotricyclo[4.2.2.0]decadiene-4-one (XIV)

In another experiment, a mixture of VIII (176 mg, 0.55 mmol) and dicarbonylchlororhodium (97.3 mg, 0.5 mmol) in cyclohexane (25 ml) was heated with stirring at 65—70°C for 66 h to give Crop-I (113.1 mg, 44%) m.p. 233.0—233.5°C (dec.). After separation the mother liquor on further heating at 83°C for 6 days gave Crop-II (110.1 mg, 43%) m.p. 243-244°C (dec.) as a mixture of XIV and XV (Found: C, 51.43; H, 3.11; Cl, 7.19, 7.17. $C_{22}H_{16}ClO_8Rh$ calcd.: C, 51.33; H, 3.13; Cl, 6.89%). Analysis of the NMR spectrum gave the ratio of XIII/XV as 2/1.

Aquacarbonylchloro-4-rhodia(III)-1,2-dicarbomethoxy-dibenzotricyclo[4.2.2.0]-decadiene-3-one (XVI)

When the mixtures, either Crop-I or Crop-II was chromatographed on preparative TLC (Silica gel; CH_3OH/CH_2Cl_2, 15/85), only one yellow band was obtained which upon extraction with CH_3OH/CH_2Cl_2 (50/50) gave complex XVI as yellow crystalline solid, m.p. 198-119°C (dec.) (Found: C, 48.45, 48.63; H, 3.54, 3.57; Cl, 5.78. $C_{22}H_{16}ClO_7Rh_{22} \cdot H_2O$ calcd.: C, 48.77; H, 3.54; Cl, 6.54%).

Acknowledgement

S.W. Tam acknowledges leave of absence from the Chinese University of Hong Kong and the award of a Senior Fellowship by the Inter-University Council.

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