Journal of Organometallic Chemistry, 77 (1974) 107—115

MIXED CARBONYL—CYCLOOCTENE COMPLEXES OF RHODIUM(I). *cis*-CYCLOOCTENE AS LIGAND

Yu. S. VARSHAVSKY, T.G. CHERKASOVA, N.A. BUZINA and V.A. KORMER
S. V. Lebedev Synthetic Rubber Research Institute, Leningrad (U.S.S.R.)
(Received March 9th, 1974)

Summary

The substitution reactions of carbonyl groups in $[Rh(CO)_2Cl]_2$, Rhacac$(CO)_2$, Rhoxq$(CO)_2$ (acac = acetylacetonate, oxq = 8-hydroxyquinolinate) by *cis*-cyclooctene, leading to the formation of $[Rh(C_8H_{14})(CO)Cl]_2$, Rhacac(C_8H_{14})CO, Rhoxq(C_8H_{14})CO respectively, are described. Other monoolefins examined do not displace carbonyl groups from rhodium(I) complexes. Mixed carbonyl—cyclooctene complexes are also formed in the ligand exchange reactions $[Rh(CO)_2Cl]_2$ + $[Rh(C_8H_{14})_2Cl]_2$ and Rhacac$(CO)_2$ + Rhacac$(C_8H_{14})_2$. On reaction with triphenylphosphine and triphenylstibine the mixed complexes give Rhacac(L)CO and Rhoxq(L)CO. (Stibine derivatives of this type have not previously been obtained). The chemical and spectroscopic evidence, as well as the thermodynamic data cited from the literature indicate that cyclooctene exhibits comparatively strong donor properties.

Introduction

The reactions of rhodium(I) carbonyl complexes with cyclic dienes are described in a number of papers [1—4]; so far the behaviour of cyclic monoolefins in these reactions has not been studied. The examination of published data on the interaction of cyclic dienes with rhodium(I) *cis*-dicarbonyl complexes enables three distinct cases to be noted:

(i) The addition of diene to form a pentacoordinated adduct. Such adducts are formed in the reaction of rhodium(I) carbonyl chloride with some conjugated dienes, both cyclic and acyclic. The example is $[Rh(CO)_2Cl]_2 \cdot$ 1,3-chd* [1].

---

* Abbreviations used: chd = cyclohexadiene, cod = cyclooctadiene, nbd = norbornadiene, nb = norbornene, dmf = dimethyl formamide, acacH = acetylacetone, oxqH = 8-hydroxyquinoline, Ph = phenyl.

(ii) The displacement of one carbonyl group. The only example of such a reaction is described [2] for the conjugated diene 1,3-cyclooctadiene behaving as a monodentate ligand:

Rhoxq$(CO)_2$ + 1,3-cod → Rhoxq(1,3-cod)CO

In the presence of HCl coordinated 1,3-cyclooctadiene isomerizes to 1,5-cyclooctadiene, the process being accompanied by the displacement of the second carbonyl group (reaction of type (iii)).

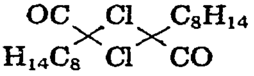
(iii) The displacement of the both carbonyl groups. Such reactions are characteristic of non-conjugated dienes having a structure favouring bidentate bonding. The products of these reactions, for example, are $[Rh(1,5\text{-cod})Cl]_2$ [3], $[Rh(nbd)Cl]_2$ [4], Rhoxq(1,5-cod) [2]. Reactions (iii) may be thought to include the reactions (i) and (ii) as consecutive stages.

We attempted to displace the carbonyl groups from rhodium(I) dicarbonyl complexes by some cyclic monoolefins.

Results and discussion

Prolonged refluxing of rhodium(I) carbonyl chloride with cyclopentene, cyclohexene or *trans*-cyclododecene gives solutions from which on evaporation the main mass of initial substance is isolated unchanged. After heating it with norbornene (in benzene) a yellow microcrystalline substance containing one mole of norbornene per rhodium has been isolated from the solution. IR spectrum of the substance in the carbonyl stretching region [$\nu(CO) = 2074, 2019, 1894, 1835\ cm^{-1}$] is similar to that of the adduct of rhodium carbonyl chloride and 1,3-cyclohexadiene [1]. The reaction appears to proceed without the carbonyl group displacement.

From the reaction with *cis*-cyclooctene (2 h refluxing in benzene or cyclooctene) a yellow crystalline substance of the formula $Rh(C_8H_{14})(CO)Cl$ can be isolated by evaporation of the solution in vacuo. In the carbonyl stretching region the substance exhibits an intense absorption band of complex shape (main maximum at 2003 cm^{-1}, sharp maxima of low intensity at 2027, 1965 cm^{-1}). There is no splitting in the spectra of the solutions; in CH_2Cl_2, and DMF $\nu(CO)$ is 2007 and 1998 cm^{-1}, respectively. Under the action of sodium acetylacetonate this product is turned into $Rhacac(C_8H_{14})CO$, which gives grounds for assigning to it the symmetric structure:



The reaction of the above dimeric complex with an excess of triphenylphosphine gives *trans*-$Rh(PPh_3)_2COCl$.

As with carbonyl chloride, the heating of acetylacetonatodicarbonylrhodium(I) and oxyquinolinatodicarbonylrhodium(I) with different cycloolefins leads to the formation of monocarbonyl derivatives only in the case of cyclooctene.

The acetylacetonate complex $Rhacac(C_8H_{14})CO$, identical with that mentioned above, is a yellow crystalline substance exhibiting ν(CO) bands at 2002 s, 1973 m and 1937 w cm^{-1} (Nujol mulls). There is no splitting in the spectra of the solutions: ν(CO) 2005 cm^{-1} in hexane, 1993 cm^{-1} in DMF. The action of triphenylphosphine and triphenylstibine on Rhacac(C_8H_{14})CO leads to the displacement of cyclooctene and the formation of yellow monocarbonyl complexes Rhacac(PPh_3)CO with ν(CO) 1981 cm^{-1} and Rhacac($SbPh_3$)CO with ν(CO) 1960 cm^{-1}. The former is readily obtained under the action of triphenylphosphine on Rhacac$(CO)_2$ [5]; by reaction of the dicarbonyl complex with triphenylstibine the authors [5] isolated the product of red colour with ν(CO) of 1969 cm^{-1} to which was ascribed the hexacoordinated formula Rhacac$(SbPh_3)_3$CO.

The oxyquinolinate complex is a yellow crystalline substance with ν(CO) 1974 cm^{-1} (in CH_2Cl_2 1980 cm^{-1}). With triphenylphosphine it gives a well-known product Rhoxq(PPh_3)CO [2, 6]. Based on the X-ray data [7] of the identical substance formed under the action of triphenylphosphine on dicarbonyl complex, it can be asserted that cyclooctene in Rhoxq(C_8H_{14})CO is *trans* with respect to the nitrogen atom. Triphenylstibine displaces cyclooctene from the oxyquinolinate complex to form Rhoxq($SbPh_3$)CO [ν(CO) 1950 cm^{-1}].

A ligand exchange reaction leading to the formation of mixed carbonyl—ethylene dimer has been described [8]:

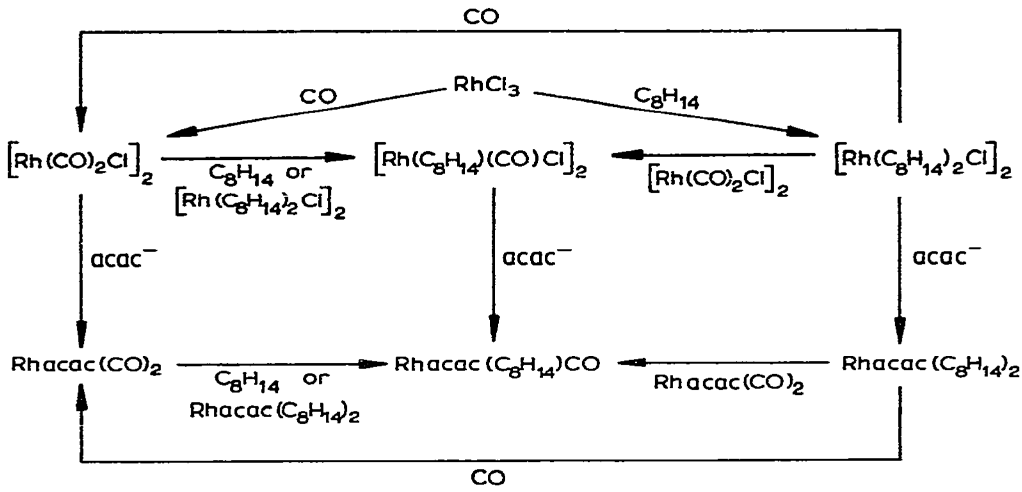
$$[Rh(CO)_2Cl]_2 + [Rh(C_2H_4)_2Cl]_2 \rightarrow 2[Rh(C_2H_4)(CO)Cl]_2$$

The carbonyl—cyclooctene complex can be obtained analogously by the interaction of equimolar amounts of $[Rh(C_8H_{14})_2Cl]_2$ [9, 10] and $[Rh(CO)_2Cl]_2$ in benzene. Analytical and IR data show that the product of this reaction is identical with the substance formed by direct displacement of carbonyl groups from rhodium(I) carbonyl chloride by cyclooctene; in reaction with sodium acetylacetonate this product gives Rhacac(C_8H_{14})CO.

Similar reactions of ligand exchange in bridged dimeric complexes of rhodium(I) have been described [11, 12]. No exchange between monomeric complexes $Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$ and $Rh(\pi\text{-}C_5H_5)(PF_3)_2$ has been established [12b]. In this connection it is of interest to know just how essential the bridged structure of initial substances is for the course of such reactions. In order to ascertain the feasibility of the ligand exchange between monomeric complexes we have carried out experiments on the interaction of Rhacac$(C_8H_{14})_2$ and Rhacac$(CO)_2$. It appears that in DMF the exchange proceeds quantitatively and practically instantaneously. In the spectrum of the solution recorded immediately after mixing of the components, there is one absorption band with ν(CO) 1993 cm^{-1}, the position and intensity of which are exactly the same as in the spectrum of the standard Rhacac(C_8H_{14})CO solution of equal concentration. In methylene chloride and benzene the reaction also takes place but not quantitatively. Thus, the monomeric complexes enter into the ligand exchange reactions as well. The mechanism of these peculiar reactions is not yet understood.

The whole set of reactions described here are represented in Scheme 1, which also shows the carbonylation reaction proceeding when carbon monoxide is purged through the solutions of bis(cyclooctene) complexes, leading to the formation of dicarbonyl derivatives.

SCHEME 1



The ability of *cis*-cyclooctene to displace carbonyl groups from rhodium(I) complexes distinguishes it from other olefins mentioned. Also available thermodynamic and kinetic data are indicative of the relatively strong tendency of cyclooctene to complex with transition metals. The stability constants [13,14] for cyclooctene complexes of Ag^I and Cu^I are markedly above those for the derivatives of most other olefins, including acyclic ones. The same relation holds for enthalpies [14]. The dissociation stage which limits the rate of the reaction:

$$(\pi\text{-}C_5H_5)Mn(CO)_2(\text{olefin}) + PPh_3 \rightarrow (\pi\text{-}C_5H_5)Mn(CO)_2PPh_3 + \text{olefin}$$

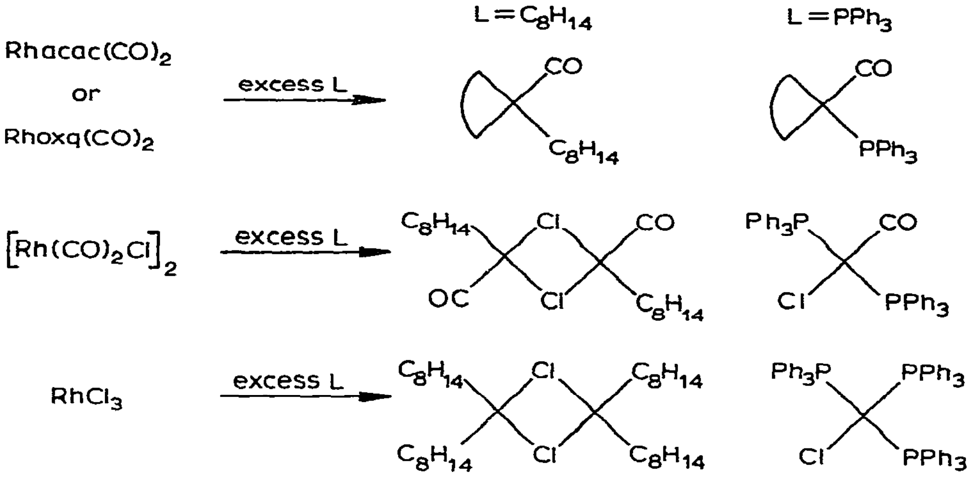
in case of cyclooctene has proved [15] to be slower than equivalent reactions with other olefins except for norbornene and ethylene.

Another distinguishing feature of cyclooctene, its ability to reduce rhodium(III) chloride to form $[Rh(C_8H_{14})_2Cl]_2$ (see Scheme 1), has been noted by us [16] while studying the interaction of rhodium chloride with a number of cycloolefins (cyclobutene, cyclopentene, cyclohexene, norbornene, cyclooctene, cyclododecene). Other authors [10] have reported analogous behaviour of cycloheptene and norbornene. According to our data [16], however, the product of the reaction of rhodium chloride with norbornene is in fact a bridged rhodium(III) complex of the formula $[Rh(C_7H_9)(C_7H_{10})Cl_2]_2$, with the C_7H_9 group being present as a bidentate, formally single-charged ligand (possible of homoallylic type).

It can be seen that cyclooctene exhibits unexpected similarities to a ligand of quite different nature, namely triphenylphosphine, both in its ability to displace carbon monoxide from dicarbonyl complexes, and in its ability to reduce rhodium(III) (Scheme 2).

The "phosphine-like" behaviour of cyclooctene in these reactions suggests that the donor properties of cyclooctene are more pronounced than those of other cycloolefins examined. On the other hand, the differences inherent in the products formed, which are associated with the inability of cyclooctene to

SCHEME 2



cleave chloride bridges in dimeric complexes, point to the fact that cyclooctene is markedly inferior to triphenylphosphine in its donor properties.

Both of these conclusions are in agreement with the data [15] on ν(CO) frequencies in the spectra of (π-C_5H_5)Mn$(CO)_2$L compounds. There are two ν(CO) frequencies in the spectra of the above compounds, one of them being more sensitive to the nature of L. The value of this latter frequency in the spectrum of cyclooctene complex (1894 cm^{-1}) falls in between ν(CO) values in the spectra of the derivatives of the other olefins (1920—1911 cm^{-1}) and triphenylphosphine (1878 cm^{-1}). In all cases the carbonyl stretching frequencies in the spectra of rhodium(I) cyclooctene complexes have been also proved to be higher than in the spectra of their triphenylphosphine analogues (Table 1). The same difference has been noted [17] for the mixed carbonyl cyclooctene complexes of iridium(I).

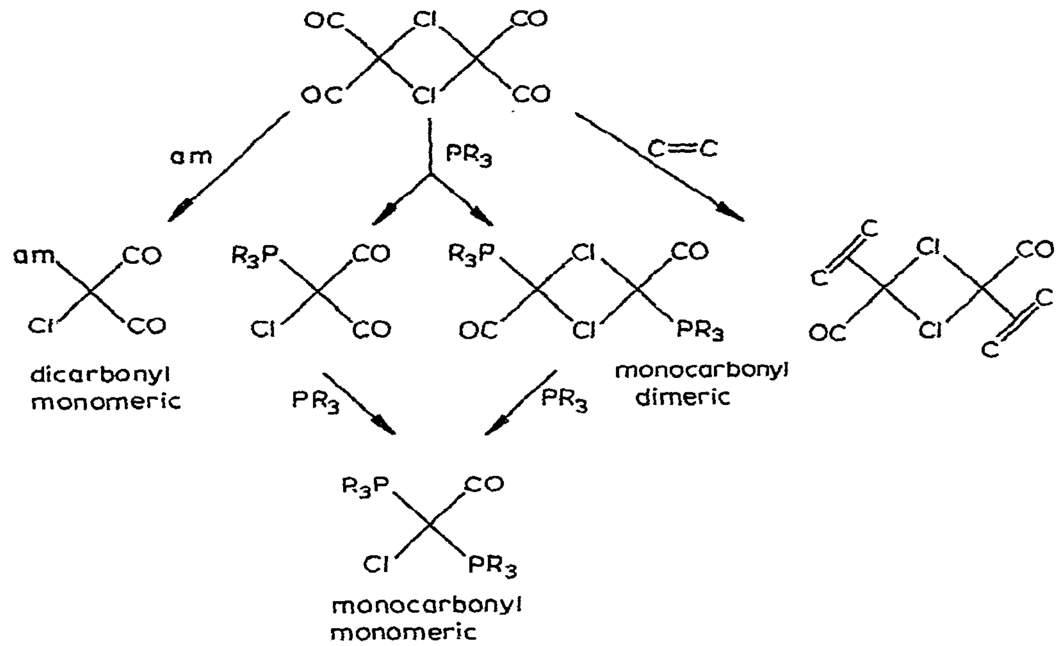
The data obtained make it possible to compare the interaction of rhodium(I) carbonyl chloride with ligands of three different types: Amines, am [18], tertiary phosphines, PR_3 [19, 20], and olefins, C=C (Scheme 3).

TABLE 1

CARBONYL STRETCHING FREQUENCIES IN THE SPECTRA OF RHODIUM(I) MONOCARBONYL COMPLEXES

Compound	L	ν(CO) (cm^{-1})	
		Nujol mull	Solution in CH_2Cl_2
$RhCOLCl_2$	PPh_3	1980	
	C_8H_{14}	2003	2007
RhacacCOL	PPh_3	1981	1982
	C_8H_{14}	2002	1999
RhoxqCOL	PPh_3	1955	1969
	C_8H_{14}	1974	1980

SCHEME 3



The comparison shows that:

(i) σ-Donor ligands with no π-acceptor properties (am) cleave the chloride bridges and are unable to displace the carbonyl groups;

(ii) Ligand with dominating π-acceptor properties (C=C) displace the carbonyl groups and are unable to cleave the chloride bridges;

(iii) Ligands with rather distinct σ-donor and π-acceptor properties (PR_3) are capable of both types of interaction (in addition, it is possible that high *trans*-activity of phosphine ligands shows up in the formation of the end product $Rh(PR_3)_2COCl$).

Analogous observations relating to the differences between bidentate ligands, namely diamines and diolefins, have also been made [21]. Differences in the direction of substitution reactions in platinum(II) complexes under the action of σ-donor and π-acceptor ligands have been noted [22].

Experimental

[Rh(C$_8$H$_{14}$)COCl]$_2$

Method (a). A solution of $[Rh(CO)_2Cl]_2$ (1 g) and *cis*-cyclooctene (3 ml) in benzene (30 ml) was refluxed for 2 h. The oily residue, formed after removal of solvent in vacuo, was dissolved in heptane and the solution again evaporated. Dissolving and evaporation were repeated several times untill a yellow or orange crystalline precipitate was formed (1.05 g, 70%). The substance is soluble in benzene, toluene, chlorinated hydrocarbons, somewhat less so in acetone, ethanol, ether, hexane (Found: Cl, 12.98; Rh, 37.60. $[Rh(C_8H_{14})COCl]_2$ calcd.: Cl, 12.83; Rh, 37.16%).

Method (b). A solution of $[Rh(CO)_2Cl]_2$ (0.5 g) in cyclooctene (8 ml) was refluxed for 2 h. (The formation of small amount of rhodium metal was observed). The solution was filtered, diluted with equal volume of heptane, and evaporated in vacuo. Dissolution and evaporation were repeated several times to give a crystalline product (0.36 g, ~50%). (Found: Cl, 12.99; Rh, 37.30%).

Rhacac(C_8H_{14})CO

Method (a). A solution of Rhacac$(CO)_2$ (1 g) and cyclooctene (5 ml) in benzene (120 ml) was refluxed for 16 h. The moment of reaction completion was determined in the following way: Small samples were taken from the solution and if the reaction was not completed, red-green needles of initial complex were isolated on evaporating the samples. After the reaction was complete, the solution was evaporated in vacuo, the oily residue dissolved in hexane and again evaporated. After the three-fold repetition of this latter operation the residue crystallised on trituration with aqueous ethanol (≈10% of water). The resultant yellow product (1.07 g, 88%) is soluble in conventional organic solvents. Recrystallization from ethanol—ether gave the substance as yellow crystals. (Found: C, 49.30; Rh, 30.42. Rhacac(C_8H_{14})CO calcd.: C, 49.11; Rh, 30.29%.)

Method (b). To a solution of $[Rh(C_8H_{14})COCl]_2$ (0.5 g) in benzene (25 ml) was added Naacac (0.33 g). The reaction mixture was refluxed for 2 h. The solution was filtered and evaporated in vacuo to an oily state. The reaction product was isolated as in Method (a). Yield: 0.7 g, 70%.

Rhoxq(C_8H_{14})CO

To a suspension of Rhoxq$(CO)_2$ (1 g) in benzene (120 ml) was added cyclooctene (8 ml). On refluxing (16 h) the initial substance dissolves completely. The disappearance of the initial dicarbonyl complex in the solution points to reaction completion. The evaporation (in vacuo) of an orange solution gave a yellow crystalline substance which was then transferred onto the filter and washed with hexane. Yield: 1.22 g, 95%. (Found: C, 55.80; Rh, 26.94. Rhoxq(C_8H_{14})CO calcd.: C, 56.20; Rh, 26.75%.)

Action of PPh_3

(a) $[Rh(C_8H_{14})COCl]_2$ (0.1 g) was dissolved in ethanol (3 ml) and triphenylphosphine (0.14 g) was added. A yellow crystalline precipitate was immediately formed and ethanol added to the solution for the complete isolation of the precipitate. The product was washed with ethanol, ether and identified by its IR spectrum as $Rh(PPh_3)_2COCl$.

(b) Rhacac(C_8H_{14})CO (0.1 g) was dissolved in hexane (3 ml) and triphenylphosphine (0.08 g) was added. The yellow precipitate was filtered, washed with hexane, and identified by its IR spectrum as Rhacac(PPh_3)CO.

(c) Rhoxq(C_8H_{14})CO (0.1 g) was dissolved in benzene and triphenylphosphine (0.07 g) was added. The orange-yellow crystalline precipitate was isolated by adding hexane to the pre-evaporated solution; the precipitate was washed with hexane and identified by its IR spectrum as Rhoxq(PPh_3)CO.

Rhacac($SbPh_3$)CO

To a solution of Rhacac(C_8H_{14})CO (0.5 g) in hexane (15 ml) was added triphenylstibine (0.52 g). The orange precipitate was washed with hexane. Yield 0.84 g, 100%. (Found: Rh, 17.21. Rhacac($SbPh_3$)CO calcd.: Rh, 17.68%.)

Rhoxq(SbPh$_3$)CO

To a solution of Rhoxq(C_8H_{14})CO (0.5 g) in acetone (30 ml) was added triphenylstibine (0.46 g). The orange solution was evaporated and the orange-yellow substance (0.81 g, 100%) was isolated by adding hexane. (Found: Rh, 17.40. Rhoxq($SbPh_3$)CO calcd.: Rh, 16.93%.)

[Rh(C_8H_{14})$_2$Cl]$_2$

The synthesis was carried out in dry argon. To a solution of $RhCl_3 \cdot 3H_2O$ (1 g) in aqueous ethanol (20 ml) was added cyclooctene (3 ml). The sealed ampoule containing the reaction mixture was allowed to stand for 16 h at 50° (a rotatory thermostat). The crystalline precipitate (0.54 g, 40%) of yellow colour was washed with ether and dried in vacuo. (Found: Cl, 10.00; Rh, 29.01. $[Rh(C_8H_{14})_2Cl]_2$ calcd.: Cl, 9.90; Rh, 28.73%.) The procedure described was proposed by M.R. Galding (our laboratory).

Rhacac(C_8H_{14})$_2$

The synthesis was carried out in dry argon. To a solution of freshly prepared $[Rh(C_8H_{14})_2Cl]_2$ (0.6 g) in benzene (50 ml) was added Naacac (0.3 g). The reaction mixture was refluxed for 1 h. The solution was filtered (a small amount of brown precipitate remained on the filter) and evaporated in vacuo. The dry residue was dissolved in ether and again evaporated. A yellow crystalline substance was isolated. Yield: 0.64 g, 90%. The product is soluble in conventional organic solvents. (Found: Rh, 24.95. Rhacac(C_8H_{14})$_2$ calcd.: Rh, 24.41%.)

Ligand exchange reactions

(a) [Rh(CO)$_2$Cl]$_2$ + [Rh(C_8H_{14})$_2$Cl]$_2$. The reaction was carried out under argon. To a solution of $[Rh(CO)_2Cl]_2$ (0.21 g) in benzene (20 ml) was added $[Rh(C_8H_{14})_2Cl]_2$ (0.4 g). After 1 h stirring the solution was filtered and evaporated in vacuo. The oil formed was triturated with aqueous ethanol. The yellow crystalline precipitate was filtered and dried in vacuo. The product, $[Rh(C_8H_{14})COCl]_2$, (0.4 g, 65%) was identified by its IR spectrum and by reaction with Naacac.

(b) Rhacac(CO)$_2$ + Rhacac(C_8H_{14})$_2$. To a solution of Rhacac(CO)$_2$ (0.61 g) in DMF (5 ml) was added Rhacac(C_8H_{14})$_2$ (0.100 g).

The IR spectrum of the solution recorded immediately after mixing exhibits one carbonyl absorption band the intensity and frequency of which are similar to those of ν(CO) band in the spectrum of the standard solution of Rhacac(C_8H_{14})CO (0.097 g in 3 ml DMF). On carrying out the reaction in methylene chloride and benzene the spectra of the solution (CH_2Cl_2) and the precipitate (isolated from C_6H_6) exhibit the starting dicarbonyl complex absorption band along with ν(CO) band of the monocarbonyl product.

Interaction of cyclooctene complexes with CO

(a) Through a solution of Rhacac(C_8H_{14})$_2$ (0.1 g) in benzene (10 ml) a stream of CO was passed for 1 h. The reaction product, Rhacac(CO)$_2$, was identified by IR spectrum of the dry residue.

(b) Through a solution of $[Rh(C_8H_{14})_2Cl]_2$ (0.1 g) in benzene (10 ml) a stream of CO was passed for 1 h. The reaction product, $[Rh(CO)_2Cl]_2$, was identified by IR spectrum of the dry residue.

Interaction of $[Rh(CO)_2Cl]_2$ *with norbornene*

To a solution of $[Rh(CO)_2Cl]_2$ (1 g) in benzene (30 ml) was added norbornene (5.4 g). The solution was refluxed for 3 h, then filtered (for separating small amount of metal) and evaporated in vacuo to the minimum volume. By adding hexane a light-yellow microcrystalline precipitate was isolated. Yield 0.4 g. (Found: Cl, 11.5; Rh, 35.10. $[Rh(CO)_2Cl(nb)]_2$ calcd.: Cl, 12.30; Rh, 35.70%.)

$[Rh(nb)(nb—H)Cl_2]_2$

To a solution of $RhCl_3 \cdot 3H_2O$ (1 g) in aqueous ethanol (30 ml) was added norbornene (6 g). The solution was refluxed for 2 h and evaporated in vacuo to the oily state. The residue was dissolved in the minimum volume of carbon tetrachloride whereupon a brownish-red microcrystalline product was isolated by adding hexane. Yield 0.66 g, 50%. (Found: Cl, 19.80; Rh, 28.85. $[Rh(C_7H_9)(C_7H_{10})Cl_2]_2$ calcd.: Cl, 19.67; Rh, 28.53%.) The reaction proceeds similarly both in air and in argon.

IR spectra were recorded using an IKS-14A model spectrophotometer with LiF and NaCl prisms. Rhodium(I) carbonyl chloride [23] and acetylacetonatodicarbonylrhodium(I) and oxyquinolinatodicarbonylrhodium(I) [6, 24] were synthesized according to previously-described procedures.

References

1 G. Winkhaus and H. Singer, Chem. Ber., 99 (1966) 3593.
2 R. Ugo, G. La Monica, S. Cenini and F. Bonati, J. Organometal. Chem., 11 (1968) 151.
3 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
4 E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 3178.
5 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 3156.
6 Yu. S. Varshavsky, N.N. Knyazeva, T.G. Cherkasova, N.V. Ivannikova and T.I. Ionina, Zh. Neorg. Khim., 15 (1970) 715.
7 L.G. Kuz'mina, Yu. S. Varshavsky, N.G. Boky, Yu. T. Struchkov and T.G. Cherkasova, Zh. Strukt. Khim., 12 (1971) 653.
8 J. Powell and B.L. Shaw, J. Chem. Soc., A, (1968) 211.
9 L. Porri, A. Lionetti, G. Allegra and A. Immirzi, Chem. Commun., (1965) 336; J. Organometal. Chem., 6 (1966) 422.
10 G. Winkhaus and H. Singer, Ber., 99 (1966) 3602.
11 D.F. Steele and T.A. Stephenson, J. Chem. Soc. Dalton, (1972) 2161.
12 (a) J.F. Nixon and J.R. Swain, J. Chem. Soc. Dalton, (1972) 1044;
(b) D.A. Clement and J.F. Nixon, J. Chem. Soc. Dalton, (1972) 2553.
13 M.A. Muhs and F.T. Weiss, J. Amer. Chem. Soc., 84 (1962) 4697.
14 J.M. Harvilchuk, D.A. Aikens and R.C. Murray, Inorg. Chem., 8 (1969) 539.
15 R.J. Angelici and W. Loewen, Inorg. Chem., 6 (1967) 682.
16 Yu. S. Varshavsky, N.V. Kiselyova, V.A. Kormer and T.G. Cherkasova, XIth All-Union Conference on the Chemistry of Complex Compounds, Alma-Ata, (1973) 269.
17 B.L. Shaw and E. Singleton, J. Chem. Soc. A, (1967) 1683.
18 D.N. Lawson and G. Wilkinson, J. Chem. Soc. A, (1965) 1900.
19 L. Vallarino, J. Chem. Soc., (1957) 2287.
20 L. Gallay, D. DeMontauson and R. Poilblanc, J. Organometal. Chem., 38 (1972) 179.
21 C. Cocevar, G. Mestroni and A. Camus, J. Organometal. Chem., 35 (1972) 389.
22 M.I. Gelfman, O.P. Kor'yakov, N.A. Kustova and V.V. Razumovsky, Zh. Neorg. Khim., 19 (1974) 2879.
23 K.S. Brenner, E.O. Fischer and C.G. Kreiter, Chem. Ber., 96 (1963) 2632.
24 Yu. S. Varshavsky and T.G. Cherkasova, Zh. Neorg. Khim., 12 (1967) 709.