Journal of Organometallic Chemistry, 168 (1979) 115—121
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CARBONYL EXCHANGE WITH ^{13}CO OF $Rh_6(CO)_{16}$ AND ITS BIDENTATE PHOSPHORUS LIGAND SUBSTITUTION PRODUCTS

KENJI NOMIYA and HISASHI SUZUKI *

Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229 (Japan)

(Received June 15th, 1978)

Summary

Reactions of $Rh_6(CO)_{16}$ with bidentate ligands, $Ph_2P(CH_2)_nPPh_2$ (n = 2: diphosE = 1,2-bis(diphenylphosphino)ethane; n = 4: diphosB = 1,4-bis(diphenylphosphino)butane) gave $Rh_6(CO)_{12}(diphosB)_2$, $Rh_6(CO)_{15}(diphosE)$ and $Rh_6(CO)_{13}(diphosE)_3$. In these clusters, each phosphorus donor site of diphosB is coordinated to adjacent rhodium atoms, while only one donor site of diphosE is coordinated to a rhodium atom. The other site is believed to be bound to a face-bridging carbonyl group.

Carbonyl exchange with carbon monoxide in these diphos-substituted clusters is affected by the mode of coordination of the ligands. In the diphosB-substituted cluster, both terminal and face-bridging carbonyl groups readily exchanged with ^{13}CO at 20° C, while in both diphosE mono- and tri-substituted clusters only a few percent of the terminal carbonyls exchanged and the face-bridging carbonyls were not observed to undergo exchange at all under similar conditions.

Introduction

Hexadecacarbonylhexarhodium, $Rh_6(CO)_{16}$, has been reported to react with thiols, halogens and carboxylic acids [1] and also with some phosphorus ligands [2,3]. We report here the substitution reactions of $Rh_6(CO)_{16}$ with bidentate phosphorus ligands, $Ph_2P(CH_2)_nPPh_2$ (n = 2: abbreviated as diphosE, n = 4: abbreviated as diphosB), in which the basic structure of the metal cluster is either retained or not, depending upon the reaction conditions. We also report the carbonyl exchange reactions of these diphos-substituted rhodium clusters with ^{13}CO.

Results and discussion

Substitution reactions with diphosB

In a closed system, the reaction of hexadecacarbonylhexarhodium with diphosB in a 1/3 molar ratio in chloroform at room temperature gave as the major product the di-substituted hexarhodium compound, $Rh_6(CO)_{12}(diphosB)_2$. The latter was recrystallized from toluene to give red crystals. Further substitution did not occur, even if more diphosB was added. Rupture of the metal cluster was observed instead. For example, a reaction in chloroform between $Rh_6(CO)_{16}$ and diphosB in a 1/4 molar ratio gave a mixture of the di-substituted compound and an unidentified yellow solid. A reaction in 1/8 molar ratio gave a high yield of the latter. Although the yellow compound has not been isolated in the pure state, its IR spectrum in chloroform solution (only a single ν(CO) band at 1974 cm^{-1}) suggests that it may be RhCl(CO) (diphosB), which corresponds to $RhCl(CO)(PPh_3)_2$ which was reported as the main product in the reaction of $Rh_6(CO)_{16}$ with an excess of triphenylphosphine in chloroform [2]. When the reaction of $Rh_6(CO)_{16}$ with a smaller excess of diphosB (molar ratio less than 1/1) was carried out at room temperature under nitrogen, the diphosB mono-substitution derivative, $Rh_6(CO)_{14}(diphosB)$, was obtained as the major product, but it could not be isolated in analytical purity.

The IR spectrum of $Rh_6(CO)_{12}(diphosB)_2$ in chloroform shows three terminal (2049, 2000 and 1970 cm^{-1}) and one face-bridging (1813 cm^{-1}) carbonyl stretching band as shown in Table 1 and Fig. 2. The band at 1970 cm^{-1} is tentatively assigned to a terminal carbonyl which is coordinated to a rhodium atom having the phosphorus ligand, and the bands at 2049 and 2000 cm^{-1} may with confidence be assigned to twin-terminal carbonyls coordinated to another rhodium atom which does not have a phosphorus ligand. Compared with those of the mono-substituted cluster, the band at about 1970 cm^{-1} is more intense and the bands around 2049 cm^{-1} weaker and simpler. The characteristic band due to face-bridging carbonyl groups is slightly shifted to higher frequency as the number of diphosB ligands coordinated to the hexarhodium cluster increases. In both di- and mono-substituted clusters, the relative intensity of the bands due to face-bridging carbonyls is nearly equal.

The ^{13}C NMR spectra of the diphosB-substituted hexarhodium clusters were measured in deuteriochloroform using ^{13}CO-enriched samples in the presence of the relaxation reagent $Cr(acac)_3$. The terminal carbonyl signals (182—189 ppm) were more complicated than those of the original cluster, $Rh_6(CO)_{16}$, because of the many possible geometric isomers of the substituted cluster and the coupling with ^{31}P as well as ^{103}Rh (*J*(P—Rh—C) 14.5 Hz; *J*(Rh—C) 49.3 Hz) [4,5]. This spectrum also showed the presence of two nonequivalent groups of face-bridging carbonyls (240.6 ppm and 246.3 ppm, in 1/1 relative intensity ratio).

The corresponding signals appeared at lower field than those of the parent cluster, $Rh_6(CO)_{16}$ (terminal carbonyls: 180.1 ppm, *J*(Rh—C) 70.2 ± 6 Hz; face-bridging carbonyls: 231.5 ppm, *J*(Rh—C) 24.4 ± 6 Hz) [4], reflecting the electronic effect of the phosphorus ligand.

In the spectrum of the mono-substituted cluster, many of the terminal carbonyl groups couple only with ^{103}Rh, but not with ^{31}P, and the coupling constant (*J*(Rh—C) 70.0 Hz at 181.0 ppm) is in accord with that of the parent cluster. The presence of three nonequivalent resonances due to face-bridging carbonyls also was apparent (232.4 ppm, 240.6 ppm and 246.5 ppm: their relative intensity ratio was 1/2/1).

From these spectroscopic data and the analogy with the triphenylphosphine-substituted cluster [2], it is suggested that each diphosB ligand in the di- and mono-substituted cluster bridges adjacent two rhodium atoms and that each phosphorus atom of the diphosB coordinates to one rhodium atom in place of one terminal carbonyl group.

Substitution reactions with diphosE

Reaction of $Rh_6(CO)_{16}$ with an equimolar amount of diphosE in chloroform gave the mono-substituted hexarhodium cluster in high yield. The reaction of $Rh_6(CO)_{16}$ with an excess of diphosE (1/6 molar ratio) in chloroform under nitrogen gave the tri-substituted hexarhodium carbonyl compound. No rupture of the metal cluster was observed, in contrast to what had been observed in the reaction of $Rh_6(CO)_{16}$ with an excess of diphosB. The IR data of these clusters are shown in Table 1, together with IR data for the diphosB-substituted clusters. The band at 1980 cm^{-1} is due to terminal carbonyl groups coordinated to a rhodium atom which also is coordinated to a phosphorus atom. Its intensity increases with the number of coordinated diphosE. The $\nu(CO)$ bands due to face-bridging carbonyl groups were mostly shifted to lower frequency and broadened, depending upon the number of coordinated diphosE. This trend contrasts with the case of the diphosB-substituted cluster.

The ^{13}C NMR spectrum of the diphosE mono-substituted, ^{13}C-enriched cluster shows the presence of three nonequivalent groups of face-bridging carbonyls at lower field (231.1 ppm, 240.1 ppm and 252.0 ppm) in relative intensity ratio 1/2/1 and a complex pattern of terminal carbonyls at higher field (180—187 ppm). The most intense and sharpest peak in the terminal carbonyl region is coupled only with ^{103}Rh, but not with ^{31}P (183.0 ppm, $J(Rh—C)$ 69.6 Hz; 184.7 ppm, $J(Rh—C)$ 69.5 Hz), and the coupling constant $J(Rh—C)$ is very close to that of $Rh_6(CO)_{16}$ (180.1 ppm, $J(Rh—C)$ 70.2 ± 6 Hz) [4].

The signal at lowest field (252.0 ppm) due to the face-bridging carbonyl group was observed in particular in the diphosE-substituted compounds. This carbonyl resonance implies that the electron density on the carbon atom of face-bridging CO ligands is less than that in the diphosB-substituted clusters. Further, the IR observations indicates that the bond distance between C and O atoms of the face-bridging CO in the diphosE compounds is lengthened more than in diphosB compounds.

As a consequence of the smaller number of bridging CH_2 groups in the

TABLE 1

IR DATA FOR RHODIUM CLUSTERS

Cluster	$\nu(CO)$ cm^{-1} (in $CHCl_3$)			
$Rh_6(CO)_{16}$	2075s,	2026w,	1801m(br)	
$Rh_6(CO)_{14}(diphosB)$	2095w,	2060S	2000w,	1975w,
	1808m,	1800m(br)		
$Rh_6(CO)_{12}(diphosB)_2$	2049S,	2000S,	1970S,	1813S
$Rh_6(CO)_{15}(diphosE)$	2086m,	2050S,	2023m,	2000(sh)
	1810(sh),	1785m,	1750(sh)	
$Rh_6(CO)_{13}(diphosE)_3$	2055s,	2030s,	2012s,	1980s
	1780(sh)	1755m,	1733m,	1710(sh)

diphosE molecule, this ligand does not seem to bridge two adjacent rhodium atoms in the Rh_6 unit, and instead it acts as a monodentate ligand. Since the IR and ^{13}C NMR spectra of the diphosE-substituted cluster imply chemical interactions between the face-bridging carbonyls and one phosphorus group of diphosE, we suggest that one donor site of the diphosE molecule is coordinated to a rhodium atom and that the other phosphorus site is not free, rather is interacting in some way with a face-bridging carbonyl group.

The coordination modes of both diphos ligands in hexarhodium clusters are shown in Fig. 1. These modes are distinguished from those of bidentate ligands such as 2,2'-bipyridine [6] and diolefins such as norbornadiene, 1,4-cyclohexadiene and 1,5-cyclooctadiene [7], which coordinate to one rhodium atom in place of two carbonyl groups at a terminal site in the hexarhodium unit.

Carbonyl exchange reactions with ^{13}CO

The rate of exchange of ^{13}CO with the carbonyl ligands in $Rh_6(CO)_{16}$ and its diphos-substituted derivatives was examined by means of IR spectroscopy. Under excess carbon monoxide, the intermolecular carbonyl exchange with the diphos-substituted clusters occurred without the elimination of the coordinated diphos ligand. In a typical experiment, a solution of the cluster (0.02 mmol) in chloroform (4 ml) was stirred under a constant pressure of ^{13}C-enriched (91 atom%) carbon monoxide (0.4 mmol) in a 85 ml-closed glass vessel at 20°C. After a constant time, the solution was frozen and then degassed. Then the IR spectrum of the solution was measured under nitrogen. ^{13}C-enriched carbon monoxide again was introduced into the thoroughly degassed solution for further exchange. This procedure was repeated. The results of these IR measurements are shown in Fig. 2.

All terminal and face-bridging carbonyl groups of $Rh_6(CO)_{12}(diphosB)_2$ exchanged readily with ^{13}CO. After 18 h, both types of carbonyl ligands were ca. 50% labelled, as indicated by the intensities of $\nu(CO)$ at 2005, 1960, 1928 (terminal) and 1755 cm^{-1} (face-bridging), which were expected from the isotopic shifts of ^{12}C—^{13}C. All carbonyl groups were exchanged at the same time.

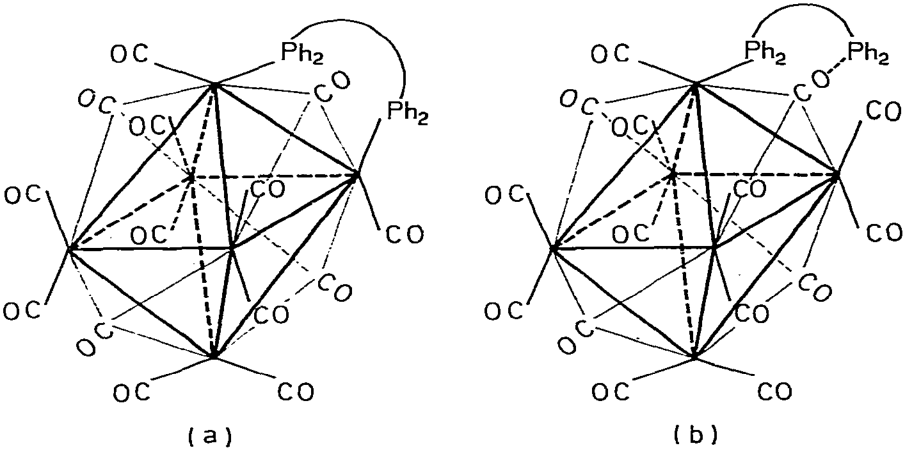

Fig. 1. Suggested coordination of diphos ligands in hexarhodium clusters: (a) diphosB and (b) diphosE.

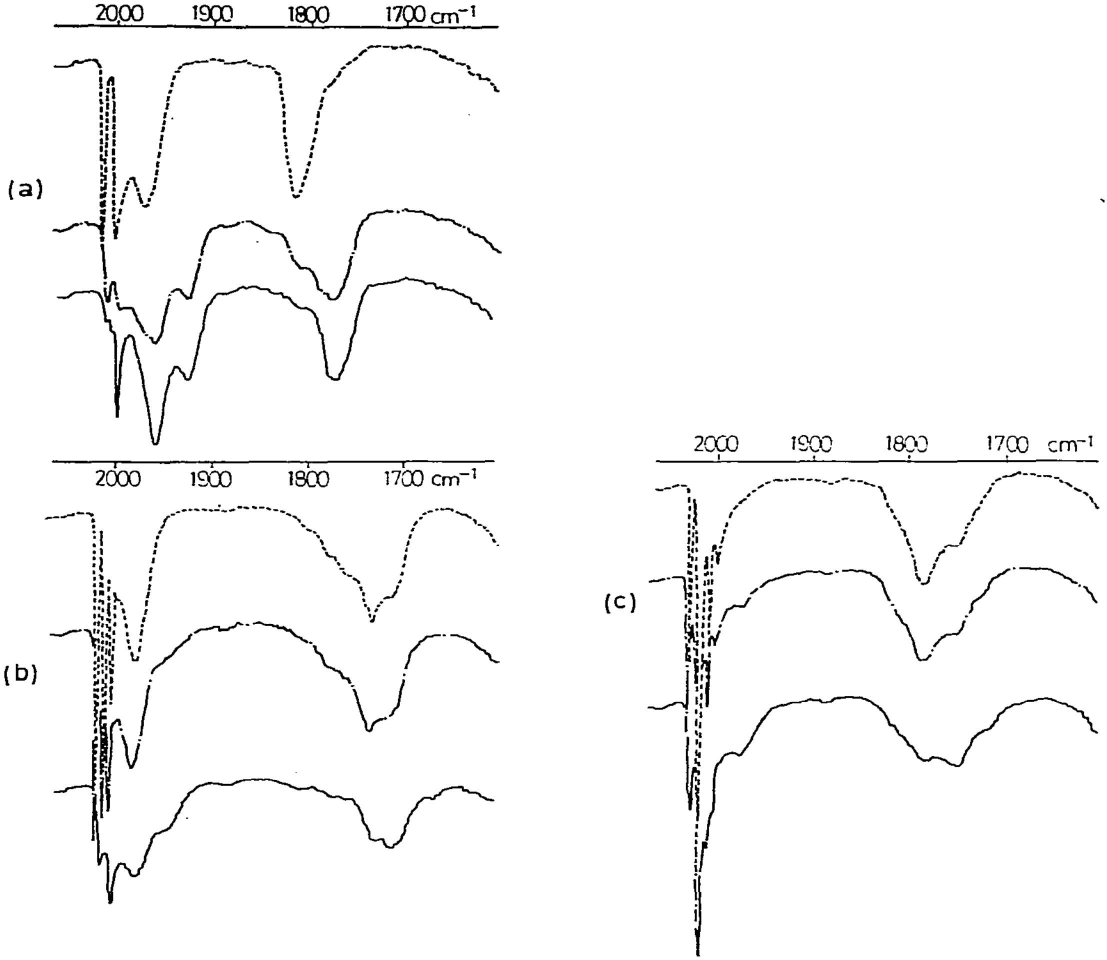

Fig. 2. The IR spectral change due to the inter-exchange between carbonyl groups in hexarhodium clusters and ^{13}CO in chloroform at 20°C; (a) $Rh_6(CO)_{12}(diphosB)_2$, (b) $Rh_6(CO)_{13}(diphosE)_3$ and (c) $Rh_6(CO)_{15}(diphosE)$. dashed line (- - - - - -): initial cluster ($t = 0$) 0.024 mmol in 4 ml $CHCl_3$, semi-dashed line (· — · — · — ·): after 18 h stirring under ^{13}CO (0.4 mmol), full line (————): further 138 h stirring under recharged ^{13}CO (0.4 mmol).

Under similar conditions, intermolecular carbonyl exchange of $Rh_6(CO)_{16}$ with ^{13}CO was extremely slow. In an 18 h reaction no exchange was observed by IR. After stirring for one month under excess of ^{13}CO, $Rh_6(CO)_{16}$ was obtained with the carbonyl ligands about 50% labelled. This was confirmed by the intensities of $\nu(CO)$ at 2020 (terminal) and 1760 cm^{-1} (face-bridging). All carbonyl groups of $Rh_6(CO)_{16}$ were exchanged, albeit extremely slowly, at the same time.

In both the diphosE mono- and tri-substituted clusters only a few percent of the terminal carbonyls were labelled and no exchange of face-bridging carbonyls was observed within 18 h. In prolonged ^{13}C-enrichment experiments (in which more than 80% of all carbonyl groups of $Rh_6(CO)_{12}(diphosB)_2$ were labelled after 138 h reaction following the preceding IR measurement) only about 10% of the terminal carbonyls and only a few percent of the face-bridging carbonyls in both the diphosE mono- and tri-substituted clusters were labelled. All carbonyls of the diphosE-substituted clusters do not exchange at the same time, and the rate of exchange of all carbonyls with ^{13}CO seems to be independent upon the number of coordinated diphosE.

As far as the exchange of face-bridging carbonyls with ^{13}CO is concerned, the diphosE-substituted clusters were slightly deactivated in comparison with $Rh_6(CO)_{16}$. On the other hand, the diphosB-disubstituted cluster was much more reactive than $Rh_6(CO)_{16}$. In qualitative experiments with a chloroform solution containing a mixture of the diphosB mono- and di-substituted clusters it was further found that the coordinated diphosB activates all carbonyl groups and accelerates their exchange with ^{13}CO.

These differences in the carbonyl exchange reactions of diphosB and diphosE derivatives might be caused by the mode of coordination of these bidentate ligands. Each phosphorus donor site of diphosB is coordinated to adjacent rhodium atoms, while only one donor site of diphosE is coordinated to a rhodium atom and the other site is possibly bound to a face-bridging carbonyl group.

The diphos-substituted hexarhodium clusters do not undergo intramolecular carbonyl exchange even at elevated temperature, being distinct from $Rh_4(CO)_{12}$ [9,10] and $Rh_4(CO)_{10}(PPh_3)_2$ [11]. They are distinct also from $Mn_2(CO)_{10}$, $Co_4(CO)_{12}$ and $Fe_3(CO)_{12}$ which undergo light-catalyzed exchange, as reported by Keely and Johnson [12]. Currently we are seeking homogeneous catalytic reactions of carbon monoxide which can be effected by these diphos-substituted clusters.

Experimental

All reactions were carried out under dry nitrogen. IR spectra were recorded on a Model EPI-G3 of Hitachi grating infrared spectrophotometer. ^{13}C NMR spectra were recorded in the Fourier transform mode on a Varian Associates XL-100-15 spectrometer in deuteriochloroform, using $Cr(acac)_3$ as relaxation reagent and using tetramethylsilane as internal standard.

Hexadecacarbonylhexarhodium, 1,2-bis(diphenylphosphino)ethane (diphosE), and 1,4-bis(diphenylphosphino)butane (diphosB) were purchased from Strem Chemicals, Inc. The ^{13}C-enriched carbon monoxide (91 atom%) enclosed in glass tube with breakable seal (250 ml, 760 Torr), purchased from B.O.C. Ltd. (Prochem), was connected to the vacuum line and used without further purification. Chloroform and deuteriochloroform were dried over P_2O_5, and were vacuum-distilled before use.

Reactions of hexadecacarbonylhexarhodium with bidentate phosphorus ligands

(a) Dodecacarbonylbis[1,4-bis(diphenylphosphino)butane]hexarhodium. The 1,4-bis(diphenylphosphino)butane (diphosB: 240 mg, 0.56 mmol) was added to hexadecacarbonylhexarhodium (200 mg, 0.19 mmol) suspended in chloroform (10 ml), with stirring, at room temperature. The mixture was stirred and the evolved carbon monoxide was evacuated from time to time and replaced with dry nitrogen. The progress of the reaction was monitored by IR

measurements at appropriate time intervals. After that no further spectral change at lower frequency (about 1800 cm^{-1}) was observed (about 42 h), the reaction mixture was evaporated to dryness. The residue was extracted with toluene and the unreacted, insoluble $Rh_6(CO)_{16}$ was filtered off. The red crystalline solid was crystallyzed from the toluene extracts; yield about 240 mg. (Found: C, 45.35; H, 3.63. $C_{68}H_{56}O_{12}P_4Rh_6$ calcd.: C, 45.18; H, 3.10%).

(b) Pentadecacarbonyl [1,2-bis(diphenylphosphino)ethane]hexarhodium. 1,2-Bis(diphenylphosphino)ethane (diphosE: 75 mg, 0.19 mmol) was added to a chloroform solution (10 ml) containing suspended $Rh_6(CO)_{16}$ (200 mg, 0.19 mmol), with stirring, at room temperature. A dark brick-red solid was obtained after 16 h reaction. Similar work-up was used. Recrystallization from benzene/n-hexane gave a yield of ca. 50 mg. (Found: C, 35.44; H, 2.14. $C_{41}H_{24}O_{15}P_2Rh_6$ calcd.: C, 34.26; H, 1.67%).

(c) Tridecacarbonyltris[1,2-bis(diphenylphosphino)ethane]hexarhodium. DiphosE (300 mg, 0.75 mmol) was slowly added with stirring to the chloroform solution (10 ml) containing suspended $Rh_6(CO)_{16}$ (200 mg, 0.19 mmol) at room temperature. A reaction time of 18 h and similar work-up gave an insoluble yellow compound and unreacted $Rh_6(CO)_{16}$. These were filtered off from the benzene solution which was evaporated. The dark brick-red product was recrystallized from benzene/n-hexane, yielding about 80 mg. (Found: C, 49.89; H, 3.79. $C_{91}H_{72}O_{13}P_6Rh_6$ calcd.: C, 50.18; H, 3.31%.)

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