Journal of Organometallic Chemistry, 96 (1975) 451—459

FIVE COORDINATE RHODIUM(I) OLEFIN COMPLEXES CONTAINING THE LIGAND BIS(BUT-3-ENYL)PHENYLPHOSPHINE

PETER W. CLARK* and GEORGE E. HARTWELL
Department of Chemistry, Indiana University, Bloomington, Indiana 47401 (U.S.A.)
(Received March 21st, 1975)

Summary

The complexes $Rh_2X_2(bbp)_2$ (X = Cl, Br or I; and bbp = bis(but-3-enyl)-phenylphosphine) have been prepared. These complexes have been characterized as five coordinate dimers in which the unsaturated phosphine acts as a tridentate ligand. Carbon monoxide reacts reversibly with the dimers forming the five coordinate monomeric compounds RhX(CO)(bbp). Mass spectral, infrared, Raman, and proton magnetic resonance data are consistent with the above formulations.

Introduction

Recently, there has been considerable interest in the isolation, characterization and reactions of unsaturated tertiary phosphine complexes of rhodium(I) [1-12]. We have taken advantage of the chelate effect of suitable unsaturated tertiary phosphines in order to study the possible intermediates occurring in the catalytic hydrogenation and isomerization reactions involving tertiary phosphine complexes of rhodium(I) [2], and following this investigation have found that the ligands $(C_6H_5)_2P(CH_2CH_2CH{=}CH_2)$ and $P(CH_2CH_2CH{=}CH_2)_3$ form the very stable five coordinate rhodium(I) complexes $RhCl[(C_6H_5)_2P(CH_2CH_2CH{=}CH_2)]_2$ [13] and $RhCl[P(CH_2CH_2CH{=}CH_2)_3]$ [3,11] respectively. Both compounds in the solid state are essentially trigonal bipyramidal in structure, with the olefins bonded to the rhodium atom. The analogous compound RhBr(tris-o-styrylphosphine) has been shown to have a similar structure [5]. The potentially multidentate ligands $(C_6H_5)P(CH_2CH_2CH{=}CH_2)_2$ [19], $(C_6H_5)As(CH_2CH_2CH_2CH{=}CH_2)_2$ [14] and $As(CH_2CH_2CH{=}CH_2)_3$ [15], act only in a bidentate or monodentate fashion in palladium(II) and platinum(II) complexes; in contrast,

---

* Present address: Chemistry Department, University of Queensland, St. Lucia, 4067, Brisbane (Australia).

we have now found that $(C_6H_5)P(CH_2CH_2CH{=}CH_2)_2$ is a very effective tridentate ligand with rhodium(I) complexes, and forms five coordinate compounds.

Experimental

Dichlorophenylphosphine, triphenylphosphine (Aldrich Chemical Company), carbon monoxide (Matheson Company) and 4- bromobut-1-ene (Pierce Chemical Company and PCR) were used without further purification. The rhodium complexes, $Rh_2Cl_2(CO)_4$ [16], $Rh_2I_2(C_8H_{12})_2$ [17] and $RhCl[(C_6H_5)_3P]_3$ [18] were prepared by the published methods. The preparation of the ligand bis(but-3-enyl)phenylphosphine has been described previously [19]. The rhodium trichloride was obtained from Engelhard.

Infrared spectra were recorded using Perkin—Elmer 137, 137G and 621 spectrometers and Raman spectra on a Cary 81 spectrometer using the He—Ne laser excitation at 6328 Å. Proton magnetic resonance spectra were obtained with Varian HA100 and HR220 spectrometers. The Varian HA100 spectrometer was normally operated in the field sweep mode. Air sensitive samples were prepared in an inert atmosphere and the NMR tube sealed under a vacuum. The temperature of the probe of the Varian HA100 spectrometer was calibrated from the chemical shifts of the protons of methanol (low temperature) and glycerol (high temperature). Molecular weights were measured using a Mechrolab Model 301-A vapor pressure osmometer and the mass spectra were recorded on a Varian MAT CH-7 and on an AEI MS-9. Melting points were obtained with a Fischer Johns Melting Point Apparatus, and are uncorrected.

Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory; West Germany, and by Huffman Laboratories, Inc., Wheatridge, Colorado.

Preparation of $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$. A stirred solution of 0.4 g (1.03 mmol) of $Rh_2Cl_2(CO)_4$ in 20 ml of dry benzene under nitrogen was heated to a gentle reflux. To this solution was added dropwise 0.52 ml (1.08 mmol) of $(C_6H_5)P(C_4H_7)_2$ in 5 ml of benzene. The solution was refluxed for 3 h giving a light brown solution. The product either precipitated during the reaction, or upon cooling, or seeding the hot solution. The yield of the golden flakes was 0.514 g, and the filtrate was concentrated to yield another 0.151 g, to give a total yield of 91%. The product was washed with benzene and dried in vacuo and could be recrystallized from methylene chloride. Analysis found: C, 44.0; H, 5.25; P, 8.29; Cl, 16.2%. M.p. 245°C. Mol. wt. 713 (M^+); 715 (vpo in chloroform). $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2 \cdot CH_2Cl_2$ calcd.: C, 43.6; H, 5.05; P, 7.76; Cl, 17.80%. Mol. wt. 713.

Preparation of $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$. (i) From $Rh_2Cl_2(CO)_4$. To a stirred solution of 0.05 g (0.13 mmol) of $Rh_2Cl_2(CO)_4$ in 8 ml of ethyl ether under nitrogen was added 0.06 ml (0.27 mmol) of $Rh_2Cl_2(CO)_4$ in 5 ml of ethyl ether. The solution was concentrated under a flow of nitrogen at room temperature to give an orange oil. The oil was redissolved in a 1/1 methylene chloride—ether mixture. Upon slow evaporation of this solution under nitrogen, 0.062 g (62.7%) of $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$ was obtained. The crystals were washed with ether and dried in vacuo.

(ii) From $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$. Carbon monoxide was bubbled through a deaerated suspension of 0.151 g (0.21 mmol) of freshly prepared $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$ in 10 ml of ethyl ether for 1 h. There was a definite reaction as both the crystal form and color of the crystals changed. The yellow crystals were collected, washed with ether and dried in vacuo to yield 0.135 g (83.5%) of the desired product. Analysis found: C, 46.9; H, 5.01; Cl, 9.17%. M.p. 101-104°C. Mol. wt. 446 (vpo in chloroform). $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$ calcd.: C, 46.8; H, 4.98; Cl, 8.05%. Mol. wt. 385.

Decarbonylation of $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$. (i) Upon heating a small quantity of $RhCl(CO)[C_6H_5)P(C_4H_7)_2]$ in refluxing acetone, methanol or benzene, carbon monoxide was evolved and the product was $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$ as identified by its infrared spectrum.

(ii) Upon heating a small quantity of $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$ in the solid state at ca. 80°C under a vacuum overnight, the majority of the carbon monoxide was removed to give mainly $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$ as identified by its infrared spectum.

Preparation of $RhCl[(C_6H_5)_3P][(C_6H_5)P(C_4H_7)_2]$. (i) To a stirred solution of 0.10 g (0.14 mmol) of $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$ in 5 ml of methylene chloride under nitrogen at room temperature was added 0.074 g (0.28 mmol) of triphenylphosphine in 5 ml of methylene chloride. The solution was heated and the product was crystallized with methanol and could be recrystallized from methylene chloride—methanol.

(ii) To a stirred suspension of 0.40 g (0.44 mmol) of $RhCl[(C_6H_5)_3P]_3$ in 2 ml of benzene under nitrogen was added 0.11 ml (0.47 mmol) of the ligand $(C_6H_5)P(C_4H_7)_2$. The solution was stirred at room temperature for ca. 1½ h and the resulting yellow crystals were separated by filtration, washed with benzene and dried in vacuo to yield 0.12 g (44%) of the complex. Analysis found: C, 62.2; H, 5.40; Cl, 5.82%. M.p. 124°C. Mol. wt. 605 (vpo in chloroform). $RhCl[(C_6H_5)_3P][(C_6H_5)P(C_4H_7)_2]$ calcd.: C, 62.1; H, 5.50; Cl, 5.75%. Mol. wt. 617.

Preparation of $Rh_2Br_2[(C_6H_5)P(C_4H_7)_2]_2 \cdot CH_2Cl_2$. To a solution of 0.30 g (0.42 mmol) of $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$ in a minimum amount of hot methylene chloride was added 0.60 g (6.9 mmol) of lithium bromide in a minimum amount of methanol. The solution was heated to boiling and the desired complex was crystallized with methanol to give 0.28 g (86%) of the bromide complex. This product was recrystallized from methylene chloride—methanol to yield 0.21 g (65%) of yellow-orange crystals. Analysis found: C, 41.2; H, 4.83%. Mol. wt. 757 (M^+). $Rh_2Br_2[(C_6H_5)P(C_4H_7)_2]_2 \cdot CH_2Cl_2$ calcd.: C, 39.3; H, 4.65%. Mol. wt. 757.

Preparation of $RhBr(CO)[(C_6H_5)P(C_4H_7)_2]$. (i) Carbon monoxide was bubbled through a suspension of 0.10 g (0.11 mmol) of $Rh_2Br_2[(C_6H_5)P(C_4H_7)_2]_2 \cdot CH_2Cl_2$ in 15 ml of ethyl ether at room temperature for 1 h. The solution was then filtered to yield 0.071 g (73.5%) of the product, which was washed with ethyl ether and dried in vacuo. Analysis found: C, 41.5; H, 4.36. $RhBr(CO)[(C_6H_5)P(C_4H_7)_2]$ calcd.: C, 42.0; H, 4.45%.

(ii) To a solution of 0.1 g (0.26 mmol) of $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$ in 3 ml of methanol under nitrogen was added 0.15 g (1.7 mmol) of lithium bromide in 1 ml of methanol. The solution was stirred at room temperature for 18 h. Upon filtering the solution, 0.022 g (20%) of the product was collected. This product so formed was shown to contain some $Rh_2Br_2[(C_6H_5)P(C_4H_7)_2]_2$ from its infrared spectrum.

Preparation of $Rh_2I_2[(C_6H_5)P(C_4H_7)_2]_2$. To a solution containing 0.20 g (0.30 mmol) of bis(cycloocta-1,5-diene)-μ,μ'-diiododirhodium in 6 ml of benzene under nitrogen was added 0.14 ml (0.61 mmol) of $(C_6H_5)P(C_4H_7)_2$. The solution was stirred at room temperature for at least 3 h. The resulting crystals were collected by filtration, washed with ether and dried in vacuo to yield 0.138 g (52%) of the product. When this compound was prepared from $Rh_2Cl_2[(C_6H_5)P(C_4H_7)_2]_2$ and sodium iodide at elevated temperatures or at room temperature, the compound was a yellow-green color due to some decomposition.

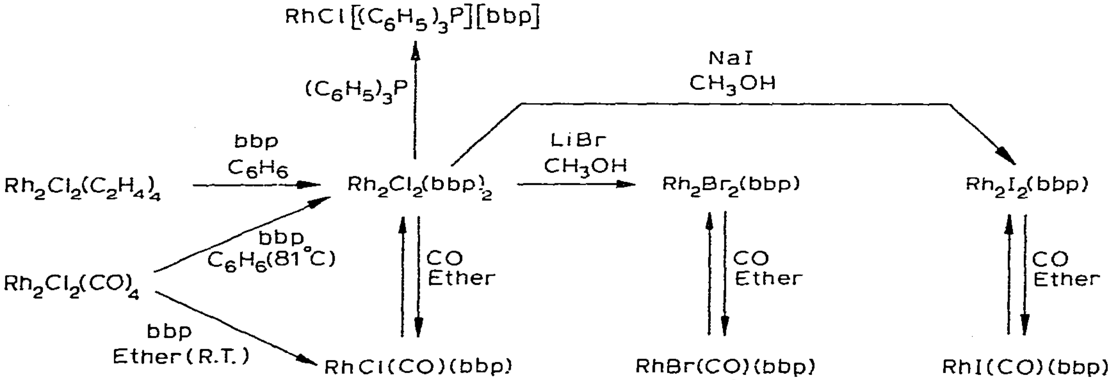
Preparation of $RhI(CO)[(C_6H_5)P(C_4H_7)_2]$. (i) Carbon monoxide was bubbled through a suspension of 0.138 g (0.154 mmol) of $Rh_2I_2[(C_6H_5)P(C_4H_7)_2]_2$ in 15 ml of ether at 0°C for 6 h. The resulting orange-yellow crystals were collected, washed with ether and dried in vacuo to yield 0.111 g (76%).

(ii) To a solution of 0.05 g (0.13 mmol) of $RhCl(CO)[(C_6H_5)P(C_4H_7)_2]$ in 3 ml of methanol was added 0.12 g (0.80 mmol) of sodium iodide in 1 ml of methanol. The light-orange precipitate that formed was collected by filtration, washed with methanol and dried in vacuo. The yield was 0.020 g (32%).

Discussion

The reaction of the ligand phenyl(bis-*o*-vinylphenyl)phosphine (dvpp) with bis(cycloocta-1,5-diene)-μ,μ'-dichlorodirhodium(I) yields an insoluble product with the stoichiometry RhCl(dvpp), assumed to be dimeric with bridging chlorine atoms [9]. By using the related tridentate ligand, bis(but-3-enyl)phenylphosphine(bbp) [19], we have isolated a similar series of complexes having the formula RhX(bbp) (X = Cl, Br or I). (The preparations and reactions are represented in Scheme 1 below.) However, due to the nature of the butenylphosphines, the isolated complexes are soluble enough to obtain accurate solution data, viz. PMR, IR and molecular weights. The molecular weights were checked with mass spectrometry, and the compounds were found to be dimeric.

SCHEME 1



The dimeric complexes $Rh_2X_2(bbp)_2$, (X = Cl, Br or I) react reversibly with carbon monoxide forming the monomeric complexes RhX(CO)(bbp). The triphenylphosphine adduct $RhCl[(C_6H_5)_3P](bbp)$ was also prepared.

The stretching frequency of the olefin in the ligand occurs at 1634 cm^{-1}

TABLE 1

INFRARED AND RAMAN DATA[a] FOR COMPLEXES OF bbp = $(C_6H_5)P(CH_2CH_2CH{=}CH_2)_2$

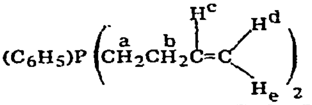
	ν(CO) KBr (IR)	ν(CO) CH_2Cl_2 (IR)	Band I (IR)	Band II (R)	$\nu(Rh—olefin)_s$ (R)	$\nu(Rh—olefin)_{as}$ (R)
bbp			1634 (oil)			
$Rh_2Cl_2(bbp)_2$			1477 w	1227	396	470 or 517
$Rh_2Br_2(bbp)_2$			1500 w	1231	405	472 or 521
RhCl(CO)(bbp)	2016 s 2004 s 1976 (sh)	2035 s	nr	1231	388	503
RhBr(CO)(bbp)	2012 s 2000 s 1976 (sh)	2045 s	nr			
RhI(CO)(bbp)	2028 s 2012 s	2033 s	1499 w	1229	394	513

[a] IR = infrared, R = Raman, s = symmetric, as = asymmetric; w = weak, m = medium, s = strong, nr = not resolved. Raman spectra taken on solid samples. All measurements are in cm^{-1}

(Table 1) and in the complexes this has been shifted to lower energy consistent with coordinated olefins. The band I frequency occurs around 1500 cm^{-1} and the band II frequency occurs around 1230 cm^{-1} in agreement with the recent assignment for bonded olefin groups [20]. For two of the complexes RhX(CO)(bbp), X = Cl or Br, band I was not resolved. It is assumed that this band is essentially coincident with the 1486 cm^{-1} band which occurs in the ligand. This phenomenon also occurs in the complexes $Rh_2Cl_2[(C_6H_5)_2P(CH_2CH_2CH{=}CH_2)]_2$ and $Rh_2Cl_2[(C_6H_5)_2P(CH_2CH_2CH_2CH{=}CH_2)]_2$ [21]. The symmetric platinum—olefin stretching frequency has been assigned in the 400 cm^{-1} region and asymmetric stretch in the 490 cm^{-1} region [22,23]. However, this latter band is either absent or very weak in other platinum and palladium complexes [24]. In the

TABLE 2

PMR[a] DATA FOR COMPOUNDS CONTAINING bbp


$(C_6H_5)P\left(\overset{a}{C}H_2\overset{b}{C}H_2\overset{H^c}{C}{=}C\begin{matrix}H^d\\H_e\end{matrix}\right)_2$

	Phenyl	a b	c	d	e	$J(H_c—H_d)$	$J(H_c—H_e)$
bbp	2.4-2.8	8.2 7.92	4.19	5.08	5.00	10.0	17.0
$Rh_2Cl_2(bbp)_2$	2.2-2.8	7.7-8.3[b]	4.86	5.81	6.72	9.0	12.0
$Rh_2Br_2(bbp)_2$	2.2-2.8	7.7-8.3[b]	4.95	5.70	6.63	9.0	12.0
RhCl(CO)(bbp)	2.45-2.65	7.2-8.1[b]	5.12	6.42	6.61	8.5	11.5
RhBr(CO)(bbp)	2.4-2.6	7.15-8.2[b]	5.06	6.31	6.62	8.5	11.5
RhI(CO)(bbp)[c]	2.4-2.6	7.15-8.2[b]	4.91	6.10	6.65	8.5	11.5
$RhCl[bbp][(C_6H_5)_3P]$	2.6-3.1	7.8-8.2[b]	5.00	6.8-7.2[b]		[b]	[b]

[a] Measured at 100 MHz; chemical shifts in ppm relative to TMS, τ = 10.0, except where noted; coupling constants in Hz. All samples were dissolved in $CDCl_3$. [b] Overlapping or not resolved. [c] Relative to C_6H_6, τ = 2.63.

complexes studied here, a strong absorbance was observed in the 400 cm^{-1} region and another absorbance was observed in the 490 cm^{-1} region in the Raman. However, in complexes of rhodium containing the ligand $P(C_4H_7)_3$, which are monomeric in solution and trigonal bipyramidal, there is no observable band in 490 cm^{-1} region [21]. The symmetric rhodium—olefin stretch occurs from 388-405 cm^{-1} for the compounds studied here. The band in the 490 cm^{-1} region is noted, but at present cannot be definitely assigned to the asymmetric rhodium—olefin stretch.

The PMR spectra (Table 2) of all the compounds exhibit the same essential points; (i) the resonances for protons a and b are overlapping, (ii) protons c, d, and e have shifted upfield compared to the free ligand and (iii) the *cis* and *trans* coupling constants of the olefin have decreased compared to the free ligand. The resonances for c protons have shifted between τ0.67-0.93, d protons between τ0.62-1.34 and e protons between τ1.61-1.72. The *cis* coupling constant has decreased from 10.0 Hz in the ligand to 9.0 or 8.5 Hz; and the *trans* coupling constant from 17.0 to 12.0 or 11.5 Hz. In all cases, little, if any, extra coupling besides $J(H_c—H_d)$ or $J(H_c—H_e)$ was resolved for protons d and e. Since the line widths of the olefinic resonances are ca. 3-4 Hz at room temperature and do not exhibit further coupling, it is assumed that the other possible coupling constants, $J(H_b—H_d)$, $J(H_d—H_e)$, $J(Rh—H_c)$, $J(Rh—H_d)$, $J(Rh—H_e)$ are less than 0.5 Hz. The coupling between b and c is of about the same order as that observed for $RhCl[P(CH_2CH_2CH{=}CH_2)_3]$ [3] (ca. 3 Hz).

The above observations are consistent with the olefins bonded to the rhodium in agreement with the infrared data in the solid state and in solution. The only exception to this could be $RhCl[bbp][(C_6H_5)_3P]$ which shows broad resonances in the PMR, but no unbonded olefin in the IR in solution. This broadening could be due to intramolecular rearrangements [25] or extra coupling or both. For the first five complexes in Table 2, the two butene chains on each phosphine are obviously magnetically equivalent as required by the simplicity of the olefinic resonances.

The proposed structure for the dimeric complexes $Rh_2X_2(bbp)_2$ is shown in Fig. 1. Since the individual olefinic protons are magnetically equivalent on the NMR time scale, and there is no evidence for bonded—non bonded olefin exchange, the olefins on each rhodium atom must be related by a plane which contains the rhodium, phosphorus and halogen atoms. This is required since

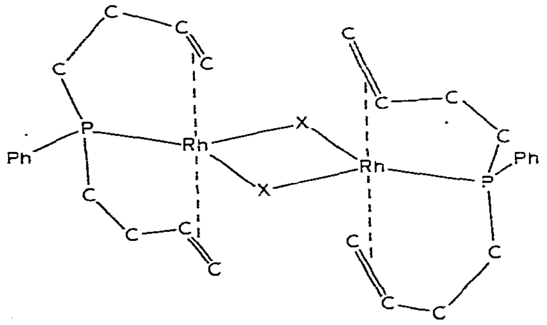


Fig. 1. Proposed structure for $Rh_2X_2[(C_6H_5)P(C_4H_7)_2]$ (*trans*-configuration).

otherwise there would be inequivalence introduced from the phenyl ring. Using the same argument for the whole molecule (i.e., the equivalence of the olefinic protons on both trigonal bipyramids), the overall sterochemistry could be *cis* or *trans*. If the stereochemistry was *cis*, the halves of the molecule would be related by a mirror plane through the bridging halides. If it was *trans*, the halves of the molecules would be related by an S_2 axis (C_2 operation along the Rh—Rh line plus a mirror plane through the bridging halides). Neither the *cis* nor *trans* configuration seem to be preferred over the other upon consideration of models of the compound. The structure drawn has the *trans*-configuration. The plane containing the two olefinic bonds on each trigonal bipyramid would be perpendicular or slightly skew of perpendicular to the Rh—Rh line. If the plane containing the two olefinic bonds on each trigonal bipyramid also contained the Rh—Rh line, there could be considerable steric interference of the olefinic protons across the bridging structure.

The proposed structure for the monomeric carbonyl complexes RhX(CO)(bbp) (Fig. 2) is quite similar to that found for $RhCl[P(CH_2CH_2CH{=}CH_2)_3]$ [11]. Indeed, this would merely involve the exchange of one olefinic group with a carbon monoxide, and the trigonal bipyramidal structure is favored by back bonding arguments. The high value for the carbonyl stretching frequencies is in agreement with the carbonyl opposite the olefinic groups. For the compounds RhX(CO)(bbp), there are distinct resonances for the methylene protons in the ratio of 1/7 at τ 7.35 and at τ 7.55-8.20 respectively at 100 MHz, while at 220 MHz, they are in the ratio of 1/3/4 upon separating (see Fig. 3). The high field resonances (area 4) are in broad quartet, the other resonances are broad and show little visible coupling. The upfield resonances most likely belong to protons a, and the downfield resonances to protons b in which there is different P—H coupling. Indeed, a similar pattern is noticed in the low temperature spectra of $RhCl[P(CH_2CH_2CH{=}CH_2)_3]$ and $RhI[P(CH_2CH_2CH{=}CH_2)_3]$ [21]. The methylene protons will be inequivalent due to the restricted rotation about the $P{-}CH_2$ and $CH_2{-}CH_2$ bonds and due to the inequivalence introduced by the phenyl ring (see Fig. 4 for the different conformations). In the temperature dependent PMR spectrum of RhCl(CO)(bbp) from room temperature (ca. 32°C) to —60°C, there is essentially no chemical shift change and no coupling constant variation in the alkene protons (a C_6H_6 lock was used and this precluded

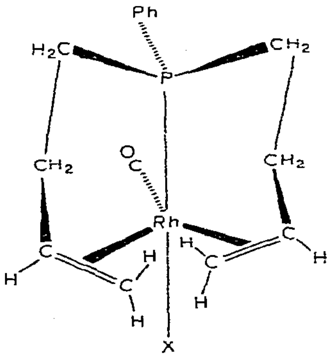


Fig. 2. Proposed structure for the complexes $RhX(CO)[(C_6H_5)P(CH_2CH_2CH{=}CH_2)_2]$.

Fig. 3. PMR spectrum of RhCl[CO][$(C_6H_5)P(CH_2CH_2CH{=}CH_2)_2$] relative to internal TMS = τ10.0, at 220 MHz in $CDCl_3$.

observations of the phenyl protons). Some broadening is observed at −60°C and this could be due to loss of resolution of partial crystallization of the sample at that temperature. These observations are in agreement with the non-observance of free olefin in the infrared for RhCl(CO)(bbp) in methylene chloride at room temperature. This indicates that between 32 and −60°C there is no fluxional behaviour between bonded and free olefin. Although the olefinic protons (c, d and e) are equivalent on both butene chains, it is not possible to conclude whether the olefins are directed towards or away from the carbonyl. (In Fig. 2 the direction of the olefins is away from the carbonyl.) In both cases the phenyl ring would lie above the carbonyl group. It would also be expected, that in the compounds RhX(CO)(bbp), the olefin—rhodium—olefin and the P—Rh—X angles would increase and decrease respectively, in order to minimize steric strain as compared to RhX[$P(CH_2CH_2CH{=}CH_2)_3$]. In this position, the olefins could more easily lie in the equatorial plane than in RhX[$P(CH_2CH_2CH{=}CH_2)_3$].

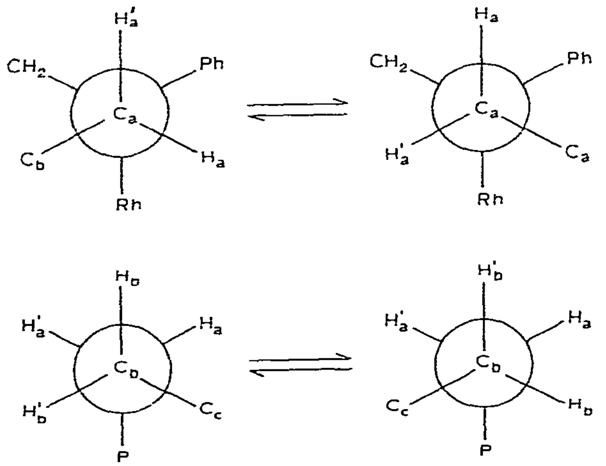
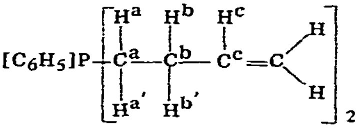


Fig. 4. Configuration of methylene protons in the complexed ligand



$$[C_6H_5]P\left[\overset{H^a}{\underset{H^{a'}}{C^a}}-\overset{H^b}{\underset{H^{b'}}{C^b}}-\overset{H^c}{C^c}{=}C\begin{matrix}H\\H\end{matrix}\right]_2$$

Acknowledgements

The authors wish to thank Dr John Cotton for his useful comments in the preparation of the manuscript and Mr Paul Koeneman for obtaining the Raman spectra.

References

1 M.A. Bennett and P.A. Longstaff, J. Amer. Chem. Soc., 91 (1969) 6266.
2 G.E. Hartwell and P.W. Clark, Chem. Commun., (1970) 1115.
3 P.W. Clark and G.E. Hartwell, Inorg. Chem., 9 (1970) 1948.
4 D.I. Hall and R.S. Nyholm, Chem. Commun., (1970) 488.
5 C. Nave and M.R. Truter, Chem. Commun., (1971) 1253.
6 M.A. Bennett and E.J. Hann, J. Organometal. Chem., 29 (1971) C15.
7 M.A. Bennett, S.J. Gruber, E.J. Hann and R.S. Nyholm, J. Organometal. Chem., 29 (1971) C12.
8 M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, Chem. Commun., (1972) 1011.
9 D.I. Hall and R.S. Nyholm, J. Chem. Soc. Dalton Trans., (1972) 804.
10 M.A. Bennett, R.N. Johnson and I.B. Tomkins, J. Organometal. Chem., 54 (1973) C48.
11 M. Orrico Visscher, J.C. Huffman and W.E. Streib, Inorg. Chem., 13 (1974) 792.
12 J.L.S. Curtis and G.E. Hartwell, J. Chem. Soc. Dalton Trans., (1974) 1898.
13 R.R. Ryan and R.O. Schaeffer, private communication.
14 M.A. Bennett, H.W. Kouwenhoven, J. Lewis and R.S. Nyholm, J. Chem. Soc., (1964) 4570.
15 C.A. McAuliffe and D.G. Watson, J. Chem. Soc. Dalton Trans., (1974) 1531.
16 J.A. McCleverty and G. Wilkinson, Inorg. Syn., 8 (1966) 211.
17 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
18 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
19 P.W. Clark, J.L.S. Curtis, P.E. Garrou and G.E. Hartwell, Can. J. Chem., 52 (1974) 1714.
20 D.B. Powell, J.G.V. Scott and N. Sheppard, Spectrochim. Acta, Part A, 28 (1972) 327.
21 P.W. Clark and G.E. Hartwell, unpublished results.
22 J. Hiraishi, Spectrochim. Acta, Part A, 25 (1969) 749.
23 J. Hiraishi, D. Finseth and F.A. Miller, Spectrochim. Acta, Part A, 25 (1969) 1657.
24 M.J. Grogan and K. Nakamoto, J. Amer. Chem. Soc., 88 (1966) 5454.
25 J.R. Shapley and J.A. Osborn, J. Amer. Chem. Soc., 92 (1970) 6978.