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OXIDATIVE ADDITION REACTIONS OF RHODIUM(I) COMPLEXES CONTAINING BIDENTATE UNSATURATED TERTIARY PHOSPHINE LIGANDS

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Summary

The oxidative addition reactions of RhCpPPh$_2$R (R = OCH$_2$CH=CH$_2$ (map) or CH$_2$CH$_2$CH=CH$_2$ (mbp)) have been investigated. RhCp(map) and RhCp(mbp) react with one mole of X$_2$ (X = Br or I) to yield stable dihalide adducts with a non-coordinated olefin. RhCp(mbp) reacts with methyl halides primarily yielding ionic compounds which do not undergo migration of the methyl group to the coordinated olefin. The isolation of these ionic intermediates, [RhCp(mbp)CH$_3$]X, is consistent with formation by a S_N2 reaction mechanism with the Rh^I complex acting as the nucleophile. The reaction of RhCp(mbp) with MeX also yields small amounts of products which contain a metallocyclic ring, RhCp[CH(CH$_2$CH$_3$)CH$_2$CH$_2$PPh$_2$]X (7%) and possibly RhCp[CH(CH$_3$)-CH$_2$CH$_2$CH$_2$PPh$_2$]X (1%). RhCp(mbp) also reacts in solution with hydrogen halides, benzyl and allyl halides but not with carbon monoxide. In contrast, RhCp(map) reacts with carbon monoxide to form RhCp(map)CO but does not react with the organohalides.

^{1}H NMR and infrared data indicate a considerably stronger rhodium—olefin interaction for the Rh^I than for the Rh^{III} complexes, and this difference is related to the reactivity of the coordinated olefin. Thus, RhCp(mbp) can be recovered unreacted from a methanolic solution of sodium methoxide while the ionic Rh^{III} complex [RhCp(mbp)CH$_3$]I, which has less electron density on the olefin, reacts with the nucleophile yielding RhCp[CH$_2$CH(OCH$_3$)CH$_2$CH$_2$PPh$_2$]-CH$_3$.

Introduction

Oxidative addition reactions of metal complexes have received considerable attention since 1965 resulting in several proposed mechanisms [1, 2, 3, 4, 5]. Although the major effort has involved the study of four-coordinate complexes, recent investigations of the formally five-coordinate, 18 electron complexes, MCp(L$_1$)(L$_2$), where M = Rh^I or Ir^I, L$_1$ = PMe$_2$Ph or PPh$_3$ and L$_2$ = CO or

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C_2H_4, has resulted in the isolation of ionic complexes indicating that the metal is functioning as a Lewis base, i.e. nucleophile [6—10]. These ionic complexes can then undergo loss of L_2 to yield neutral M^{III} complexes or migration of X to L_2 (L_2 = CO) to form neutral M^{III} complexes with attachment of Y to the metal. A study of the reaction of $RhCp(PPh_3)(C_2H_4)$ with alkyl halides should,

$$MCp(L_1)(L_2) + XY \rightarrow [MCp(L_1)(L_2)X]Y \begin{cases} \rightarrow MCp(L_1)XY \\ \rightarrow MCp(L_1)(L_2X)Y \end{cases}$$

in principle, allow both an investigation of the oxidative addition mechanism and the behavior of the coordinated olefin. This reaction, however, resulted in the direct formation of $RhCp(PPh_3)(R)(X)$ with loss of the coordinated ethylene and no indication of olefinic interaction with the coordinated alkyl group [9], although alkyl migration to coordinated olefins is well documented in the Ziegler—Natta catalytic systems and has also been proposed for the conversion of $RhCp(C_2H_4)(C_2H_5)Cl$ to $RhCp[(CH_2)_3CH_3](PPh_3)Cl$ in the presence of triphenylphosphine [11].

In order to facilitate such studies of rhodium—olefin complexes, the olefin can be incorporated as part of a tertiary substituted phosphine in which the potentially bidentate ligand may allow the isolation of complexes that would otherwise be unstable. The coordinated olefin might be expected [12] to (1) undergo hydride, methyl or halogen transfer from the metal to the olefin resulting in a metal—alkyl bond, (2) become unbonded as the alkyl halide oxidatively adds to the metal, or (3) undergo attack by Lewis bases (e.g. methoxide ion).

We have synthesized the complexes $RhCp(PPh_2OCH_2CH{=}CH_2)$ and $RhCp(PPh_2CH_2CH_2CH{=}CH_2)$ [13], and wish to report on the results of several reactions which could have involved the coordinated olefin.

Experimental

^1H NMR spectra were measured with a Varian HR220 spectrometer. The ^{31}P NMR spectra were obtained at 40.5 MHz using a Varian XL100 spectrometer and Fourier transform pulse methods with random noise decoupling of the protons. IR spectra (4000—670 cm^{-1}) were obtained using Perkin—Elmer 137 and 621 instruments. Melting points (uncorrected) were measured with a Fisher—Johns hot stage apparatus. Molecular weights were determined by mass spectrometry at 70 eV using a Varian MAT CH-7 mass spectrometer. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee or by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim, Germany.

All preparations and reactions were carried out under an argon atmosphere using degassed reagent grade solvents which had been dried previously over sodium wire. The ligands [14] and the starting compounds [13], (3-butenyldiphenylphosphine)-π-cyclopentadienylrhodium(I), RhCp(mbp) and (2-allyldiphenylphosphinite)-π-cyclopentadienylrhodium(I), RhCp(map), were prepared as previously reported. The gases, H_2, CO, MeBr, MeCl, HCl and HBr were passed through a solution of benzene prior to introduction into the reaction flask in order to remove impurities and to saturate the incoming gas with benzene. Benzyl iodide, benzyl bromide, methyl iodide, allyl bromide and allyl iodide were

TABLE 1

π-CYCLOPENTADIENYLPHOSPHINERHODIUM(III) DERIVATIVES PREPARED IN THIS WORK

Compound	Color	M.p. (°C)	Yield (%)	Analyses found (calcd.) (%)[a]			
				C	H	X	P
$RhCp(mbp)Br_2$	orange	136–138	59	44.20 (44.37)	3.97 (3.90)	28.45 (28.16)	5.30 (5.46)
$RhCp(mbp)I_2$	violet	170–172	69	38.37 (38.07)	3.40 (3.35)	38.18 (38.37)	
$RhCp(map)Br_2$	orange	126–128	60	42.54 (42.11)	4.36 (3.54)	27.22 (28.08)	
$RhCp(map)I_2$	violet	178–180	56	36.10 (36.14)	3.08 (3.04)	38.44 (38.25)	
$[RhCp(map)(CH_3)]I$	yellow	102–104	92	47.85 (48.00)	4.65 (4.58)	22.95 (23.09)	5.51 (5.63)

[a] In addition, a peak corresponding to the parent ion was present in the mass spectrum of each compound except the ionic complex. $[RhCp(mbp)(CH_3)]I$, which had the expected parent ion at 423 corresponding to $[RhCp(mbp)CH_3]^+$.

distilled immediately before use. Chlorine was introduced by saturation of a 5 ml benzene solution at 25° C.

The compounds prepared and their analytical data are listed in Table 1.

Preparation of $RhCp(mbp)Br_2$

The dropwise addition of 2 ml of a benzene solution containing 0.320 mmol of bromine to a stirred solution of RhCp(mbp), 0.130 g (0.32 mmol), in 10 ml benzene resulted in an immediate color change. After complete addition of the bromine (ca. 5 min) the solution was orange. This solution was stirred at room temperature under argon for 2 h. Reduction of the solvent volume to ca. 5 ml caused precipitation of orange microcrystals. The precipitate was collected by filtration, washed three times with 1 ml portions of ether, and vacuum dried for 12 h. The compound may be recrystallized from benzene/ether.

Preparation of $RhCp(map)Br_2$

This compound was prepared as described above. A precipitate formed immediately upon addition of bromine, but redisolved after 2 min. The compound may be recrystallized from benzene/ether.

Preparation of $RhCp(mbp)I_2$

The dropwise addition of 2 ml of a benzene solution containing 0.063 g (0.248 mmol) of I_2 to a stirred solution of RhCp(mbp), 0.100 g (0.245 mmol), in 10 ml of refluxing benzene resulted in an immediate color change from yellow to violet. After refluxing for 2 h, the solution volume was reduced to 2 ml and 5 ml of ether was added, resulting in precipitation of violet microcrystals. The crystals were collected by filtration, washed twice with 1 ml portions of ether and vacuum dried for 12 h. They are moderately soluble in ether and very soluble in benzene or chloroform.

Preparation of $[RhCp(mpb)CH_3]I$

An excess of methyl iodide, 0.30 ml (0.685 g, 4.8 mmol) was injected into a solution of RhCp(mbp), 0.125 g (0.31 mmol) in 15 ml of benzene. The yellow solution underwent a color change during the first minute, became cloudy, then after 4 min of stirring at room temperature, slowly precipitated a yellow microcrystalline powder. After 8 h, the crystals were collected by filtration, washed 3 times with 1 ml portions of ether, and vacuum dried for 12 h. The complex is insoluble in benzene, hexane and ether; slightly soluble in $CHCl_3$ and CH_2Cl_2. In addition to a peak at mass 423 for the ion $[RhCp(mbp)CH_3]^+$, a peak at mass 550 which may be assigned to the rearranged complex, $RhCp[CH(CH_2CH_3)CH_2CH_2PPh_2]I$, was observed.

Preparation of [RhCp(mbp)CH₃]Br

A slow stream of methyl bromide was passed for 4 h through a solution of RhCp(mbp), 0.125 g (0.31 mmol), in 15 ml of benzene leading to the slow precipitation of yellow microcrystals. The crystals were collected by filtration in air, washed 3 times with 1 ml portions of ether, and vacuum dried for 12 h. The complex has the same solubility properties as $[RhCp(mbp)CH_3]I$, and essentially the same IR spectrum. In addition to a peak at mass 423 for the ion $[RhCp(mbp)CH_3]^+$, a peak at mass 503 which may be assigned to the rearranged complex, $RhCp[CH(CH_2CH_3)CH_2CH_2PPh_2]Br$, was observed.

Results and discussion

RhCp(mbp) and RhCp(map) react with 1 mole equivalent of X_2 (X = Br or I) resulting in the cleavage of the rhodium(I)—olefin bond without halogen transfer to the free olefin (Fig. 1). The addition of a second mole of X_2 primarily results in halogenation of the nonbonded olefin, i.e. $RhCp[PPh_2CH_2CH_2CHXCH_2X]X_2$. Similar complexes with Cl_2 could not be isolated at room temperature due to decomposition including the loss of the cyclopentadienyl group. The ^1H NMR assignments of these complexes are based on data published for related systems and are fully internally consistent for the whole range of complexes studied. Chemical shifts for the protons, labeled as shown in Fig. 1, are given in Table 2. The ^{31}P NMR data are useful in differentiating rhodium oxidation states; the phosphorus resonance for Rh^I complexes is at lower field versus corresponding Rh^{III} complexes, consistent with the behavior of similar rhodium complexes upon increasing coordination number and oxidation state [15]. The expected reduction in $^1J(Rh—P)$ for the Rh^{III} versus the Rh^I complexes can also be noted.

The reaction of RhCp(mbp) with methyl halides takes place allowing the isolation of the cationic Rh^{III} complexes, $[RhCp(mbp)CH_3]X$, X = Br of I, similar to the reactions of $RhCp(PMe_2Ph)(CO)$ [6] and $RhCp(AsPh_3)(C_2H_4)$ [9]. The relative rates of reaction of the methyl halides are $CH_3I > CH_3Br > CH_3Cl$. Very little of the CH_3Cl adduct could be isolated from the decomposition products that accompanied the extended reaction time. The ^1H NMR data of the cationic complexes are shown in Table 2. The methyl group attachment to Rh^{III} is verified by the magnitude of $^2J(Rh—H)$ and $^3J(P—H)$.

Comparison of the infrared and ^1H NMR data for these Rh^{III} complexes with that of the corresponding Rh^I complexes is consistent with significantly different degrees of rhodium—olefin interaction. The coordinated olefin can be detected in the infrared by the presence of an absorption at 1474 ± 5 cm^{-1} in RhCp(mbp). The large shift of this absorption from that of the free olefin,

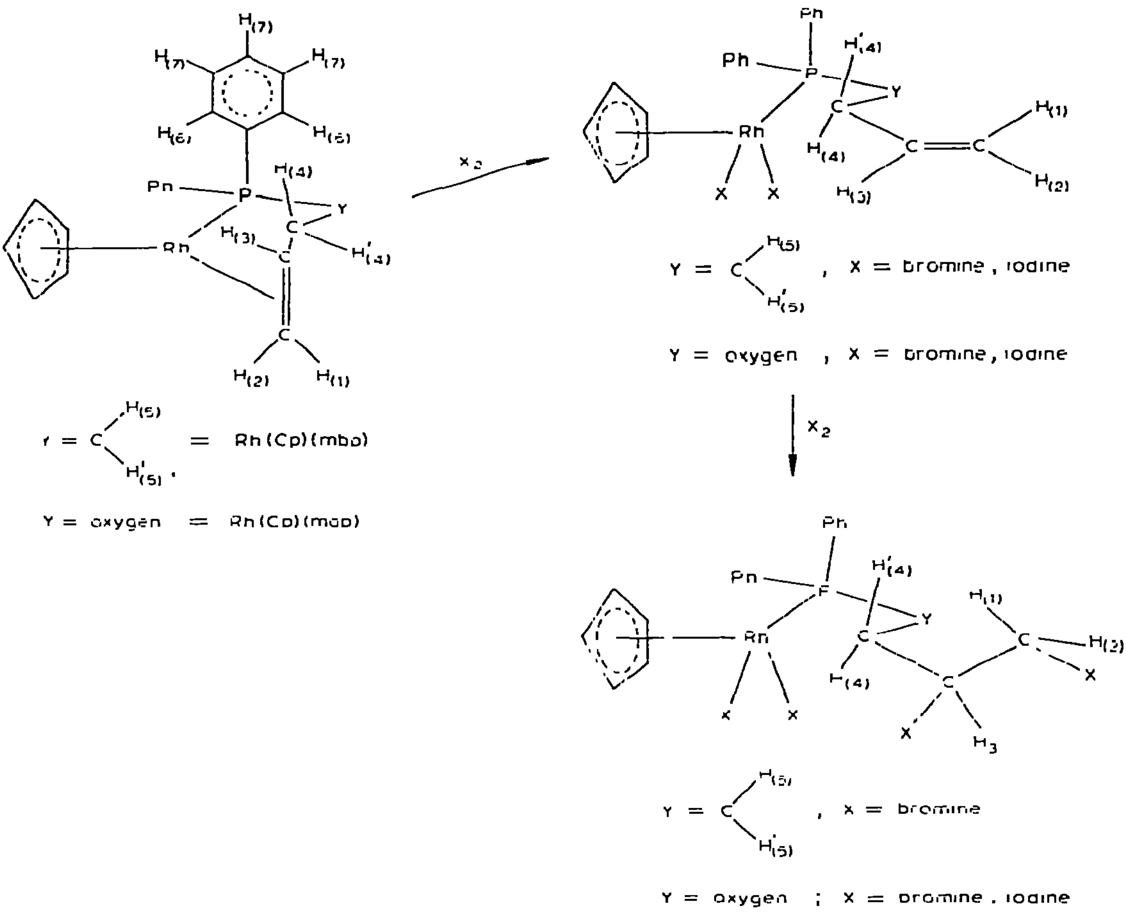

Fig. 1. Reaction of RhCp(mbp) and RhCp(map) with X_2 (X = Br, I).

1641 cm^{-1}, is indicative of a strong rhodium—olefin interaction (δ_ν = 167 ± 5 cm^{-1}). The absorption of the coordinated olefin in the ionic complexes, [RhCp(mbp)CH_3]X, is at 1502 cm^{-1} (δ_ν = 139 cm^{-1}) indicating a weaker rhodium—olefin interaction [12]. A similar conclusion is indicated by the ^{1}H NMR data as each olefinic proton is shifted to lower field versus the corresponding proton in the Rh^I complex, e.g. compare [RhCp(mbp)CH_3]I with RhCp(mbp). Similar chemical shift trends for these olefinic protons can be noted for RhCp(C_2H_4)(C_2H_5)Cl versus RhCp$(C_2H_4)_2$ [16].

The ionic complexes, [RhCp(mbp)CH_3]X, are insoluble in benzene but soluble in chloroform, methylene chloride, and methanol. When the ionic iodide complex is dissolved in either chloroform or methanol and stirred for ca. 2 h at room temperature, even with an excess of methyl iodide, no change in the ^{1}H NMR of the initial complex occurs. In these ionic complexes, no indication of methyl transfer to the coordinated olefin has been observed. If the solution containing methyl iodide is allowed to stir for longer periods, 16 to 25 h, RhCp(mbp)(CH_3)I and RhCp(mbp)I_2, both having an uncoordinated olefin, may be identified by ^{1}H NMR. Similarly, RhCp(C_2H_4)(PPh_3) has been reported to react with methyl iodide to yield RhCp(PPh_3)(CH_3)I and small amounts of RhCp-

TABLE 2

NMR AND IR DATA [a]

Compound	H(1)	H(2)	H(3)	H(6)	H(7)	H(Cp)	$J(1,3)$ (Hz)	$J(2,3)$ (Hz)	$J(P-Cp)$ (Hz)	$\delta(^{31}P)$	$J(Rh-P)$ (Hz)	$\nu(C=C)$ (cm^{-1})
$PPh_2OCH_2CH{=}CH_2$ (map) [b]	4.72 d	4.88 d	4.24 m	2.51 m	2.72 m		17.0	10.3		−113.0		1649
RhCp(map) [c]	8.97 d	7.58 d	6.12 m	2.30 m 2.66 m	2.66 m	4.75 s	10.0	7.5	1.1	−169.0	216.0	1475
$RhCp(map)Br_2$ [d]	4.66 d	4.82 d	4.1 m	2.14 m	2.55 m	4.65 s	17	10	2.0	−115.5	140.0	1649
$RhCp[PPh_2OCH_2CHBrCH_2Br]Br_2$ [e]	6.2 (br)	6.2 (br)	5.7 (br)	2.09 m	2.56 m	4.61 s			2			
$RhCp(map)I_2$ [f]	4.66 d	4.79 d	4.1 m	2.24 m	2.55 m	4.52 s	17	10	2.1	−118.1	152.4	1649
$RhCp[PPh_2OCH_2CHICH_2I]I_2$	6.07 q	6.20 t	5.9 m	2.2 m	2.5 m	4.45 s			2			
RhCp(map)CO	4.65 d	4.8	4.1 m	2.3 m	2.6 m	4.85 s	17		0.8			1639
$PPh_2CH_2CH_2CH{=}CH_2$ (mbp) [g]	5.06 d	5.11 d	4.24 m	2.60 m	2.70 m		17.0	10.3		+16.5		1641
RhCp(mbp) [h]	8.80 d	7.66 d	5.96 m	2.31 m 2.63 m	2.63 m	4.84 s	10.0	7.5	1.0	−77.2	206.0	1475
$RhCp(mbp)Br_2$ [i]	5.13 d	5.18 d	4.35 m	2.22 m	2.53 m	4.74 s	17	10	1.8	−28.4	182.1	1640
$RhCp[PPh_2CH_2CH_2CHBrCH_2Br]Br_2$ [j]	6.32 q	6.52 t	5.91 m	2.24 m	2.52 m	4.73 s			2			
$RhCp(mbp)I_2$ [k]	5.08 d	5.11 d	4.33 m	2.28 m	2.54 m	4.69 s	17	10	1.8	−24.3	137.1	1640
$[RhCp(mbp)(CH_3)]Br$ [l]	7.76 d	5.32 d	3.43 m	2.48 m	2.18 m	4.20 s	13	7.8	<2			1502
$[RhCp(mbp)(CH_3)]I$ [m]	7.73 d	5.36 d	3.46 m	2.49 m	2.49 m	4.19 s	13	8	<2			1502
$[RhCp(mbp)(\pi\text{-}C_3H_5)]Br$ [n]	4.96 m	4.96 m	4.33 m	2.48 m	2.48 m	4.18						
$RhCp[CH_2CH(OCH_3)CH_2CH_2PPh_2]CH_3$ [o]				2.2 m	2.6 m	5.00						

[a] The ^1H NMR spectra were analyzed at 220 MHz in $CDCl_3$ with TMS as reference at τ 10.0. ^{31}P chemical shifts ± 0.3 ppm are relative to 85% H_3PO_4. Abbreviations: s, singlet; d, doublet; m, multiplet; t, triplet; q, quartet. All peak intensities were checked by integration. [b] $\tau(H(4))$ 5.74 m (2). [c] $\tau(H(4))$ 5.9 m (2) see ref. 13 for additional couplings. [d] $\tau(H(4))$ 5.45 (2), $^3J(P-H(4))$ 6 Hz, $^3J(H(4)-H(3))$ 5.5 Hz [e] $^3J(H(1)-H(2))$ and $^3J(H(1)-H(3))$ 10Hz, $^3J(H(2)-H(3))$ 4 Hz. [f] $\tau(H(4))$ 5.55 m (2), $^3J(P-H(1))$ 6 Hz, $^3J(H(4)-H(3))$ 5.5 Hz. [g] τ(methylene) 7.9 (4) [h] $\tau(H(4))$ 8.4 m (2), $\tau(H(5))$ 8.0 m (2), see ref. 13 for additional couplings. [i] $\tau(H(4))$ 8.01 m (2), $\tau(H(5))$ 7.03 m (2). [j] $\tau(H(4))$ 8.22 m (1), $\tau(H(4'))$ 7.78 m (1), $\tau(H(5))$ 6.91 m (2), $^2J(H(1)-H(2))$ and $^3J(H(1)-H(3))$ 10 Hz, $^3J(H(2)-H(3))$ 4 Hz. [k] $\tau(H(4))$ 7.97 (2), $\tau(H(5))$ 6.85 m (2). [l] The methylene protons, H(4), H(4'), H(5), H(5') are at 7.6–7.8 m τ(1), $\tau(Rh-Me)$ 9.34 d (3), $^3J(P-Me)$ 5.4 Hz, $^2J(Rh-Me)$ 1.8 Hz. [m] τ(methylene) 7.6–7.8 m (4), $\tau(RH-Me)$ 9.33, $^3J(P-Me)$ 5.6 Hz, $^2J(Rh-Me)$ 1.8 Hz. [n] τ(H–allyl) 4.72 m (1), 5.78 d (2), 8.36 t (2), τ(methylene) 7.40 m (2), 7.79 m (2). [o] $\tau(O-Me)$ 6.70 s, 6.71 s, $\tau(CH(OMe))$ 6.33, $\tau(Rh-Me)$ 8.54, $^3J(P-Me)$ 5 Hz

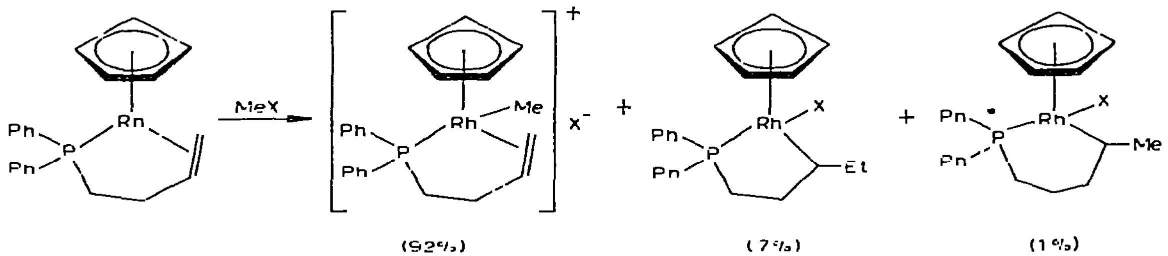

Fig. 2. Reaction of RhCp(mbp) with methyl halides (X = Cl, Br and I).

$(PPh_3)I_2$ [9]. Attempts to induce methyl transfer by adding either PPh_3 or NaI to a chloroform solution of $[RhCp(mbp)CH_3]I$ were unsuccessful and the unreacted ionic complex may be recovered from the solution after 1 h.

In addition to these ionic compounds formed in the reaction of RhCp(mbp) with methyl halides, neutral species can be detected in low yield, $RhCp[CH(CH_2CH_3)CH_2CH_2PPh_2]X$ (ca. 7%) and $RhCp[CH(CH_3)CH_2CH_2CH_2PPh_2]X$ (ca. 1%). A complex triplet in the ^1H NMR at ca. τ 9.00 is consistent with the CH_3 of a five-membered metallocycle and a complex doublet at ca. τ 9.14 ppm with the six-membered metallocycle, see Fig. 2.

In contrast, RhCp(map) does not react with methyl halides, and can be recovered, after one day, at room temperature, from a benzene solution containing excess methyl iodide.

The reaction of RhCp(mbp) with HBr or HCl resulted in a color change from orange to yellow. The analysis of the product by ^1H NMR indicated that loss of the π-cyclopentadienyl group had occurred. The reaction of $RhCp(CO)(PPh_3)$ with hydrochloric acid results in hydrogen transfer to the π-cyclopentadienyl group and subsequent loss of cyclopentadiene [17], and the reaction of $RhCp(C_2H_4)_2$ with HCl must be done at —60° C to observe the formation of $RhCp(C_2H_4)(C_2H_5)Cl$, which then decomposes when warmed to —10°C [16].

The room temperature reaction of RhCp(mbp) with excess benzyl bromide in benzene resulted in a color change over a 24 h period. The ^1H NMR spectrum of the orange crystalline product proved it to be $RhCp(mbp)Br_2$; yield based on rhodium 24%. Under the same reaction conditions RhCp(mbp) reacts with excess benzyl iodide to yield the red complex, $RhCp(mbp)I_2$; yield based on rhodium 67%.

The reaction of RhCp(mbp) with excess allyl bromide in benzene resulted in the precipitation of a yellow powder; yield ca. 20%. The ^1H NMR spectrum of this compound in $CDCl_3$ has absorptions which may reasonably be assigned to a π-allyl ionic complex $[RhCp(mbp)(\pi\text{-}C_3H_5)]Br$ with the olefin of the phosphine ligand nonbonded. The chemical shift values are very similar to those reported for $[RhCp(PPh_3)(\pi\text{-allyl})]Cl$ [10]. Attempts to purify the ionic compound lead to decomposition, with $RhCp(mbp)Br_2$ as one of the products. A similar reaction of RhCp(mbp) with allyl iodide resulted in the precipitation of a yellow powder; yield ca. 50%. The ^1H NMR spectrum of the sparingly soluble product, (2 mg/ml of $CDCl_3$) allows identification as a mixture of ionic π-allyl complex, $[RhCp(mbp)(\pi\text{-}C_3H_5)]I$ and neutral diiodide addition complex, $RhCp(mbp)I_2$.

The attempted reaction of RhCp(map) with both benzyl and allyl bromide or iodide for a 24 h period in benzene at room temperature only resulted in the recovery of the unreacted complex.

A benzene solution of RhCp(mbp) or RhCl(map) is unaffected by contact with an atmosphere of hydrogen gas over a 24 h period. After removal of the solvent under vacuum, the yellow powder which resulted was proved by ^1H NMR to be the appropriate starting complex.

The reactivity of the two complexes toward the various reagents implies several characteristics of the complexes that can be best discussed in terms of the Lewis acid—base character of the metal and/or the coordinated olefin. The rather subtle change from the phosphine-olefin to the phosphinite-olefin ligand appears to have an effect upon the basicity (nucleophilic character) of the metal in these two complexes. The previously reported formation of complexes such as $RhCp(C_2H_4)_2 \cdot HgCl_2$ [18] confirms the nucleophilic character of this type of complex, and the reaction between RhCp(mbp) and RX undoubtedly is the result of a nucleophilic attack by the metal upon the alkyl group. The absence of such a reaction for RhCp(map) even with CH_3I indicates the rhodium is a much weaker nucleophile in this complex.

Although RhCp(mbp) does not react with carbon monoxide, RhCp(map) establishes an equilibrium mixture: RhCp(map)/RhCp(map)(CO) = 60/40 in CHCl under 1 atmosphere of carbon monoxide. This adduct cannot be isolated, even under an atmosphere of carbon monoxide, but the ^1H NMR spectrum clearly shows both coordinated and free olefin and its infrared spectrum in $CHCl_3$ has $\nu(CO)$ 1940 cm^{-1} and $\nu(C=C)$ 1639 cm^{-1}. Such a difference in behavior has been previously noted, e.g. $RhCp(CO)_2$ exchanges CO rapidly, while $RhCp(C_2H_4)_2$ does not exchange C_2H_4 nor will CO replace an ethylene molecule [19]. $RhCp(C_2H_4)_2$ is the better nucleophile and $RhCp(CO)_2$ appears to allow the coordination of a third carbon monoxide in an intermediate species in which the basic character of the metal can be directed into the π-antibonding orbitals of the carbon monoxide. In a similar manner, RhCp(map) is able to establish an equilibrium with carbon monoxide while RhCp(mbp) does not. The possibility of an S_N1 mechanism, dissociation of the olefin prior to CO addition, appears less reasonable since ^1H NMR and IR data of the two complexes indicate essentially equal metal—olefin bond strengths and similar molecular structures [13].

There was no evidence for attack on the olefin while coordinated to Rh^I with the possible exception of a small amount of product from the direct reaction of RhCp(mbp) with CH_3X and there was no evidence for migration to the olefin of a group once it is bonded to rhodium.

As mentioned earlier, the ^1H NMR and infrared data indicate a considerably stronger rhodium—olefin interaction for the Rh^I than for the Rh^{III} complexes. The chemical shift data and olefinic coupling constants for the Rh^{III} complexes are, in fact, similar to those for related Pt^{II} complexes [20]. The coordinated olefin of such Pt^{II} complexes is susceptible to nucleophilic attack by species such as the methoxide ion [21—23] while the olefin in a Rh^I complex is less susceptible because of a greater amount of electron density put onto the olefin by back-bonding. Thus, RhCp(mbp) can be recovered unreacted from a methanolic solution of $NaOCH_3$, while the ionic Rh^{III} complex, $[RhCp(mbp)CH_3]I$, yields the neutral complex, $RhCp[CH_2CH(OCH_3)CH_2CH_2PPh_2]CH_3$; the result of attack on the β carbon of the coordinated olefin and the formation of a rhodium—carbon σ bond to the α carbon. This complex was identified by its ^{1}H NMR spectrum and has two peaks of equal intensity for OCH_3, at τ 6.70 and 6.71, since there are two conformers.

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