Inorganica Chimica Acta, 122 (1986) 175–184

Protonation and Dimerization Reactions of Cyclopentadienylrhodiumcarbonylphosphine and Phosphite Derivatives

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(Received June 16, 1986)

Abstract

Eight cyclopentadienylrhodiumcarbonylphosphine and phosphite complexes have been prepared and their IR, ^{1}H, and ^{31}P NMR spectra recorded. A good correlation between carbonyl stretching frequencies and rhodium–phosphorous coupling constants has been observed. Reaction of these compounds with trifluorosulfonic acid, HCF_3SO_3, forms the expected cationic rhodium–hydride species which were examined using ^{1}H and ^{31}P NMR spectroscopy. Similar reactions between trifluoroacetic acid, HCF_3CO_2, and the phosphine compounds gave evidence of rapid proton exchange at the metal. Reaction between trifluoroacetic acid and cyclopentadienylrhodiumcarbonylphosphite compounds yielded new sets of rhodium–hydride resonances which were shown to be due to the formation of dinuclear rhodium complexes and cyclopentadienylrhodiumbis(phosphite) complexes which arise under the reaction conditions. A Scheme for the formation of these reaction products is presented which is consistent with all of the experimental data.

Introduction

Protonation studies of the half-sandwich complexes, $(h^5\text{-}C_5H_5)MLL'$, of the cobalt triad have established that the metal-basicity of these complexes follows roughly in the order Co < Rh < Ir. For a given element, the basicity is strongly dependent on the identity of the ligands L and L′. For the rhodium compounds, it has been found that the order of increasing basicity is

$$CpRh(CO)_2 < CpRh(CO)PR_3 < CpRh[P(OR)_3]_2 < CpRh(PR_3)_2$$

where $(h^5\text{-}C_5H_5) = Cp$. The chemistry of these compounds has recently been reviewed by Werner [1, 2].

A large number of cyclopentadienylrhodiumcarbonylphosphines and phosphites have been reported in the literature [3–7], but only in two cases have the protonation reactions been examined. In those cases, Werner and his coworkers [6, 7] reported the isolation of $(h^5\text{-}C_5H_5)Rh(CO)(PMe_3)H^+$ and its pentamethylcyclopentadienyl analog as BF_4^- and $CF_3SO_3^-$ salts. IR carbonyl stretching frequencies were reported for the former compound, and ^{1}H NMR spectral data was reported for the latter. In a related investigation, Graham [8] has reported the isolation of $(h^5\text{-}C_5H_5)Ir(CO)(PPh_3)H^+$.

No direct protonation studies of $(h^5\text{-}C_5H_5)Rh(CO)_2$ have been reported, although Herrmann and his coworkers [9] have described attempts to protonate $(h^5\text{-}C_5Me_5)Rh(CO)_2$ which led to the formation of $(\mu\text{-}CO)(\mu\text{-}H)[h^5\text{-}C_5Me_5)Rh(CO)]_2^+$. Similarly, we have found [10] that $CH_2[(h^5\text{-}C_5H_4)Rh(CO)_2]_2$ reacts with trifluoroacetic acid to yield $(\mu\text{-}CO)(\mu\text{-}H)CH_2[(h^5\text{-}C_5H_4)Rh(CO)]_2^+$.

In the present work we have prepared a series of cyclopentadienylrhodiumcarbonyl derivatives incorporating phosphines and phosphites which exhibit a broad range of electronic and steric properties, and have examined the protonation reactions of these compounds in trifluoromethylsulfonic acid, HCF_3SO_3, and trifluoroacetic acid, HCF_3CO_2. The unexpected appearance of dinuclear species in reactions with HCF_3CO_2 caused us to expand the investigation to include the protonation of dinuclear, monophosphine compounds and $(h^5\text{-}C_5H_5)Rh(CO)_2$. Reactions of these protonated species with excess phosphite has also been examined.

Results and Discussion

$(h^5\text{-}C_5H_5)Rh(CO)L$ complexes are readily prepared as described by Schuster-Woldan and Basolo [3] by refluxing $(h^5\text{-}C_5H_5)Rh(CO)_2$ with an appropriate phosphine or phosphite in benzene for 10–18 h. Compounds **1**–**8** were prepared in this manner. Compounds **9** and **10** were prepared by the procedure of Hill and Knox [11]. All of the compounds are sufficiently air-stable to be handled for brief periods in air without protection. These compounds are best stored under nitrogen, and their solutions must be protected from air to avoid decomposition.

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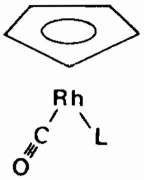
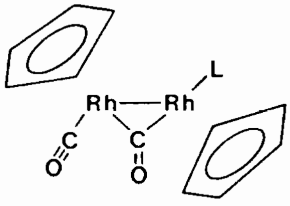


1, L = PMe_3
2, L = PBu_3
3, L = $P(i\text{-}Pr)_3$
4, L = $P(C_6H_5)_3$
5, L = $P(OMe)_3$
6, L = $P(OCH_2)_3CC_2H_5$
7, L = $P(OC_6H_5)_3$
8, L = $P(O\text{-}o\text{-}CH_3C_6H_4)_3$



9, L = $P(OC_6H_5)_3$
10, L = $P(OCH_2)_3CC_2H_5$

The ^1H and ^{31}P NMR spectral parameters and IR carbonyl stretching frequencies of compounds **1**–**8** are presented in Table I. The variation of carbonyl stretching frequencies with the identity of the phosphines and phosphites follow the series reported by Tolman [12] and reflect the relative abilities of the phosphorous ligands to modify the electron density at the metal atom.

Although the ^{31}P chemical shifts do not follow any apparent pattern, the magnitude of the $^1J(Rh–P)$ coupling constants was found to vary uniformly with the carbonyl stretching frequencies to give a high correlation coefficient of $R = 0.988$.

Grim and his coworkers [13] have reported a similar correlation between carbonyl stretching frequencies and $^1J(W–P)$ coupling constants in $W(CO)_5PR_3$ complexes, which they interpreted as evidence for a back-bonding interaction between the metal d orbitals and the empty phosphorous d orbitals. Tolman [14] has suggested that steric effects may also contribute to the coupling constants and has argued that the large uncertainties (±8 Hz) in the coupling constants and limited range of cone angles (130–157°) of the phosphine compounds examined by Grim may mask these contributions. Although the present data cannot answer the question of the nature of the metal-to-phosphine interaction, the low uncertainty in the coupling constant assignments (about ±1 Hz) and large range of phosphine and phosphite cone angles (106–160°) seems to eliminate any significant contribution to the coupling constants from steric factors in these compounds. As a case in point, the triphenylphosphite and tri(*o*-cresol)-phosphite ligands have almost identical carbonyl stretching frequencies and Rh–P coupling constants but have cone angles of 128° and 141°, respectively.

Protonation of compounds **1**–**8** in $CDCl_3$ with trifluoromethylsulfonic acid, HCF_3SO_3, was studied by recording the ^1H and ^{31}P NMR spectra of the compounds over about a one-half hour time period. In general, an initial ^1H spectrum was recorded prior to acid addition and then a second within 2 min of acid addition. The spectrometer was reconfigured for ^{31}P NMR and data collection initiated. After a satisfactory ^{31}P NMR spectrum was obtained (10–20 min), the spectrometer was returned to the ^1H configuration and a third ^1H NMR spectrum recorded. In one case, compound **7**, new resonances were observed indicating the formation of a secondary product. Further observations on these secondary species are described below. ^1H and ^{31}P NMR spectral parameters are presented in Table I for all compounds.

Addition of trifluoromethylsulfonic acid to compounds **1**–**8** resulted in rapid changes in color with the initially orange–red solutions of the neutral compounds giving solutions which ranged from pale yellow to red. The cyclopentadienyl ring resonance was found to shift downfield upon protonation. Rhodium–hydride resonances are found at high-field (−9 to −11 ppm) and are generally resolved into a doublet-of-doublets or a triplet in those cases where the hydride coupling constant to the rhodium atom and to the phosphorous atom are similar.

^{31}P NMR spectra of the protonated species were recorded. In all cases the spectra consisted of a simple doublet whose chemical shifts followed no apparent pattern. Comparison of the coupling constants of the protonated and unprotonated compounds revealed that the ratio of protonated to unprotonated coupling constants is surprisingly uniform, averaging 0.640 for the eight compounds examined. Within this set, the phosphine compounds tended to have slightly smaller ratios while the phosphites were among the larger values. The change in coupling constant probably reflects the reduction in 's' orbital character of the rhodium orbitals accompanying the change in metal geometry from pseudo-trigonalplanar to pseudo-tetrahedral upon protonation. Also, protonation of the metal would be expected to withdraw electron density from the metal which would further lower the coupling constants.

Protonation of compounds **1**–**8** in HCF_3SO_3 results in formation of the metal-protonated species indicating that this acid is sufficiently strong to drive the protonation equilibrium to completion. Since this limiting effect makes it impossible to distinguish the relative basicities of the various compounds, it was decided to examine the same series of compounds in the weaker acid, trifluoroacetic acid.

TABLE I. Spectral Parameters for Neutral and Protonated Rhodium Complexes

Compound	L	$(h^5\text{-}C_5H_5)^a$	L	Rh–H	$^{31}P^b$	Solvent^c	Ir (cm^{-1})^d
$(h^5\text{-}C_5H_5)Rh(CO)L$							
1	PMe_3	5.30 (s)	1.56, CH_3 (d of d, J = 10.05, J = 1.30)	–	2.88 (d, J = 186.01)	1	1932
1	PMe_3	5.80 (s)	1.82, CH_3 (d of d, J = 12.42, J = 2.75)	–10.60 (d of d, J = 19.66, J = 24.76)	11.00 (d, J = 114.45)	2	
2	PBu_3	5.28 (s)	1.54, $(CH_2)_3$ (broad) 0.93, CH_3 (t, J = 5.90)	–	36.06 (d, J = 185.98)	1	1928
2	PBu_3	5.80 (s)	1.90, $P(CH_2)$ (m) 1.45, $(CH_2)_2$ (broad) 0.96, CH_3 (t, J = 6.15)	–10.61 (t, J = 20.00)	44.33 (d, J = 113.51)	2	
3	$P(i\text{-}Pr)_3$	5.30 (s)	2.03, $C\underline{H}(CH_3)_2$ (septet, J = 7.05) 1.30, CH_3 (d, J = 6.93) 1.12, CH_3 (d, J = 6.94)	–	80.41 (d, J = 189.38)	1	1927
3	$P(i\text{-}Pr)_3$	5.94 (s)	2.31, $C\underline{H}(CH_3)_2$ (septet, J = 7.30) 1.39, CH_3 (d, J = 6.87) 1.19, CH_3 (d, J = 6.95)	–10.52 (t, J = 18.58)	87.55 (d, J = 115.25)	2	
4	$P(C_6H_5)_3$	5.17 (s)	7.70–7.28, C_6H_5 (complex multiplet)	–	52.71 (d, J = 199.50)	1	1940
4	$P(C_6H_5)_3$	5.70 (s)	7.63–7.35, C_6H_5 (complex multiplet)	–9.34 (d of d, J = 17.17, J = 21.45)	43.68 (d, J = 121.89)	2	
5	$P(OMe)_3$	5.37 (s)	3.60, CH_3 (d, J = 13.06)	–	47.05 (d, J = 299.38)	1	1962

(continued)

TABLE I. *(continued)*

Compound	L	$(h^5\text{-}C_5H_5)^a$	L	Rh–H	$^{31}P^b$	Solvent^c	Ir $(cm^{-1})^d$
$(h^5\text{-}C_5H_5)Rh(CO)L$							
5	$P(OMe)_3$	5.89 (d, J = 2.07)	3.77, CH_3 (d, J = 13.24)	−10.09 (t, J = 18.15)	123.77 (d, J = 195.13	2	
6	$P(OCH_2)_3CC_2H_5$	5.44 (s)	4.17, OCH_2 (d, J = 5.04) 1.14, CH_2 (multiplet) 0.84, CH_3 (multiplet)	–	127.07 (d, J = 318.41)	1	1970
6	$P(OCH_2)_3CC_2H_5$	5.90 (d, J = 2.52)	4.45, OCH_2 (d, J = 5.52) 1.28, CH_2 (multiplet) 0.82, CH_3 (multiplet)	−9.92 (d of d, J = 19.28, J = 16.70)	119.12 (d, J = 211.72)	2	
7	$P(OC_6H_5)_3$	4.81 (d, J = 1.45)	7.27–7.19, C_6H_5 (multiplet)	–	62.70 (d, J = 328.77)	1	1977
7	$P(OC_6H_5)_3$	5.45 (d, J = 2.74)	7.53–7.13, C_6H_5 (multiplet)	−9.82 (d of d, J = 19.98, J = 16.23)	120.73 (d, J = 212.09)	2	
8	$P(O\text{-}o\text{-}MeC_6H_4)_3$	4.85 (s)	7.47–7.08, C_6H_4 (multiplet) 2.27, CH_3 (s)	–	66.44 (d, J = 328.21)	1	1975
8	$P(O\text{-}o\text{-}MeC_6H_4)_3$	5.52 (d, J = 2.58)	7.34–7.22, C_6H_4 (multiplet) 2.27, CH_3 (s)	−9.77 (d of d, J = 21.00, J = 16.68)	117.55 (d, J = 210.70)	2	
$(\mu\text{-}CO)[(h^5\text{-}C_5H_5)Rh(CO)][(h^5\text{-}C_5H_5)RhL]$							
9	$P(OC_6H_5)_3$	5.59 (s) 4.67 (d, J = 2.23)	7.37–7.25, C_6H_5 (multiplet)	–	136.02 (d of d, J = 342.01 J = 100.60)	1	1979, 1815^e
9	$P(OC_6H_5)_3$	5.83 (s) 5.00 (d, J = 2.65)	7.49–7.13, C_6H_5 (multiplet)	−11.92 (d, of t, J(Rh–H) = 19.86 J(P–H) = 11.18)		2	

(continued)

TABLE 1. *(continued)*

Compound	L	(h^5-C_5H_5)[a]	L	^{31}P[b]	Rh–H	Solvent[c]	Ir (cm^{-1})[d]
(μ-CO)[(h^5-C_5H_5)Rh(CO)][(h^5-C_5H_5)RhL]							
10	$P(OCH_2)_3CC_2H_5$	5.44 (broad s)	4.17, OCH_2 (d, J = 5.27) 1.14, CH_2 (multiplet) 0.84, CH_3 (multiplet)	128.92 (d, J = 311.92)	–	1	1973, 1970
10	$P(OCH_2)_3CC_2H_5$	5.72 (broad s)	4.26, OCH_2 (d, J = 5.27) 1.18, CH_2 (multiplet) 0.80, CH_3 (multiplet)		−11.73 (d of t, J(Rh–H) = 19.45 J(P–H) = 12.88)	2	

[a] ^1H NMR chemical shifts are relative to tetramethylsilane, TMS. [b] ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 in a coaxial capillary. [c] Solvent 1 = $CDCl_3$; solvent 2 = $CDCl_3$ + HCF_3SO_3. [d] Ir spectra were recorded as solutions in CH_2Cl_2 except where noted (see e). [e] Hexane solvent.

Reaction of compounds **1**–**8** with HCF_3CO_2 was conducted as previously described for HCF_3SO_3. A solution of the weaker acid with **3** was found to give an ^1H NMR spectrum which was similar to that observed with HCF_3SO_3 except for slight broadening of the cyclopentadienyl ring resonance and the Rh–H resonance. Reaction of **1**, **2** and **4** with HCF_3CO_2 gave solutions in which the ring resonance was broadened and the Rh–H resonances broadened and unresolved.

Protonation of compounds **5**–**8** with HCF_3CO_2 gave solutions whose ^1H NMR spectra contained a broad ring resonance with the same chemical shifts as found in the stronger acid, but there was no evidence for an Rh–H quartet or broadened resonance at the chemical shifts which were observed in the stronger acid. These observations are entirely consistent with the expectation that the phosphite derivatives are less basic than the phosphine derivatives.

Examination of the spectra of the solutions of compounds **5**–**7** with HCF_3CO_2 over a period of several minutes after acid addition revealed that a new set of Rh–H resonances and additional cyclopentadienyl ring resonances were growing into the spectrum. Examination of the Rh–H resonances showed them to consist of one or two sets of doublets of triplets. The spectra of **5** and **7** were found to contain two sets of doublets of triplets while that of **6** had only one set. Spectra of **8** did not exhibit any observable resonances in the Rh–H region. The metal–hydride spectra of several compounds are presented in Fig. 1.

It was noted above that in the case of compound **7** new hydride resonances were found to arise in the spectra of this compound in HCF_3SO_3. Comparison of these additional hydride resonances in the HCF_3SO_3 spectra with those found in the HCF_3CO_2 spectra showed them to be identical. Extended examination of the protonated species in the stronger acid was not possible because of extensive H/D exchange between the acid and the $CDCl_3$ solvent.

The small samples used in the NMR studies were insufficient to permit recovery of products from the trifluoroacetic acid reactions, so a larger scale preparative reaction was undertaken. A methylene chloride solution of **7** was reacted with trifluoroacetic acid for 2 h, after which the reaction was quenched by the addition of solid Na_2CO_3 and the methylene chloride solution eluted on a small alumina column. A yellow band and a red band were eluted from the column while a dark band remained on the column. The yellow band was shown by IR and ^1H NMR spectroscopy to be identical to **7**. An IR spectrum of the red band showed both terminal and bridging carbonyl bands. A ^1H NMR spectrum of this compound contained phenyl resonances and two equivalent cyclopentadienyl resonances, one of which was split into a doublet and the second into a triplet. ^{31}P NMR showed a low-field doublet-of-doublets.

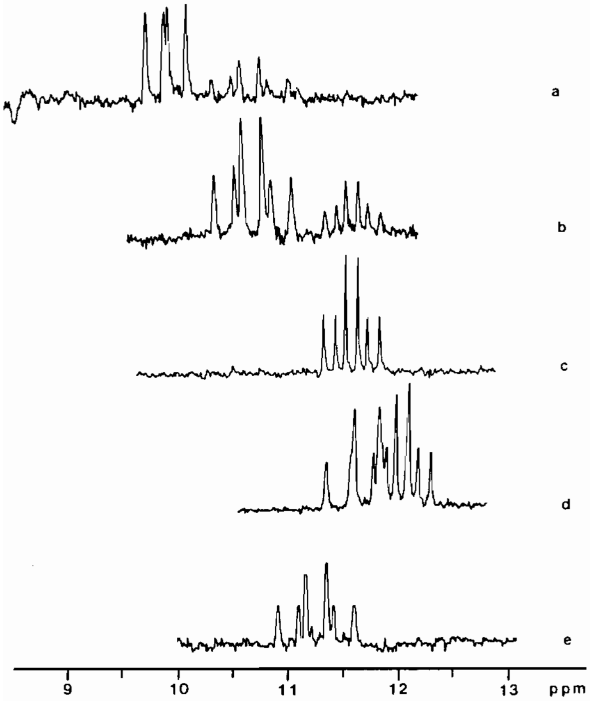


Fig. 1. Rhodium–hydride spectral region of cyclopentadienyl rhodiumcarbonylphosphite compounds in $CDCl_3$–acid solutions. (a) 7 and HCF_3SO_3 after 10 min. Note: small amounts of secondary reaction species are observed. (b) 7 and HCF_3CO_2 after 10 min. (c) 9 and HCF_3CO_2. (d) 5 in HCF_3CO_2 after 10 min. (e) 6 in HCF_3CO_2.

The spectral features of the red compound from above were consistent with a dinuclear, monophosphite complex. Such a compound, **9**, has been reported by Johnson and his coworkers [15] and comparison of the red compound with an authentic sample of **9** showed the two compounds to be identical. Protonation of **9** in $CDCl_3$ with HCF_3CO_2 resulted in the formation of a μ-hydride species whose hydride resonance is identical to that of the upfield doublet-of-triplet set found in the protonation of **7**. Two cyclopentadienyl resonances were observed for the protonated dinuclear compound which matched resonances found in the earlier protonation study.

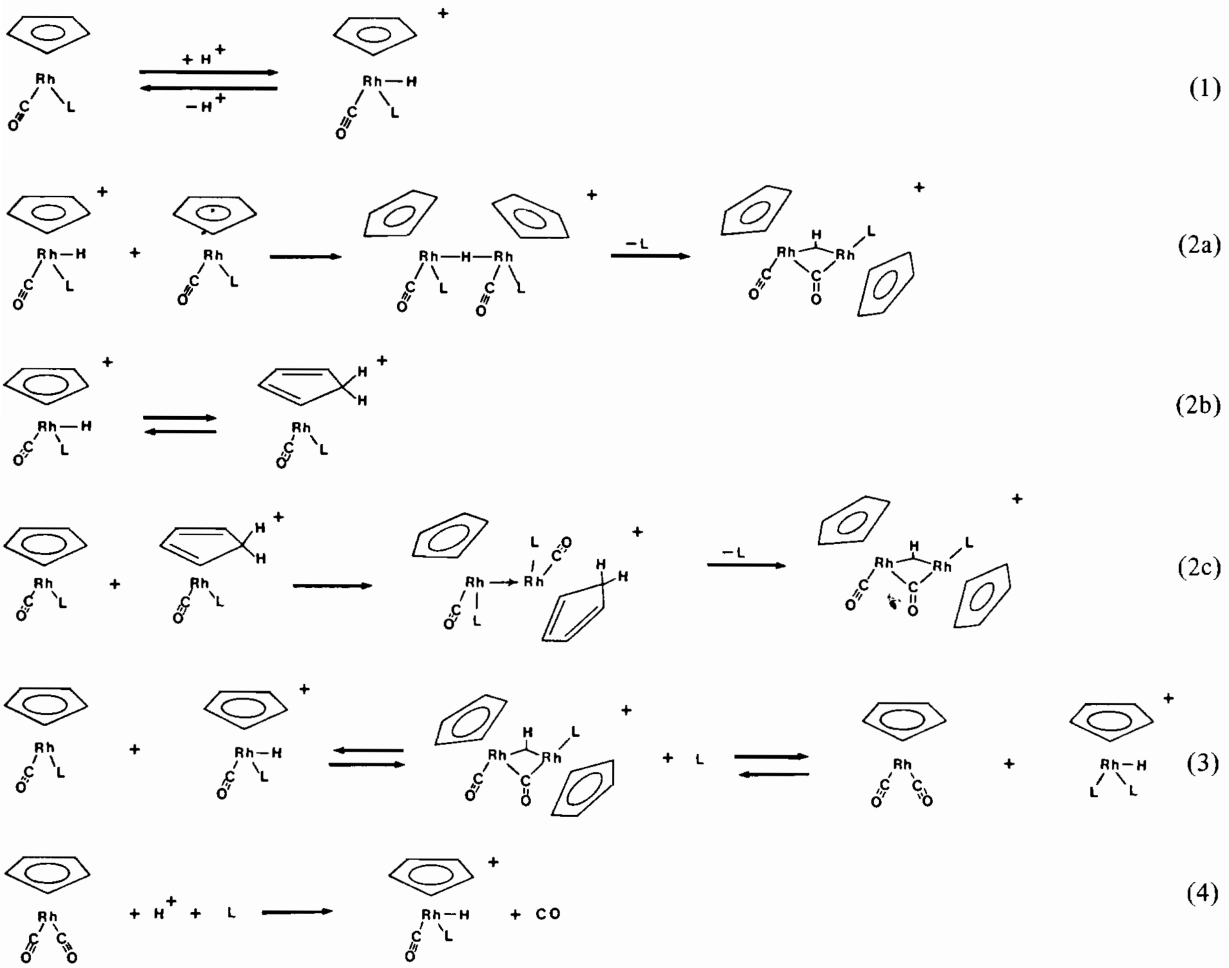
Addition of excess $P(OC_6H_5)_3$ to the solution of **9** in trifluoroacetic acid resulted in an immediate reaction and appearance of a new set of ring and hydride resonances. The hydride resonance was identical to the lower field doublet-of-triplets and a triplet cyclopentadienyl resonance was observed. Examination of the literature has shown these resonances to be very similar to those reported by Werner [16] for $(h^5\text{-}C_5H_5)Rh[P(OC_6H_5)_3]_2H^+$. Similarly, the lower hydride doublet-of-triplets in the spectrum of **6** in HCF_3CO_2 is consistent with that reported for the analogous $(h^5\text{-}C_5H_5)Rh[P(OCH_3)_3]_2H^+$ cation.

Compound **10**, the ethylbicyclophosphite analog of **9**, was readily prepared by adaptation of the procedure of Hill and Knox [11]. IR, ^1H and ^{31}P NMR spectra and elemental analysis of this new compound are in agreement with its formulation. Protonation of **10** resulted in the formation of a previously unobserved species whose ^1H NMR spectrum was fully in accord with its assignment as a μ-hydrido species in which the Rh–Rh bond has been protonated by the acid. Reaction of this protonated species with excess ethylbicyclophosphite gave an immediate color change and the ^1H NMR spectrum of the reaction mixture showed only one major cyclopentadienyl containing species. The cyclopentadienyl resonance of this species was split into a triplet and the rhodium–hydride resonance was a doublet-of-triplets. These resonances matched the major resonances observed in the protonation of **6** by HCF_3CO_2. The spectrum of this new species indicates that it is the ethylbicyclophosphite analog of the $(h^5\text{-}C_5H_5)RhL_2H^+$ cations described above.

Herrmann, Plank and Reidel [9a] have reported that $(\mu\text{-CO})[(h^5\text{-}C_5H_5)Rh(CO)]_2$ is protonated by HBF_4 in diethyl ether to give the dinuclear cationic complex $[(\mu\text{-CO})(\mu\text{-H})\{(h^5\text{-}C_5H_5)Rh(CO)\}_2]BF_4$. The μ-hydride in this species was found to have a triplet resonance at -10.67 ppm with a $J(Rh\text{–}H) = 18.3$ Hz. The chemical shifts and coupling constants of the dinuclear phosphite complexes examined here are in keeping with these values.

The fate of the expected $(h^5\text{-}C_5H_5)Rh(CO)_2$ fragment from the attack of triphenylphosphite or ethylbicyclophosphite on the protonated dinuclear compounds was not clear because several small, unidentified resonances were observed in the cyclopentadienyl region of the protonated species. When triphenylphosphite was added to the solutions of $(h^5\text{-}C_5H_5)Rh(CO)_2$ in either acid, signals of $(h^5\text{-}C_5H_5)Rh[P(OC_6H_5)_3]_2H^+$ were observed within a few minutes. The facile reaction of $(h^5\text{-}C_5H_5)Rh(CO)_2$ with the phosphite compounds under these conditions accounts for the depletion of this species in the reaction mixtures of the carbonyl–phosphine compounds with excess ligand. The details of this acid-catalyzed substitution reaction are now under investigation.

The overall process which has emerged from these studies of the protonation of cyclopentadienylrhodiumcarbonylphosphine and phosphite complexes is summarized in Scheme 1. As expected, reaction of the rhodium compounds with acids results in the formation of rhodium–hydride cationic species according to reaction (1). In HCF_3SO_3 this reaction lies far to the right, while in the weaker HCF_3CO_2 both species are present in solution and rapid hydrogen exchange is occurring. When L is a phosphite, a secondary reaction (2) occurs in HCF_3CO_2 which



Scheme 1. Proposed reaction scheme for dimerization and rearrangement of cyclopentadienylrhodiumcarbonylphosphite complexes in acid media.

results in the formation of a protonated dinuclear species. The mechanism of formation of the dinuclear complex is not yet known, but two routes may be suggested. In one route, (2a), the dinuclear species may form via an intermediate in which two CpRh(CO)L fragments are held together by a bridging hydride. Loss of a phosphite from this species would result in Rh–Rh bond formation to give the observed protonated dinuclear product. Alternatively, the metal-bound phosphite may stabilize a transient 16-electron, h^4-C_5H_6 species generated by transfer of the metal-hydride to the cyclopentadienyl ring (2b). Nucleophilic attack by a neutral CpRh(CO)L on this 16-electron intermediate would form a dinuclear complex which could lose phosphite and generate the observed product (2c). Werner and Hofmann [17] have suggested that a similar 16-electron intermediate might be formed in the facile electrophilic substitution of $(h^5\text{-}C_5H_5)Co(PMe_3)_2$ by alkyl halides. Additionally, evidence presented by Basolo and his coworkers [3, 18] indicates that 16-electron fulvenic resonance structures may be important in the substitution of carbon monoxide by triphenylphosphine in $(h^5\text{-}C_5H_4R)Rh(CO)_2$ derivatives.

Reaction of the protonated dinuclear compound with phosphite can lead to either the dissociation of the complex into its starting materials, or formation of $(h^5\text{-}C_5H_5)RhL_2H^+$ and $CpRh(CO)_2$ according to reaction (3). For the ethylbicyclophosphite compound (**6**), formation of $(h^5\text{-}C_5H_5)RhL_2H^+$ is apparently dominant since there is no evidence for the dinuclear intermediate in those solutions. In the presence of excess phosphite, $(h^5\text{-}C_5H_5)Rh(CO)_2$ can react to give mixed carbonyl, phosphite products according to reaction (4).

This sequence of reactions appears to be general for three of the phosphite complexes examined. The failure of the tris(*o*-cresol)phosphite complex **8** to follow this reaction pathway may be due to the steric bulk of the phosphite which may block formation of the intermediate required for dinuclear complex formation. The apparent failure of the phosphine

TABLE II. Summary of Reactions of Rhodium Phosphite Complexes with Trifluoroacetic Acid and Excess Phosphite[a]

	$(h^5\text{-}C_5H_5)$	Rh–H	Comments
Reaction: $(h^5\text{-}C_5H_5)Rh(CO)P(OMe)_3 + HCF_3CO_2$			
Species 1	5.68 (d, J = 2.12)	–	Rapid exchange of $(h^5\text{-}C_5H_5)Rh(CO)P(OMe)_3$ and its metal protonated product.
Species 2	5.76 (s) 5.65 (s)	–12.04 (d of t, J(Rh–H) = 20.02 J(P–H) = 11.65)	Protonated dinuclear species $(\mu\text{-}CO)(\mu\text{-}H)[(h^5\text{-}C_5H_5)Rh(CO)]\text{-}[(h^5\text{-}C_5H_5)RhP(OMe)_3]^+$
Species 3	not found	–11.63 (d of t, J(Rh–H) = 22.45 J(P–H) = 25.47)	Protonated bis(phosphite) species $(h^5\text{-}C_5H_5)Rh[P(OMe)_3]_2\text{-}H^+$. Identical species formed in reaction of $(h^5\text{-}C_5H_5)Rh(CO)_2$ with excess $P(OMe)_3$ in trifluoroacetic acetic acid. Werner and coworkers [16] report very similar values for an authentic sample of the protonated bis(phosphite) complex.
Reaction: $(h^5\text{-}C_5H_5)Rh(CO)P(OC_6H_5)_3 + HCF_3CO_2$			
Species 1	5.24 (broad s)		Rapid exchange of neutral and protonated species.
Species 2	5.83 (s) 5.00 (d, J = 2.85)	–11.91 (d of t, J(Rh–H) = 19.91 J(P–H) = 11.46)	Protonated dinuclear species $(\mu\text{-}CO)(\mu\text{-}H)[(h^5\text{-}C_5H_5)Rh(CO)]\text{-}[h^5\text{-}C_5H_5)RhP(OC_6H_5)_3]^+$. Identical to species formed by protonation of compound 9.
Species 3	4.85 (t, J = 2.49)	–10.78 (d of t, J(Rh–H) = 18.41 J(P–H) = 25.92)	Protonated bis(phosphite) species $(h^5\text{-}C_5H_5)Rh[P(OC_6H_5)_3]_2\text{-}H^+$. Identical species is generated upon addition of excess phosphite to protonated dinuclear complex. Similar chemical shifts and coupling constants reported by Werner and coworkers [16] for an authentic sample of protonated bis(phosphite) complex.
Reaction: $(h^5\text{-}C_5H_5)Rh(CO)P(OCH_2)_3CC_2H_5 + HCF_3CO_2$			
Species 1	5.88 (d, J = 2.68)		Rapid exchange of neutral and protonated species.
Species 2	5.63 (t, J = 2.87)	–11.26 (d of t, J(Rh–H) = 18.63 J(P–H) = 25.10)	Protonated bis(phosphite) species. Also generated by addition of excess phosphite to solutions of the dinuclear complex in trifluoroacetic acid.

[a] Only major species present in the reaction mixtures have been reported. Ligand resonances are generally too complex to interpret and have been omitted. Resonances attributable to $(h^5\text{-}C_5H_5)Rh(CO)_2$ are also observed.

compounds to form dinuclear products may be due to their higher relative basicity since the cone angle of PMe_3 is similar to that of the phosphites and precludes a steric contribution. Additional work on the mechanism of these reactions and on their potential for synthetic applications is proceeding.

Experimental

IR spectra were recorded in methylene chloride solution using a Perkin-Elmer Model 1750 FTIR Spectrometer. ^1H and ^{31}P NMR spectra were recorded on a Varian Associates FT 80 A NMR Spectrometer operating at 79.542 MHz and 32.197 MHz, respectively. ^{31}P NMR spectra were proton decoupled. Tetramethylsilane (TMS) and 85% phosphoric acid in a coaxial capillary were used as reference standards for the NMR spectra. Elemental analyses of new compounds were conducted by Galbraith Laboratories, Inc. of Knoxville, Tenn. All reactions and chromatographic purifications were conducted under nitrogen in solvents which were freshly distilled under nitrogen.

Compound Preparation

$(h^5\text{-}C_5H_5)Rh(CO)_2$ was prepared from cyclopentadienylthallium and rhodiumcarbonylchloride dimer according to the procedure described by Knight and

Mays [19]. $(\mu\text{-CO})[(h^5\text{-}C_5H_5)Rh(CO)]_2$ was obtained in moderate yield as a side product in the preparation of $(h^5\text{-}C_5H_5)Rh(CO)_2$ and could be easily separated from the mononuclear derivative by column chromatography on alumina. Petroleum ether rapidly elutes the mononuclear product from the column and the dinuclear product is recovered by elution with methylene chloride. Small amounts of higher rhodium oligomers can also be recovered. $(\mu\text{-CO})[(h^5\text{-}C_5H_5)Rh(CO)]_2$ was also prepared by reaction of $(h^5\text{-}C_5H_5)Rh(CO)_2$ with Me_3NO in acetone as described by Lawson and Shapley [20].

$(h^5\text{-}C_5H_5)Rh(CO)L$ derivatives **1**–**8** were prepared by refluxing $(h^5\text{-}C_5H_5)Rh(CO)_2$ with a stoichiometric quantity of the phosphine or phosphite ligand in benzene solution according to the procedure described by Schuster-Woldan and Basolo [3]. The reactions were followed by IR spectroscopy. When the carbonyl bands of the starting material were no longer observed, the reaction mixtures were cooled, stripped of benzene at reduced pressure, and the resulting solid chromatographed on alumina using 10% methylene chloride in petroleum ether. Some decomposition on the column was observed for the phosphite derivatives. Yields were generally in excess of 80%. Spectral parameters for compounds **1**–**8** are reported in Table I. Analytical data and melting points are recorded below for the new compounds.

3. $L = P(i\text{-}Pr)_3$, red–brown oil. The small quantities of this compound which were available precluded preparation of an analytical sample.

6. $L = P(OCH_2)_3CC_2H_5$, yellow crystalline solid, melting point (m.p.) 141–142 °C (dec.). Calc. for $C_{12}H_{16}RhO_4P$: C, 40.11; H, 4.46. Found: C, 40.22; H, 4.58%. The analogous $P(OCH_2)_3CCH_3$ compound has been reported by Schuster-Woldan and Basolo [3].

7. $L = P(OC_6H_5)_3$, yellow oil.

8. $L = P(O\text{-}o\text{-}CH_3C_6H_4)_3$, yellow solid, m.p. 66–69 °C. Calc. for $C_{27}H_{26}RhO_4P$: C, 59.02; H, 4.74. Found: C, 59.01; H, 4.87%.

$(h^5\text{-}C_5H_5)_2Rh_2(CO)_2L$ compounds **9** and **10** were prepared by slow addition of a stoichiometric quantity of L in hexane to a refluxing solution of $(\mu\text{-CO})[(h^5\text{-}C_5H_5)Rh(CO)]_2$ in hexane according to the procedure described by Hill and Knox for $L = P(OMe)_3$. Both **9** and **10** are recovered as red microcrystalline solids in analytical purity from the cooled reaction mixtures. The spectral parameters of compounds **9** and **10** are listed in Table I. The analytical and physical properties of **10** are listed below.

10. $L = P(OCH_2)_3CC_2H_5$, red crystalline solid, m.p. 147–149 °C (dec.). Calc. for $C_{18}H_{21}Rh_2O_5P$: C, 38.84; H, 3.78. Found: C, 39.12; H, 3.91%.

Protonation Studies

NMR samples of the rhodium compounds were prepared in the usual manner except that the NMR tubes were evacuated and backflushed with nitrogen after introduction of the rhodium compounds. Deuterochloroform and TMS were added to the tubes against a nitrogen countercurrent.

After initial ^1H and ^{31}P NMR spectra were recorded, about 10–20 μl of HCF_3SO_3 or HCF_3CO_2 were added to the tubes. A ^1H NMR spectrum was recorded immediately, after which the instrument was reconfigured for ^{31}P NMR and a spectrum recorded. When a satisfactory ^{31}P NMR spectrum had been recorded (10–20 min) the instrument was returned to the ^1H mode and another ^1H NMR spectrum recorded. In some cases, excess phosphite dissolved in deuterochloroform was added to the NMR sample and additional spectra recorded.

Preparative Reaction of $(h^5\text{-}C_5H_5)Rh(CO)P(OC_6H_5)_3$ with HCF_3CO_2

A 100 mg sample of **7** was taken up in 10 ml of degassed methylene chloride and 0.25 ml of HCF_3CO_2 was added. The reaction mixture was stirred at room temperature under nitrogen for 2 h after which it was quenched with sodium carbonate. The methylene chloride solution was chromatographed on a 15 cm × 1 cm alumina column with methylene chloride. A yellow band eluted rapidly and was shown by IR and ^1H NMR spectroscopy to be unreacted **7**. A red band which was eluted slowly yielded a red solid which was shown by IR, ^1H and ^{31}P NMR spectroscopies to be **9**.

Acknowledgements

We wish to thank the Johnson-Matthey Co. for its generous loan of rhodiumtrichloride hydrate and The Research Corporation for their support of this research. We thank Professor Sam Grim of the University of Maryland for his helpful suggestions on interpretation of the phosphorous spectral data. We thank Professor Joyce Shade of the U.S. Naval Academy for the generous gift of a large sample of ethylbicyclophosphite.

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