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VARIABLE TEMPERATURE NMR STUDIES OF CARBONYL-(PHOSPHONIUM-BIS-METHYLIDE)RHODIUM(I) COMPLEXES

R.L. LAPINSKI, H. YUE and R.A. GREY

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960 (U.S.A.)

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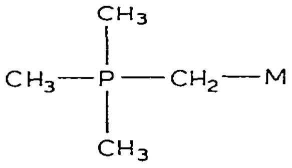
Summary

A phosphorus-ylide-rhodium complex of empirical formula $[RhC_6H_{10}PO_2]$ has been investigated by nuclear magnetic resonance. Both the ^1H and ^{31}P magnetic resonance measurements indicate two species present simultaneously in a toluene-d_8 solution. From these studies, these species have been assigned to monomeric and dimeric structures. The assignments are further confirmed by a ^1H nuclear magnetic resonance temperature dependence study. The ^1H NMR temperature data fits the Van 't Hoff equation indicating a true equilibrium between the monomeric and dimeric species at different temperatures. A value of —10.5 kcal/mol for the heat of reaction (ΔH^0) is calculated from a least squares fitting. The temperature profile indicates the dimer is the more preferred species at lower temperatures.

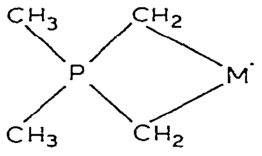
Introduction

In recent years, phosphorus ylides have been found to form stable transition metal complexes. In general, there are three ways in which the phosphorus ylide has been found to bond to transition metals [1]. These are known as the monodentate (A), chelating (B) and bridging (C) linkages. In addition, the ylide

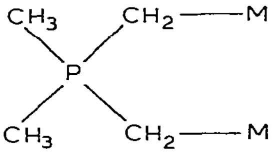


$CH_3{-}\overset{CH_3}{\underset{CH_3}{P}}{-}CH_2{-}M$

(A)



(B)

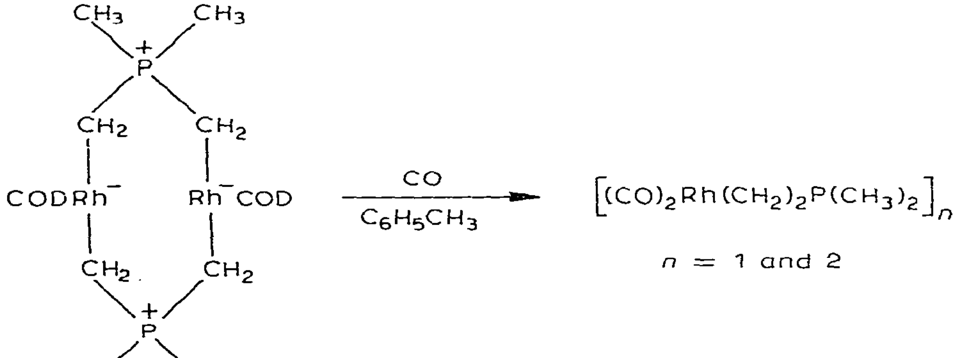


(C)

can bind in mixed type linkages, i.e. binding the same central metal atom in both a monodentate and chelating fashion or in other combinations.

Schmidbaur [1] has prepared stable phosphorus-ylide complexes of the monodentate type with Au and Ni; the chelating type with Co and Rh [2], the bridging type with Ni, Ag, Cu, Au and Ti [2], and mixed types with Ni, Pt, and Pd. Work in this area by Kurras has led to the isolation of stable phosphorus-ylide complexes of chromium(II), chromium(III) [4] and molybdenum(II) [5]. Manzer has reported the isolation and characterization of the phosphorus-ylides of titanium(III), scandium(III) and vanadium(III) [6].

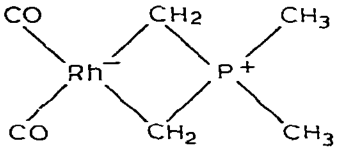
The carbonyl-bis-methylide-rhodiums * which are the subject of this paper were prepared by the reaction of carbon monoxide with the recently prepared cyclooctadiene dimethylphosphonium-bis-methylide-rhodium(I) dimer ** as shown in the following equation [7]:



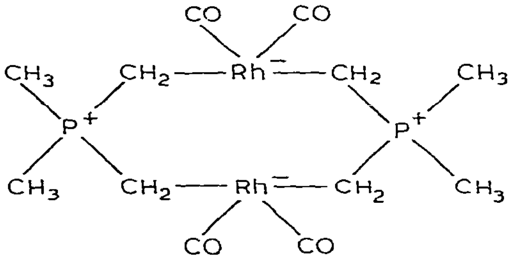
(1)

(COD = cyclooctadiene)

In this paper, we present the data and our conclusions concerning the results of the structure determination of the monomeric (I) and dimeric (II) phosphorus-ylide-rhodium complexes (as shown below) by a multi-nuclear magnetic resonance technique.



(I)



(II)

Also we report nuclear magnetic resonance evidence for an equilibrium between the monomeric and dimeric species. In addition, the $J(CH_2P)$ coupling constant appears to be diagnostic in most cases for the type of metal to phosphorus ylide linkage.

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* Elemental analyses and mass spectral data indicate species of empirical formula $RhC_6H_{10}PO_2$ [7].

** A single crystal X-ray investigation has shown this compound to to be a dimer [13].

Results and discussion

The ^{1}H NMR spectrum of the phosphorus-ylide-rhodium is illustrated in Fig. 1. The spectrum was recorded using a Varian HA-100 NMR spectrometer. The sample was dissolved in toluene-d_8 containing 2% benzene to provide an internal lock. The concentration of the sample was 4%. The most downfield peaks observed in Fig. 1 belong to the CD_2H impurity in toluene-d_8. The CD_2H quintet was used as an internal standard to measure the chemical shifts. The use of tetramethylsilane (TMS) as an internal standard was deliberately avoided since the chemical shift of tetramethylsilane is only 0.10 ppm away from the chemical shift of methylene absorptions for the rhodium complex. The spectral parameters for both the monomeric structure I and the dimeric structure II are given in Table 1.

On careful examination of the resonance peaks shown in Fig. 1, one notices the peaks can be divided into two groups on the basis of integrated intensities, splitting patterns and line widths. In this manner one can easily separate the doublet of doublets (dd) at —1.32 ppm and the doublet (d) of —0.96 ppm as belonging to one group and the peaks at —1.25 ppm (d) and —2.44 ppm (dd) as belonging to another. The NMR data is separated in Table 1 into two groups from which one can conclude the sample is a mixture of two components. Two

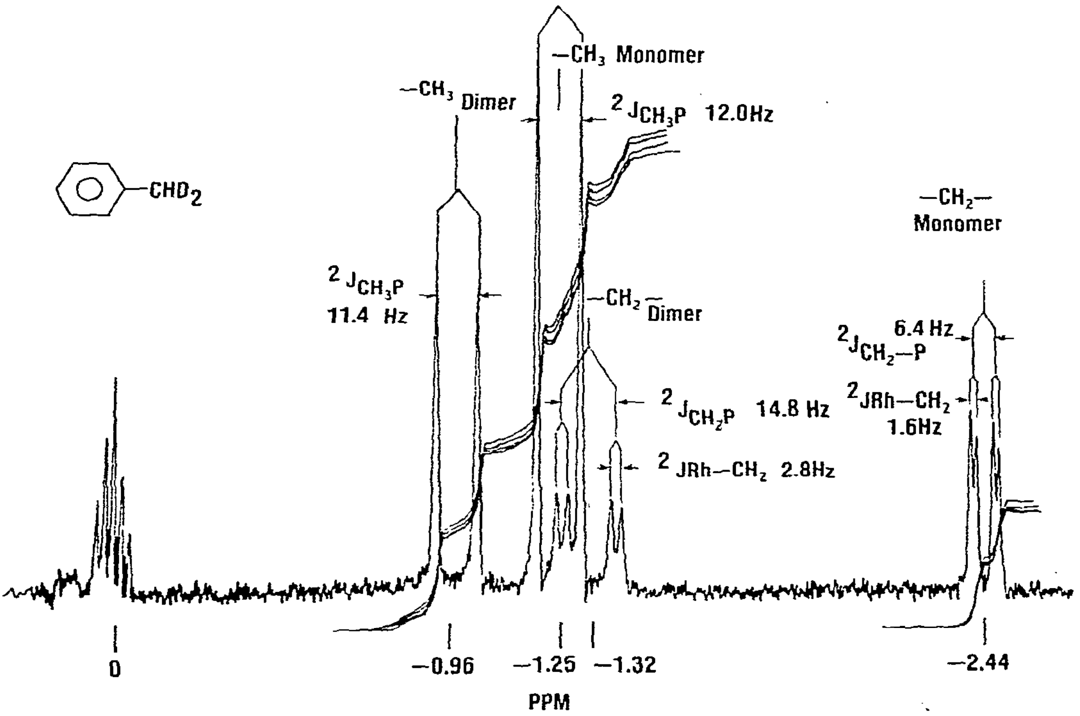

Fig. 1. ^{1}H NMR spectrum of the phosphorus-ylide-rhodium complex.

TABLE 1

^{1}H AND ^{31}P NMR PARAMETERS IN COMPOUNDS I AND II

		I	II
^{1}H	$\delta(CH_3)$ [a]	−1.25(d)ppm	−0.96 ppm
	$\delta(CH_2)$	−2.44(dd)ppm	−1.32(dd)ppm
^{31}P	$\delta(P)$ [b]	−28.5(d)ppm	−30.6(t)ppm
	$^2J(CH_3P)$	−12.0 Hz	−11.4 Hz
	$^2J(CH_2P)$	−6.4 Hz	−14.8 Hz
	$^2J(RhCH_2)$	$|1.6|$ Hz	$|2.8|$ Hz
	$^2J(Rh{-}P)$	$|24.9|$ Hz	$|2.0|$ Hz

[a] Proton chemical shifts were measured relative to the methyl peak in toluene-d_8, concentrations were 4% with a small amount of benzene for an internal lock. [b] The ^{31}P chemical shifts were measured relative to an external H_3PO_4 standard also decoupled from protons.

questions immediately arise, namely what are the structures of each component and also what is the dynamic relation of the two components with temperature. The information obtained from magnetic resonance provides a satisfactory answer to both questions. The details are presented in the following sections.

A. Structure determination

Having separated the ^{1}H NMR spectrum into the two groups listed in Table 1 the doublet in each group can be assigned to the CH_3 resonances split by the ^{31}P nucleus. The doublet of doublets (dd) in each group can be assigned to the ylide-CH_2 resonances split by the interaction of the methylene group with the ^{31}P and ^{103}Rh nuclei both of which have a spin value of $|\frac{1}{2}|$. In both cases the

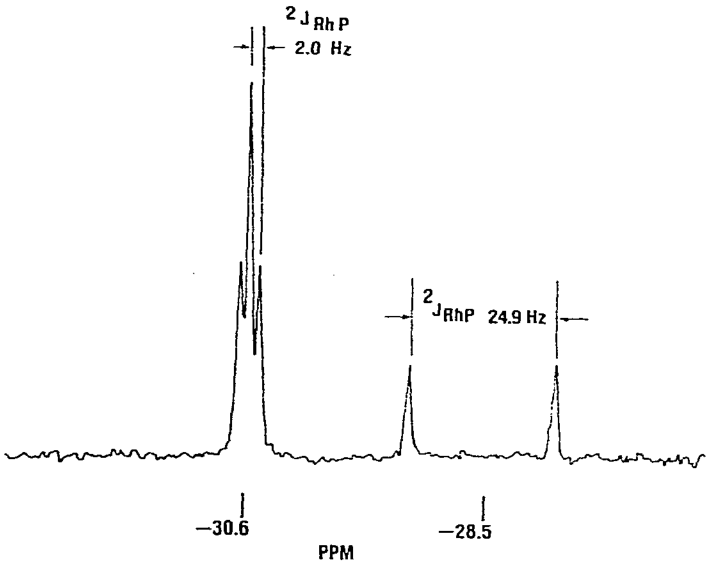

Fig. 2. ^{31}proton decoupled NMR spectrum recorded at 24 MHz of the phosphorus-ylide-rhodium complex.

integrated intensities of the CH_3 and CH_2 areas are in the expected ratio of 3/2. The observation of ^{103}Rh coupling with the protons of ylide-methylene groups clearly establish a covalent metal—carbon bond. The assignment of the monomeric and dimeric structure can now be made to the proper group of ^{1}H NMR parameters on the basis of the ^{31}P NMR spectrum.

The ^{31}P proton decoupled NMR spectrum recorded at 24.2 MHz and given in Fig. 2 shows the presence of a doublet and a triplet. Since ^{103}Rh, with a natural abundance of 100% has a spin of $-\frac{1}{2}$, one can easily see the doublet corresponds to the monomer, and the triplet belongs to the dimer. The presence of the triplet indicates two ^{103}Rh nuclei are coupled to the ^{31}P nuclei as given in the dimer. Since coupling constants are unaffected by a change in the magnetic field intensity, the ^{31}P spectrum was also recorded at 40.3 MHz to further confirm the ^{31}P spectral splittings are due to coupling and not due to mixtures. The relative intensities of the two absorptions in the ^{31}P NMR spectrum indicates that the dimer is the predominant species at 35° C. Therefore, on examination of the relative intensities of the ^{1}H NMR spectrum at 40° C, the absorptions centered at —0.96 and —1.32 ppm were assigned to the dimer and the absorptions centered at —1.25 and —2.44 ppm are assigned to the monomer. This assignment is also consistent with the observed line widths in the ^{1}H NMR spectrum since the larger molecule gives the larger line widths as expected.

B. Dynamic temperature dependence

The temperature dependent study was carried out using a Varian HA-100 nuclear magnetic resonance spectrometer equipped with a Varian temperature controller. Spectra were recorded at 10° C increments from 40 to 80° C. The relative concentrations of the monomeric and dimeric complexes were measured by integrating the resonance peaks. For this purpose, the concentration of the individual species were calculated from the relative intensities of the methyl peak of the dimer II (—0.96 ppm) and the methylene peak of the monomer I (—2.44 ppm). These peaks were chosen because they are free from interference of other resonance peaks. The experiments were also carried out by cooling from 80 to 40° C using the same temperature intervals to insure reproducibility and reversibility. The recorded temperatures are corrected temperatures calibrated by using a copper-constantin thermocouple. The data obtained from the temperature study is plotted in Fig. 3 assuring the following equilibrium $2[M] \rightleftharpoons [D]$, from which an equilibrium constant can be calculated by

$$K = [D]/[M]^2 \qquad (2)$$

where K is the equilibrium constant, $[D]$ represents the concentration of dimer and $[M]$ the concentration of monomer.

Using the Van 't Hoff equation, $\ln K = \Delta H^0/RT + \Delta S^0/R$ the data plotted as $\ln K$ vs. $1/T(K)$ in Fig. 3 was obtained. This straight line plot indicates eq. 2 is valid, and also helps confirm the structural assignments since it indicates a relationship exists between the two species. The slope of the straight line plot obtained from a least squares fit of the data provides a value of —10.5 kcal/mol for the thermodynamic quantity ΔH^0. Also from the Van 't Hoff equation, the intercept of this plot provides a value of —32.9 cal mol^{-1} deg^{-1} for ΔS^0. The

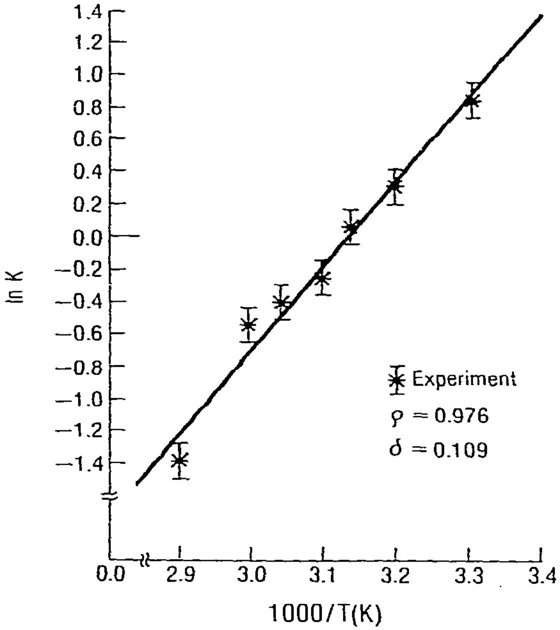

Fig. 3. Plot of ln K vs. $\frac{1}{T(K)} \times 10^3$.

standard free energy, for the reaction as written $2[M] \rightleftharpoons [D]$, using the equation $\Delta G^0 = \Delta H^0 - T\Delta S^0$ was calculated to be —0.7 kcal. The value of the equilibrium constant K was found to be 3.3 at 25° C.

Since ΔS^0 is negative, it can be seen from the equation $\Delta G^0 = \Delta H^0 - T\Delta S^0$ that as the temperature is increased, ΔG^0 will become more positive and therefore the tendency of the reaction to proceed toward the dimer decreases. Thus as seen from the data plotted in Fig. 3, the dimer is the predominant species at lower temperatures and the monomer is the more predominant species at higher temperatures. At 57° C the concentrations of monomer and dimer are equal.

C. Ylides with similar structures

A survey of the literature for the NMR parameters of similar phosphorus-ylide compounds having chelating and bridging structures has revealed the coupling constant values listed in Table 2. These coupling values are listed along with the values obtained for the rhodium-phosphorus-ylide complexes obtained in this study. A brief look at these values at this time would be appropriate since coupling constants may be diagnostic for the presence of either a chelating or a bridging structure in phosphorus-ylide-metal compounds.

An examination of the $^2J(CH_3P)$ coupling shows this particular coupling constant to be practically constant for both the chelating and bridging structures, but it appears that the $^2J(CH_2P)$ coupling constants are diagnostic for the type of metal to ligand linkage in the phosphorus ylides. By consulting the values

TABLE 2

COUPLING CONSTANTS IN BRIDGING AND CHELATING PHOPHORUS YLIDES

	Coupling constant (Hz)			Bridging (C)				
	Rh	Cu	Ag	Au	Ti	Ni	Ni [a]	Mo
$^2J(CH_3P)$	—11.9	—11.6	—11.6	—11.9	—12.0	—11.9	—11.3	—12.3
$^2J(CH_2P)$	—14.8	—13.4	—12.0	—12.3	—13.5	—4.8	—14.4	—10.5
$^2J(MCH_2P)$	$\lvert 1.6 \rvert$	—	$\lvert 9.7 \rvert$	—				
$^2J(MCH_2)$	$\lvert 2.8 \rvert$	—	$\lvert 9.8 \rvert$	—				

	Coupling constant (Hz)			Chelating (B)		Rh—P(CH$_3$)$_3$[2]
	Rh	Co	Ni [a]	Rh—COD[2]	Rh—CO[2]	
$^2J(CH_3P)$	—12.0	—11.7	—11.9	—	—	—
$^2J(CH_2P$	—6.4	—5.2	—6.3	—3.7	—4.9	—4.1
$^2J(MCH_2P)$	$\lvert 24.9 \rvert$			$\lvert 25.6 \rvert$	$\lvert 25.6 \rvert$	$\lvert 21.4 \rvert$
$^2J(MCH_2)$	$\lvert 1.6 \rvert$			$\lvert 1.95 \rvert$	$\lvert 1.9 \rvert$	$\lvert 1.7 \rvert$

[a] This nickel complex contains both chelating and bridging phosphorus ylides.

listed for $^2J(CH_2P)$ one notices the coupling constants reported for the bridging structures of Cu [8], Ag [8], Au [9], Rh and Ti [2] are approximately twice as large as those reported for the chelating structures of the Rh reported here, Schmidbaur's Rh complexes, Co [10] and Ni [11]. Thus one observes values in the range of —12.0 to —14.8 Hz for the bridging and from —3.7 to —6.4 Hz for the chelating structures. The only exception to this is in the case of the isomer of the above nickel dimer which contains four bridging ylides [11]. We offer no explanation as to why nickel appears to be the exception. In the molybdenum complex [4], the phosphorus ylides could not be assigned by Kurras to be bridging or chelating. On the basis of our observation that large coupling constants are diagnostic for bridging ylide structures and the reported $^2J(CH_2P)$ of —10.5 Hz, we would predict this complex to contain bridging bis-methylide ligands. A recent crystal structure has been published for the analogous chromium complex and found to contain bridging bis-methylide ligands [12].

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