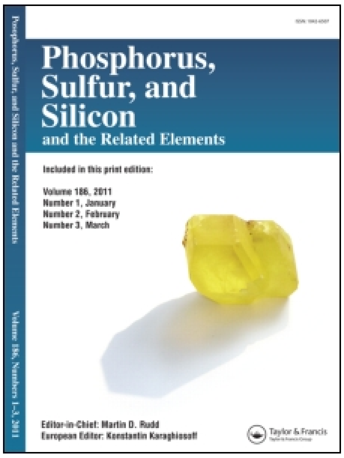

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BISPHOSPHANYLHYDRAZIDES AS NOVEL CHELATING PHOSPHINES IN TRANSITION METAL CHEMISTRY - SYNTHETIC AND CATALYTIC STUDIES

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Abstract: The synthesis of alkoxy- and aryloxy- functionalized bisphosphanyl hydrazides, $(RO)_2PN(Me)N(Me)P(OR)_2$, is described. Interaction of these ligands with transition metals, particularly rhodium(I), has been investigated. The steric effects around P^{III} centers have pronounced effects on the pathway of reactions of Rh(I) precursors. For example, the reactions of these ligands with $[RhCl(CO)_2]_2$ leads to the formation of carbonyl free, chlorobridged dinuclear complexes when the groups are relatively smaller (*e.g.*, CH_2CF_3, Ph), whereas mononuclear carbonyl-containing complexes are formed with bulky substituents (e.g., $C_6H_3Me_2$-*2,6*, $C_6H_3(OMe)_2$-*2,6*).

Key words: Bisphosphanyl Hydrazides, Rhodium Complexes, Bisphosphites, Catalysts.

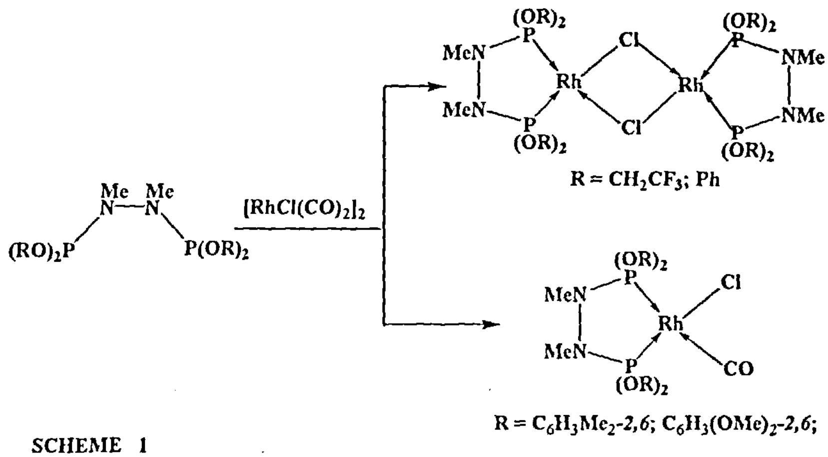
INTRODUCTION

Since the early 80's the application of phosphites as ligands in the rhodium-based hydroformylation of olefins has been a field of active interest. The mediation of electronic and steric effects of oxygen substituents (of phosphites) on to the interacting Rh(I) center in the rhodium-phosphite-based hydroformylation reactions is of fundamental importance. Chelating phosphites may provide contrasting binding properties with Rh(I), wherein even if one of the phosphite-rhodium bond is reversibly broken (in the presence of a substrate molecule) the other P^{III}-Rh bond will provide access to a reactive intermediate. Therefore, effective catalysts my be generated from chelating bisphosphites if synthetic routes to such ligands are developed. Toward this objective, we have developed synthetic strategies to a new genertion of bisphosphites of the general structure: $(RO)_2PN(Me)N(Me)P(OR)_2$.[1-4] This paper reports the coordination chemistry of a new class of bisphosphites with Rh(I) precursors.

The alkoxy- and aryloxy-functionalized dinitrogen-bridged bisphosphanes. $(RO)_2PN(Me)N(Me)P(OR)_2$ (R = Me, Et, CH_2CF_3, $CH_2CH{=}CH_2$, $(CH_2)_7CH_3$, $CH(CH_3)_2$, C_6H_5, C_6H_4Me-*p*, $C_6H_4(CH_2CH{=}CH_2$-*o*)) were obtained from the reactions of the corresponding alcohols or phenols with $Cl_2PN(Me)N(Me)PCl_2$ in the presence of Et_3N in 75-90% yields (Equation 1). These alkoxide and aryloxide derivatives are air-stable and are colorless viscous liquids. All the compounds were characterized by various spectroscopic and analytical methods. The ^{31}P NMR spectra of all the compounds consisted of single resonance(s) in the range between 137-148 ppm.

$$Cl_2PN(Me)N(Me)PCl_2 \xrightarrow[-4Et_3N.HCl]{4ROH/4Et_3N} \underset{R = \text{Alkyl or Aryl}}{(OR)_2PN(Me)N(Me)P(OR)_2} \quad (1)$$

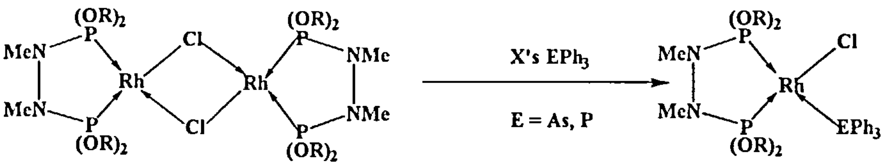
The reactions of bisphosphanylhydrazides $(RO)_2PN(Me)N(Me)P(OR)_2$ (R = CH_2CF_3, Ph) with $[RhCl(CO)_2]_2$ afford the chlorobridged Rhodium(I) dimers, $[RhCl\{(RO)_2PN(Me)\text{-}N(Me)P(OR)_2\}]_2$ in near quantitative yields (Scheme 1). The absence of bands due to ν(CO) in their IR spectra confirmed complete decarbonylation in these reactions. Observation of single resonances in the ^{31}P NMR spectra ($^1J_{RhP}$ = 287.0 Hz for R = CH_2CF_3; 296.5 Hz for R = Ph) indicated chelate structures with *cis* dispositions for P^{III} centers around Rh(I) as shown in Scheme 1. The chloride bridge in



SCHEME 1

these dimeric 16-electron species can be readily cleaved upon reactions with triarylphosphines or arsines (Scheme2) providing an efficient synthetic avenue for the mixed phosphine-bisphosphite complexes of Rh(I).

It is important to note that the integrity of the five-membered P-N-N-P-Rh rings in both the complexes were retained even when 4-10 fold excess of ER_3 (E = As or P) were used in these reactions. These mononuclear 16-electron species may be considered as 'hybrids' to the Wilkinson catalyst $[RhCl(PPh_3)_3]$.



SCHEME 2

Reactions outlined in Scheme 1 also demonstrate that the steric bulk on the phosphorus will change the course of reactions with $[RhCl(CO)_2]_2$. For example, the reactions of $(RO)_2PN(Me)N(Me)P(OR)_2$ (R = $C_6H_3Me_2$-*2,6* and $C_6H_3(OMe)_2$-*2,6*)) with $[RhCl(CO)_2]_2$ afford the mononuclear carbonyl complexes $[RhCl(CO)\{(RO)_2PN(Me)\text{-}N(Me)P(OR)_2\}]$ in near quantitative yields (Scheme 1). All these complexes were characterized by various spectroscopic and analytical methods. The structures of the dimeric and monomeric rhodium complexes were confirmed by X-ray crystallography (Figure 1).

The N-N bonds in the simple hydrazine and its derivatives tend to be unstable toward hydrolysis, metallation reactions and also in common orgnic solvents at elevated temperatures. In sharp contrast the bisphosphanyl hydrazides, especially the ones with the bulky substituents on the P^{III} centers, are stable in common organic solvents even at

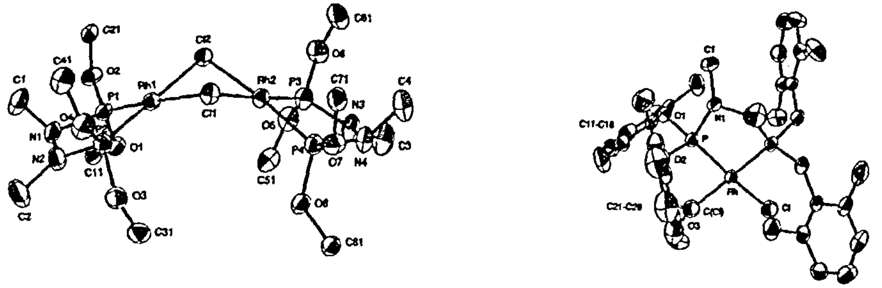


FIGURE 1

elevated tempertures (up to 140 °C). In addition the N-N bonds are inert toward reactions with various early and late transition metallic precursors. These observations suggest that the bisphosphanyl hydrazides will find applications as a new generation of bisphosphites for use in transition metal/organometallic chemistry.

Preliminary studies suggest that Rh(I) complexes of bisphosphites derived from bulky substituents ($(RO)_2PN(Me)N(Me)P(OR)_2$; R = $C_6H_3Me_2$-*2,6* and $C_6H_3(OMe)_2$-*2,6*)) catalyze the hydroformylation of propylene to *n* and *i* butanal with good selectivity and catalytic efficiency.

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