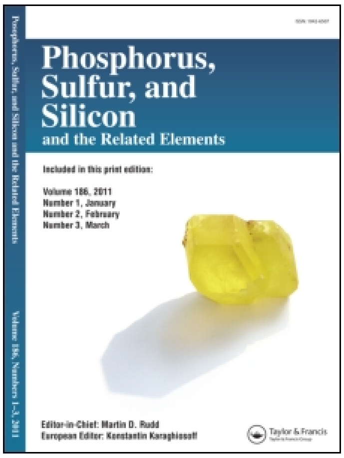

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Interaction of Metal Bis(Phosphane) Fragments with Phosphirene and Phosphirane Complexes

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INTERACTION OF METAL BIS(PHOSPHANE) FRAGMENTS WITH PHOSPHIRENE AND PHOSPHIRANE COMPLEXES.

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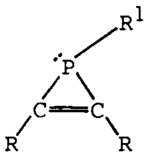
Abstract Different types of interactions of platinum, palladium and nickel complexes with phosphirene and phosphirane rings are presented and discussed.

INTRODUCTION

The novel phosphirene ring system (1) is of considerable



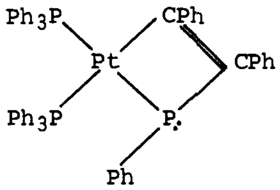
(1)

current interest[1] and its organic chemistry has been the subject of numerous recent investigations which have demonstrated its versatility as a synthon for organophosphorus chemistry[2]. Its coordination chemistry has so far remained relatively undeveloped and we have therefore undertaken a study of the reactivity of (1), ($R=R^1=Ph$), with nickel, palladium and platinum complexes.

RESULTS AND DISCUSSION

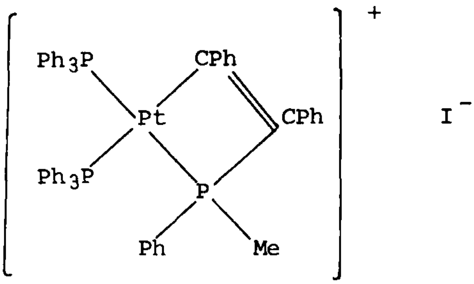
The isolation of the complexed phosphirenes $[M(CO)_n\overline{PPh-CPh=CPh}]$ (2)M=Cr,n=5;(3)M=Mo,n=5;(4)M=W,n=5;(5)M=Fe,n=4; by Marinetti et al[3] suggested that (1) should react as a phosphane, and reaction with the platinum (II) complexes $[Pt(COD)Cl_2]$ and $[Pt(PEt_3)Cl_2]_2$ yields the anticipated η^1-phosphirene complexes cis-$[Pt(\overline{PPhCPh=CPh})_2Cl_2]$ and cis-$[Pt(\overline{PPhCPh=CPh})(PEt_3)Cl_2]$ (7). The structure of (7) has been confirmed by a single crystal X-ray diffraction study[4] which reveals a short platinum-phosphirene distance (2.21Å). The relationship between the structural parameters and spectroscopic data for (7) will be presented and discussed.

Our recent development of a simple new route to $[M(PR_3)_2C_2H_4]$ (M=Ni,Pd,Pt R= alkyl,aryl) compounds[5] led us to investigate their reactions with (1) ($R=R^1=Ph$). Treatment with $[Pt(PPh_3)_2C_2H_4]$ yielded the anticipated η^1- product $[Pt(PPh_3)_2(\overline{PPh-CPh=CPh})_2]$, (8) at low temperatures which was characterised by ^{31}P nmr spectroscopy (triplet, $\delta(^{31}P)=-125.1$ p.p.m. $^1J_{PtP}=4222Hz$; triplet, $\delta=-296.9$p.p.m., $^1J_{PtP}=3927Hz$; $^2J_{PP}=59Hz$, (ref. TMP.)) Interestingly (8) is converted quantitatively to the ring-opened compound (9) upon warming to room temperature.

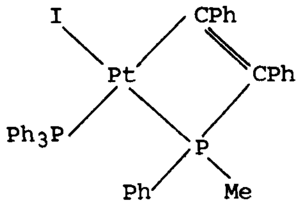


(9)

This remarkable reaction provides an extremely mild route to activated phosphirene complexes and is clearly a consequence of the strain inherent in the 3-membered ring. Complex (9) is best regarded as a metallated phosphane and undergoes quaternisation with methyl iodide to give the unusual complexes (10) and (11)

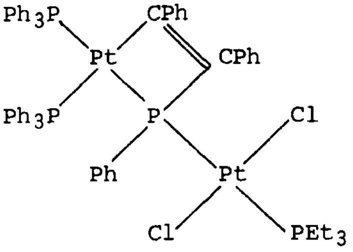


(10)



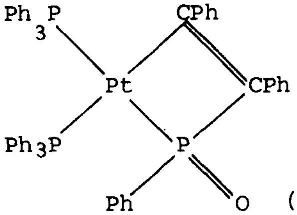
(11)

whilst with $[Pt(PEt_3)Cl_2]_2$ it forms the trans-complex (12)

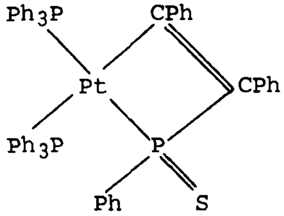


(12)

Oxidation of (9) with trimethylamine-N-oxide or sulphur yields (13) and (14) respectively.

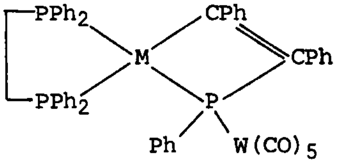


(13)



(14)

It is important to note that we find (14) is also formed by the direct insertion of a $[Pt(PPh_3)_2]$ fragment into $[\mathrm{S{=}\overline{PPh{-}CPh{=}C}Ph}]$[1] and therefore coordination of the phosphorus lone pair to the metal fragment is not essential to the ring opening process. Similarly [M(dppe)] fragments (M=Ni,Pd,Pt) have been shown[6] to insert into (4) to give the bimetallic phosphorus bridged complexes (15) - (17).



(15) M=Ni
(16) M=Pd
(17) M=Pt

(15) undergoes further insertion reactions and treatment with carbon monoxide (25°C, 1 atm) readily affords $[W(CO)_5\overline{PPhC(O)CPh{=}CPh}]$ (18) previously described by Marinetti *et al*[7]. Finally our recent observations that phosphirane pentacarbonyl tungsten (O) complexes also readily incorporate [M(dppe)] fragments[8] suggests that this type of insertion reaction may offer a general route to metallacyclobutane and -butene compounds. Possible extension of this methodology to other ring systems will also be discussed.

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