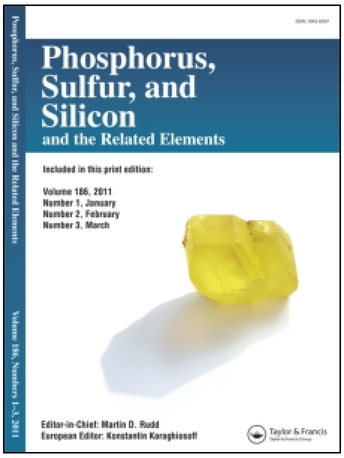

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Cyclometallaphosphiniminatopxosphane (and Arsane) Complexes of "Early" and "Late" Transition Metals Derived from Novel Heterodifunctional Phosphorus and Arsenic Ligands

Kattesh V. Katti[a]; Ronald G. Cavell[a]
[a] Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

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CYCLOMETALLAPHOSPHINIMINATOPHOSPHANE (AND ARSANE) COMPLEXES OF "EARLY" AND "LATE" TRANSITION METALS DERIVED FROM NOVEL HETERODIFUNCTIONAL PHOSPHORUS AND ARSENIC LIGANDS.

KATTESH V. KATTI and RONALD G. CAVELL
Department of Chemistry, University of Alberta, Edmonton,
Alberta, Canada T6G 2G2

Abstract A new heterodifunctional ligand system $Me_3EN{=}PPh_2(CH_2)_nQPh_2$ (E = Si, Ge; Q = P, As; n = 1, 2) has been developed. These heterodifunctional ligands provide hard (N) and soft (P, As) base character appropriate for combination with "early" and "late" transition metals respectively to form chelate and monodentate complexes. In addition M-N σ bond formation by means of metathetical Me_3EX elimination leads to a variety of useful functionalized phosphanes. Interactions with Ti(IV), Mo(O), W(O), Pd(II), Rh(I) and Ir(I) indicate the versatility of these ligands

INTRODUCTION

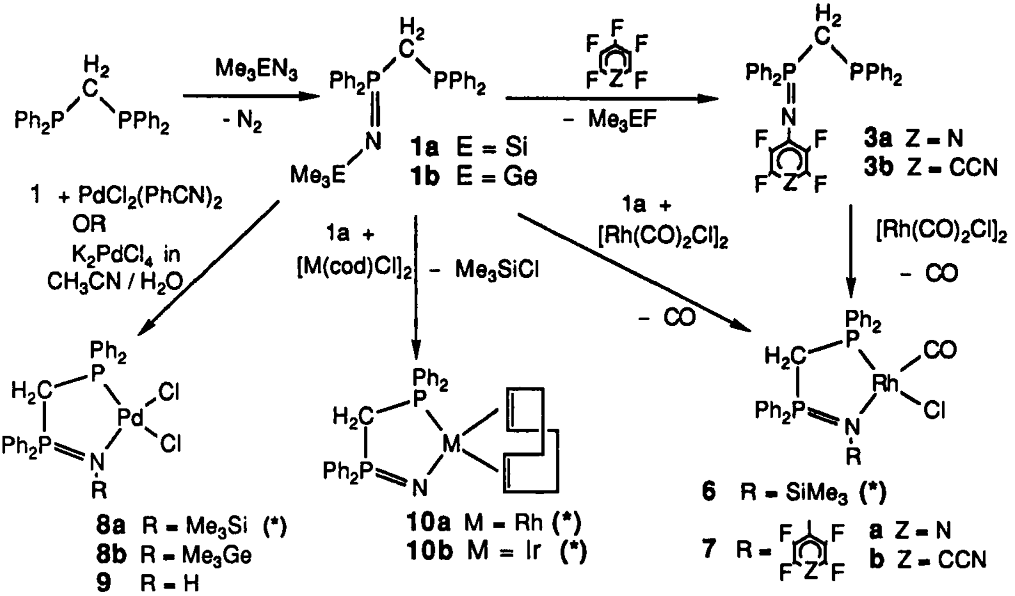
We have developed[1] a new series of heterodifunctional ligands *via* partial oxidation of alkane bridged diphosphanes such as dppm with Me_3SiN_3 to give **1a** (Scheme), a reaction which introduces a reactive trimethylsilyl functionality on the nitrogen. This application of the Staudinger reaction[2] is general for diphosphanes of any alkane chain length. Arsinophosphanes (e.g. ARPHOS: $Ph_2PC_2H_4AsPh_2$) are oxidized only at phosphorus to give, for example $Me_3SiN{=}PPh_2C_2H_4AsPh_2$, **2**. Use of Me_3GeN_3 or organic azides, RN_3, provides easy routes to germyl (**1b**) or organic analogs of **1**. Further chemistry can be developed readily from **1** and its analogs by carrying out metathetical reactions with halides in which Me_3EX (E = Si or Ge) is eliminated (e.g., **1** → **3** in the Scheme).

RESULTS AND DISCUSSION

1. *Fluorocarbon Substitution*

The reactions (**1** → **3**) proceed virtually quantitatively with exclusive *para* substitution on the ring. In contrast to **1**, which gave a mixture of rotameric components, **3** shows a simple ^{31}P NMR spectrum indicative of one rotameric configuration. The crystal structure of **3** shows that

Scheme

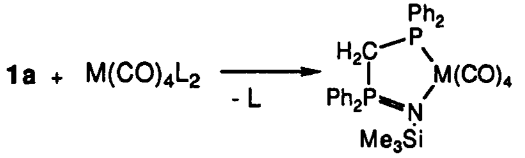


(*) Parallel products have been prepared with the $Me_3SiN{=}PPh_2(CH_2)_2AsPh_2$ ligand.

the molecule adopts a conformation in which the fluorocarbon substituent is aligned with one of the phenyl rings on the trivalent phosphorus. In a similar fashion $CpTiCl_3$ reacted with **1** to form an "early" transition metal derivative, $Cl_2CpTi{-}N{=}PPh_2CH_2PPh_2$, **4**, in which the free phosphane is available for further reaction.

2. Cyclometallaphosphiniminatophosphanes of Early Transition Metals

Tungsten and molybdenum carbonyls reacted with **1a** to give the new **5a** and **5b** in good yields as air stable crystalline solids of monomeric constitution (eqn 1). Although in general the presence of easily



5a L = pip; M = Mo

5b L = CO; M = W

(1)

replaceable functionalities (such as nitriles or amines) is required for the facile elimination of more than one CO group from $W(CO)_6$, ligands of this system with basic nitrogen (e.g., **1a**) do not require such enhancement. Notably **3b** did not displace CO from $W(CO)_6$ because of the much reduced basicity at nitrogen. The large ^{31}P NMR shielding of the phosphane unit compared to the phosphiniminato centre in **5a** (two doublets centred at 18.17 and 40.02 ppm (the latter signal showing a large coupling of $^1J(^{31}P-^{183}W)$ of 235 Hz indicating that this signal arises from the coordinated P(III) group) relative to sharp doublets centred at -28.20 (P(III)) and -1.38 (P(V)) ppm is probably a consequence of the interplay of two effects: (a) the delocalization of electronic charge in the $Ph_2P=N-W(O)$ framework, and (b) the net transfer of electron density from W(O) to the phosphane. The $^{31}P\{^1H\}$ NMR spectrum of **5b** and ^{29}Si (INEPT) NMR spectroscopy of both **5a** and **5b** support the suggested electronic delocalization within these five membered ring systems. Carbonyl IR stretching frequencies indicate that the P-N coordination is *cis*.

3. Cyclometallaphosphiniminatophosphanes of the Late Transition Metals

(a) *Complex formation*: Reactions of **1** and **3** with $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 at 25°C gave new metallacycles **6** and **7**. Again introducing significant differences in basicity at nitrogen by altering the substituent exerts a control over the properties of the complex. Here the effect is manifested by the contrasting P(III)-P(V) chemical shift difference which is reduced from 43 ppm in **6** to *ca*. 4 ppm in **7**. Such small differences in the chemical shifts of formally P(III) and P(V) centres appears to be unprecedented. We suggest that the decrease in basicity of the phosphiniminato nitrogen induced by the fluoroaromatic substituent in turn reduces the strength of the coordinate donation to the Rh(I) centre. Additional electron density from the electron rich Rh(I) centre may also drift *via* the iminato nitrogen into the fluoroaromatic substituent. These electronic effects lead to poor back bonding of Rh(I) with the P(III) phosphane group and this is manifested by the unusual proximity of the shifts for the two kinds of phosphorus in **7**. Further characterization of **7** was provided by ^{13}C nmr spectroscopy which showed $^2J(^{13}C-^{31}P)$ of 18.55 and 19.20 Hz (**7a** and **7b** respectively) indicative of a *cis* relationship between the CO and the phosphane groups. In addition, ν_{CO} values of 1972 and 1970 cm^{-1} for **7a** and **7b** are consistent with the proposed *cis* structures.

Another variation in the chemistry of the system is shown by reactions of **1** with palladium complexes (Scheme). In the absence of water $PdCl_2(PhCN)_2$ gave the expected chelate complexes $Me_3\overline{EM=PPh_2CH_2PPh_2Pd}Cl_2$ **8**. In the presence of water Pd(II) complexes or salts (K_2PdCl_4) formed the imine complex $H\overline{N=PPh_2CH_2PPh_2Pd}Cl_2$, **9**, the structure of which has been confirmed by X-ray crystallography. Water reacts with **8** to yield **9**. The latter represents the first example of a complex containing the parent phosphoraniminephosphane ligand. The imine itself can be obtained by reaction of **1** with alcohol.

(b) M-N σ Bond Formation: The presence of a reactive Si-N bond in **1a** presents the possibility of σ bond formation with metals *via* elimination of Me_3SiCl. This aspect has been demonstrated in the reactions of **1** with $CpTiCl_3$[1] and with $[MCl(cod)]_2$ complexes (Scheme) wherein facile elimination of Me_3SiCl occurred at 25°C to give good yields of the monomeric, air-stable, crystalline solid metallacycles containing a M-N σ bonds. The $^{31}P\{^1H\}$ NMR spectrum of **10a** showed two sharp doublets centered at 33 and 52 ppm, the high field signal being due to the P(III) moiety as it shows a large $^1J_{RhP}$ coupling (169 ppm).[2] The Ir complex **10b** likewise showed sharp doublets at 20.1 (P(III)) and 61.2 (P(V)) ppm respectively with $^2J_{PP}$ of 35 Hz (*vs.* $^2J_{PP}$ of 44 Hz in **10a**).[2] The marked deshielding of the P(V) phosphorus which accompanies the removal of the Me_3Si group with concomitant formation of the M-N σ bond (the P(V) chemical shift changes are accompanying the transformation **1** to **10** are 53 (**10a**) and 63 (**10b**) ppm to low field respectively) is notable in that the remote P(V) atom now deshielded by an extent similar to that accompanying the direct coordination of P(III) to the metal. This substantial effect on P(V) may be due to delocalization within the $Ph_2P=N-M$ unit and it is clear from comparisons of **7** and **10** that bond formation or the introduction of electronically modifying substituents can have a profound influence on the properties of the compounds. This in turn may lead to useful applications in catalytic processes.

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