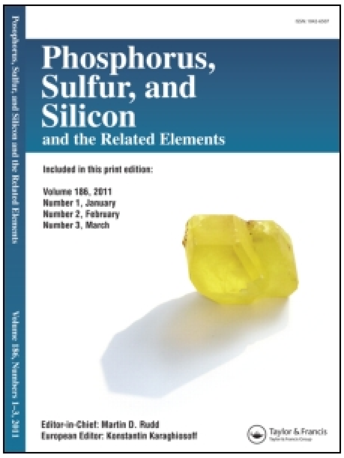

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FUNCTIONALIZED PHOSPHINES: SYNTHESIS, REACTIVITY AND TRANSITION METAL CHEMISTRY

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FUNCTIONALIZED PHOSPHINES: SYNTHESIS, REACTIVITY AND TRANSITION METAL CHEMISTRY

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Ten-membered heterocycles of the type $PhN(PCl_2)\{OC_6H_2(R)_2$ $(\mu$-S-$(CH_2))((R)_2—C_6H_2O—)\}$ *(R = Me,* ^{i}*Pr or* ^{t}*Bu) have been prepared and their transition metal chemistry is explored. Functionalised phosphines react with transition metals to give interesting metallacycles. Several Group 6, ruthenium, platinum metals and novel titanium(IV) metallacycles have been structurally characterized.*

Keywords: Aminophosphines; funcationalized phosphines; hemilabile; inorganic heterocycles; metallacycles; phosphine ethers; transition metals

AMINOPHOSPHINES

Bis(phosphino)amine embedded inorganic heterocycles of the type, **I–IV** can be obtained by reacting $Cl_2PN(R)PCl_2$ with appropriate reagents followed by the nucleophilic substitutions at the trivalent phosphorus centers.[1] The crystal structure of **I** ($R' = R'' = {}^tBu$; X = Cl) indicates that the geometry around the nitrogen is planar with sum of the bond angles around the nitrogen is 355. 77°. The P—N—P bond angle of 109.2 (2)° is larger than the average P—N—P bond angles observed in cyclodiphosphazanes. With Q = S, the ten-membered heterocycles with as many as five heteroatoms act as potentially bi- or tridentate ligands when reacted with transition metal organometallic derivatives, and exhibit different coordination modes. Interestingly, in these heterocycles, the sterically bulky substitutents on phosphorus centers are folded in such a way that the coordination properties of phosphorus donor

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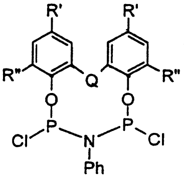
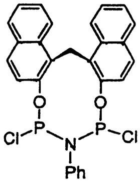
centers are least affected and the versatility in their coordination behavior is retained. The reaction of **I** or **II** with $Mo(CO)_4NBD$ afford tricarbonyl complexes with the ligand exhibiting tridentate mode of coordination involving sulfur and two phosphorus centers. The structure of **V** is confirmed by x-ray diffraction studies. The ligand **II** is puckered in such a way that the sulfur and two phosphorus centers occupy two equatorial and one axial position in a facial orientation.


Q = S, I; CH_2, II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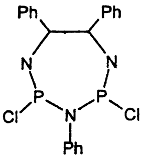
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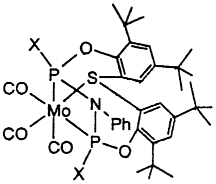
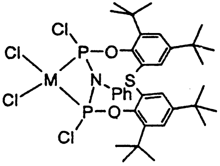
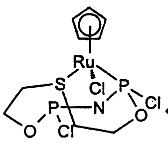
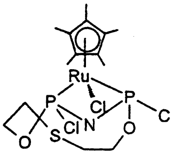
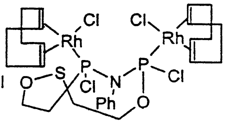

V (X=Cl, F)


VII (M=Pd or Pt)


VIII


IX


X

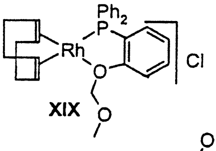
HEMILABILE PHOSPHINE LIGANDS WITH ETHER FUNCTIONALITIES

Transition metal catalysts with fairly small differences in their coordination sphere can cause marked change in the selectivity and activity of the catalytic processes. Hence the physico chemical properties of the metal complexes can be correlated to the structure of the ligand, which has been the subject of many investigations in recent years.[2] Hemilabile phosphines with pendant ether groups are of considerable interest, in particular with respect to the development of potential catalysts due to the following advantages: (a) Hemilabile phosphines can coordinate to the low valent metal centers and stabilize it in lower oxidation state and enhance the chelating possibilities through ether O-center; (b) The labile M—O coordinate bond in the chelate complex can be readily cleaved as and when it is required during the catalytic and biological processes.[3] The hemilabile phosphine ligands with ether functionalities, $Ph_2PC_6H_4OCH_2OCH_3$ (**XI**) and $PhP(C_6H_4OCH_2OCH_3)_2$ (**XII**) show interesting coordination behavior when reacted with transition metal organometallic derivatives.[4]

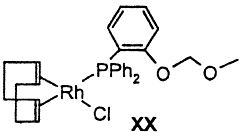
The reactions of **XI** or **XII** with $Mo(CO)_6$ and $[M(CO)_4L_2]$ (M = Cr, Mo or W; L_2 = (piperidine)$_2$, NBD) afford penta- or tetracarbonyl derivatives $[M(CO)_4(PPhRC_6H_4OCH_2OCH_3)_2]$ (M = Cr, R = Ph or $OCH_2O–CH_3$, **XIII**; M = Mo, R = Ph, **XIV**; M = W, R = Ph or OCH_2OCH_3, **XV**) exhibiting monodentate mode of coordination. The tetracarbonyl complexes of chromium prefer *trans* geometry whereas the molybdenum and tungsten complexes form stable *cis* isomers. The ether functionality does not show any interaction with the metal centers. The structures of complexes, $Mo(CO)_5(PhPRC_6H_4OCH_2OCH_3)$ (R = Ph or $C_6H_4OCH_2O–CH_3$, **XVI)** have been established by single crystal x-ray diffraction studies.

When ligand **XI** was treated with $RuCl_3{\cdot}3H_2O$, a neutral trischelate Ru(III) complex, $[Ru(Ph_2PC_6H_4O\text{-}\kappa O, \kappa P)_3]$ (**XVII**) was obtained in good yield. The ether linkage is cleaved during complexation leading to the formation of phenolate ion with the metathetical elimination of methoxymethyl chloride. The phenolate oxygens bind to the ruthenium center forming three five-membered metallacycles. The structure of complex **XVII** is confirmed by single crystal x-ray diffraction studies.

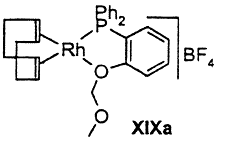
The reaction of **XI** with $[Rh(CO)_2Cl]_2$ affords a neutral complex, $[Rh(CO)Cl(PPh_2C_6H_4OCH_2OCH_3\text{-}\kappa P,\kappa O)]$ (**XVIII**) whereas the reaction with $[Rh(COD)Cl]_2$ gives a mixture of both neutral and cationic complexes as confirmed by its ^{31}P NMR spectral data. However, after crystallization, complex **XX** was obtained exclusively and attempts to isolate the cationic complex **XIX** have been unsuccessful. Similar cationic complex **XIXa** was obtained in a separate reaction of **XI** with $[Rh(COD)Cl]_2$ in presence of $AgBF_4$.



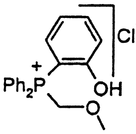
XIX



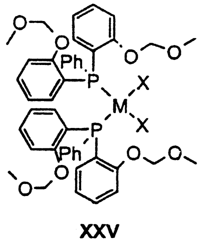
XX



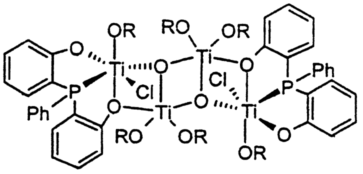
XIXa



XXIII



XXV



R = *i*Pr XXVI

The reaction of **XI** with $[Pd(COD)Cl_2]$ in 2:1 molar ratio leads to the formation of a mixture of products which are separated by fractional crystallization. Formation of complexes, [PdCl(PPh$_2$C$_6$H$_4$O-κP,κO)(PPh$_2$C$_6$H$_4$OH-κP)] (**XXI**) and [Pd(PPh$_2$C$_6$H$_4$O)$_2$-κP,κO] (**XXII**) involve metathetical elimination as observed in the case of Ru(III) complex, **XVII**. The structure of complex **XXI** co-crystallized with phosphonium salt **XXIII** having extensive hydrogen bonding was established by single crystal x-ray diffraction studies. The reaction of **XI** with [Pd(COD)Cl$_2$] in the presence of 2 mmol of AgBF$_4$ resulted in the formation of cationic complex, [Pd(PPh$_2$C$_6$H$_4$OCH$_2$OCH$_3$-κP,κO)$_2$](BF$_4$)$_2$ (**XXIV**). The reactions of **XII** with [M(COD)X$_2$] (M = Pd or Pt; X = Cl, I) afford [M{PPh(C$_6$H$_4$OCH$_2$OCH$_3$)$_2$}$_2$X$_2$] (**XXV**) in good yield.

The reaction of PhP(C$_6$H$_4$OH-*o*)$_2$ with TiCl$_4$ in the presence of ^{i}PrOH affords a mixture of products as confirmed from the ^{31}P NMR spectroscopic data. However, the tetranuclear complex, [{(^{i}PrO)$_2$Ti(μ^3-O)TiCl(^{i}PrO)((OC$_6$H$_4$)$_2$PPh)}$_2$] (**XXVI**), was isolated from the reaction mixture in low yield by crystallizing it in diethyl ether at room temperature. The x-ray structure reveals the centrosymmetric and dimeric nature of the molecule where the phenolato oxygen and oxo groups bridge the metal centers to result in three four-membered Ti$_2$O$_2$ rings. The interesting feature of these rings is their arrangement in three-dimensional space, which resemble a flat chair where alternate corners are occupied by titanium and oxygen atoms.

In summary, the heterocyclic diphosphanes and hemilabile phosphines exhibit different modes of coordination with various transition metal derivatives. The phosphorochloridite readily react with Pd(II), Pt(II), and Ru(II) derivatives, demonstrating η^2 modes of coordination and with Rh(I) derivative it forms dinuclear complex. We have synthesized a novel heptacyclic tetranuclear titanium complex containing four different types of oxygen bindings with formal titanium-phosphorus bonds. The preferential binding of soft π-phosphorus atoms to oxophilic titanium centers is due to the diphenolate substitutents on phosphorus centers, which bring the Ti and P atoms in close proximity to establish Ti—P bonds.

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