Symbiotic reactions between five- and six-membered hypervalent spirobicyclic phosphoranes and transition metal carbonylates†

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The nucleophilic substitution reactions of five- and six-membered hypervalent phosphorus containing spirobicyclic phosphoranes with metal carbonylates of high nucleophilic character result in the isolation of the corresponding metallated phosphoranes. The presence of five- and six-membered rings in their structures inhibits the ionising of these compounds into their phosphonium cations in solutions. These have been characterised by elemental analysis, molar conductance and spectroscopic (mass and $^1$H NMR) and TG studies.

The reported synthesis of both cyclic and acyclic metallated phosphoranes1-4 has brought about not only the symbiotic merger of transition metal and hypervalent chemistry5 of phosphorus, but has also extended the scope of hypervalent bonding theory. However, synthesis of cyclic species has been limited to five-membered metallophosphoranes in which the hypervalent phosphorus besides being directly bonded to transition metal is bonded only to oxygen. Though four-membered metallophosphoranes are known6, where the metallated pentacordinate phosphorus is bonded to heteroatoms other than oxygen, such moieties are not known in case of five- and six-membered bicyclic metallophosphoranes. We report here the synthesis and characterisation of these species.

Materials and Methods

All reactions were carried out in an atmosphere of nitrogen gas, purified by passage over hot BASF catalyst R-3-11 and supported by $P_4O_{10}$ (aquasorb). Solvents and reagents were degassed by repeated evacuation and flushing with pure nitrogen before use. Glassware was flame-dried in vacuo before use. Tetrahydrofuran (THF) was distilled from Na/benzophenone under nitrogen. N,N'-Dime-thylformamide was purified by reported methods7. Phosphorus, sulphur and manganese were estimated gravimetrically by reported methods8.

(i) Preparation of pentacarbonyl-(1,1',3,3'-tetrahydro-2,2'-spirobi-[2H-1,3,2λ^5-benzodiazaphosphol]-2-y1) manganese (5)

The compound [Mn$_2$(CO)$_{10}$] (1.47g, 3.8 mmol) in tetrahydrofuran (THF) (75 cm$^3$) was treated with sodium metal 0.27g (7.6 mmol + 50% excess) in mercury (100g). The resulting Na[Mn(CO)$_3$] solution was filtered and added dropwise to a solution of 1 (2.12g, 7.6 mmol) in THF at -78°C with continuous stirring. The dropwise addition was done through a pressure equalising (teflon stop-cocked) dropping funnel. The three-necked reaction flask was fitted with a nitrogen inlet stop cock and a rubber septum. The stirring was continued for 2h at this temperature. The reaction mixture was then allowed to warm slowly to ambient temperature with continuous...
stirring overnight. It was then filtered through a filtration unit in a stream of dry nitrogen. The solvent was removed from filtrate in vacuo and the residue dried. The residue was further purified by crystallising from THF and petroleum ether (60-80°C) to finally obtain a very light brown crystalline material; yield 1.86g (60%), m.pt. 160°C (decomposed); molar conductance in N,N'-dimethylformamide = \( 18.83 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1} \) [Found: C,47.02; H,2.80; N,10.79; P,6.10, Calcd for C\(_{19}\)H\(_{21}\)MnN\(_2\)O\(_3\): C,46.15; H,2.42; N,11.33 and P,6.27]. Its mass spectrum exhibited a molecular ion peak \((m/z\) 493, 1\% relative intensity) and peaks corresponding to \((\text{C}_9\text{H}_4\text{NHCONH})_2\text{P-Mn(CO)}_5^+ (465,1\%); (\text{C}_9\text{H}_4\text{NHCONH})_2\text{P-Mn(CO)}_5^+ (437,3\%); (\text{C}_9\text{H}_4\text{NHCONH})_2\text{P-Mn(CO)}_5^+ (381,5\%); (\text{C}_9\text{H}_4\text{CO(NH})_2\text{P-Mn}^+ (310,100\%) and (\text{C}_9\text{H}_4)_2\text{P-Mn}^+ (237,11\%).

**Results and Discussion**

Compounds 1-4 undergo nucleophilic substitution reactions with Na\(^+\)Mn(CO)_5 in 1:1 mole ratio in THF at -78°C to form five- and six-membered metallated spirobicyclic phosphoranes 5-8. The reactions show the cleavable nature of P - Cl bond\(^{\circ}\) in 1-4.

The reactions could be visualised as shown in Scheme 1.

Such type of substitution reactions are very well documented in literature\(^1\) and are more general and straightforward in comparison to the synthetic route reported by Ebsworth and coworkers\(^2\) for the synthesis of this class of compounds. However, these nucleophilic substitution reactions are highly specific in terms of nucleophilicity of metal carbonylates. The corresponding reactions of 1-4 with Na\(^+\)Co(CO)_4 were not successful, since the products isolated were sticky materials with variable compositions. The failure of these reactions is attributed to the low nucleophilicity of cobalt tetracarbonylate\(^1\). These compounds behave as true phosphoranes as is evidenced from the molar conductance values\(^1\) of their millimolar solutions in N,N'-dimethylformamide, thus ruling out the possibility of their existence as phosphonium salts in solution. This may be because of the fact that pentacovalent structure is stabilized by the incorporation of five- and six-membered ring\(^1\) as well as because of the well known Thorpe-Ingold effect\(^1\). These compounds...
are sufficiently volatile and give a good mass spectra. All these compounds exhibit signals of very low intensities (1-5% of the base peak) corresponding to molecular ion peaks. The fragmentation pattern further show signals corresponding to loss of CO. However, the loss of CO, unlike in pure metal carbonyls, is not stepwise. The non-sequential loss of CO was also observed while studying the thermal behaviour of these compounds. For example, in the derivatogram of 6 (Fig. 1) obtained by projecting DTG curve on TG, it is possible to identify the inflexion points on TG, which correspond to various intermediates. It starts decomposing around 40°C, and between 40 and 100°C, a mass loss equivalent to two molecules of CO is observed in the first step of decomposition. It then loses the remaining three molecules of CO in a single step. This second step of decomposition is completed at 170°C. The loss of CO is also evidenced by DTA curve corresponding to these steps which indicate an exothermic decomposition process. The compound then decomposes through some unidentified intermediates to yield ultimately a stable residue of composition Mn$_2$P$_2$O$_7$ between 610 and 700°C, through the formation of slightly less stable MnHPO$_4$ (ref. 18). This type of decomposition pattern is observed for compounds 5, 7 and 8.

The vP-Cl band in 1-4 observed in the infrared region in the range 500-530 cm$^{-1}$ is of diagnostic value in monitoring these reactions. The fact that Cl is completely substituted in 1-4 by Mn(CO)$_5$ is exhibited not only by the disappearance of the signal due to vP-Cl but also by the appearance of additional bands in the region 2100-2000 cm$^{-1}$ (Table 1) due to vCO of Mn(CO)$_5$ group. The solution spectra (in THF) of Mn$_2$(CO)$_{10}$ show three principal carbonyl stretching absorption bands at 2060 cm$^{-1}$ (b$_2$ mode), 2020 cm$^{-1}$ (e$_1$ mode) and 1983 cm$^{-1}$ (b$_3$ mode). The patterns and positions of CO stretching bands in these compounds (Table 1) are basically no different from those of the parent carbonyl. It is thus presumed that there is no change of electron density on the transition metal as a consequence of its bonding to the pentacoordinate phosphorus.

$^1$H NMR data are presented in Table 1. Compounds 5-8 exhibit a broad and complex multiplet in the aromatic region. This multiplet shows a small upfield shift when compared with the position of multiplets for 1-4. The N-H protons in these compounds seem to overlap with aromatic protons and D$_2$O exchange studies to locate the position of N-H protons were not successful as all these compounds are hydrolytically unstable.

The frequencies of the CO stretches in the IR, as well as the ability to obtain a mass spectrum, eliminate the possibility of formation ionic species, viz., [C$_6$H$_4$(NH)$_2$]$_2$P$^+$-[Mn(CO)$_3$]$^-$, [C$_6$H$_4$SNH$_2$]$_2$P$^+$-[Mn(CO)$_3$]$^-$, [C$_6$H$_4$(ONH)$_2$]$_2$P$^+$-[Mn(CO)$_3$]$^-$, [C$_6$H$_4$NH(CONH)$_2$]$_2$P$^+$-[Mn(CO)$_3$]$^-$. The nature of transition metal-pentacoordinate phosphorus bond can be viewed in two ways. Riess and coworkers described it in terms of phosphoranides (R$_4$P$^-$) in

![Fig. 1—TG-DTGA-DTA of 6](image-url)
their bidentate polycyclic systems — since it involved an abstraction of proton from the coordinated nitrogen, thus allowing the ligand to donate a pair of electrons to the metal. However, by referring to 5-8 as substituted phosphoranes, the opposite is implied here which is consistent with the mode of synthesis. Unfortunately, even after persistent efforts, it has not been possible to grow good quality crystals of any of these species. The final and definitive assignment of their structure would be possible only after X-ray diffraction studies are carried.

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References