Synthesis and Characterization of Four-membered, Spirobicyclic, Transition-metal-substituted Phosphoranes

Badri N. Anand,* Rajwant Bains, and Km. Usha
Department of Chemistry, Panjab University, Chandigarh 160014, India

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The nucleophilic substitution reactions of $\overline{\mathrm{P[RNC(O)N}}\mathrm{R'}]_2\mathrm{Cl}$ [R = R' = CH_3, (**1a**); C_6H_5, (**1b**); R = CH_3, R' = C_6H_5, (**1c**)] with $Na[Mn(CO)_5]$ in tetrahydrofuran at −78 °C result in the synthesis of a new class of four-membered spirobicyclic transition-metal-substituted phosphoranes in which the five-co-ordinated phosphorus is bonded to heteroatoms other than oxygen. These compounds have been characterized by elemental analysis, n.m.r. spectroscopy (^{1}H and ^{31}P), and thermal analysis.

The symbiosis of hypervalent[1] and transition-metal chemistry has been achieved by the reported synthesis of both cyclic and acyclic transition-metal-substituted phosphoranes.[2–5] The cyclic species[2] consisted of five-membered spirobicyclic oxyphosphoranes and contained a direct bond between the transition metal and five-co-ordinated phosphorus. However, there are no reports regarding the nature of the corresponding four-membered metallophosphoranes. We report herein the synthesis and characterization of such moieties.

Experimental

All reactions and sample preparations were carried out in a Pyrex vacuum line under a dry nitrogen atmosphere using dry and degassed solvents. Glassware was flame dried under vacuum before use.

Phosphorus and manganese were estimated gravimetrically by reported methods.[6] Microanalyses for C, H, and N were performed by the microanalytical service of Panjab University. Thermal analysis was carried on a MOM Budapest Derivatograph (type Paulik, Paulik, and Erdey). Conductances of millimolar solutions were measured on a Century CC 601 conductivity bridge. Molecular weights were determined cryoscopically. Mass spectral measurements were done on a VG Micromass MM 70/70F spectrometer both at 70 and 20 eV (eV ≈ 1.60×10^{-19} J). Proton n.m.r. spectra were recorded at 90 MHz on a Varian EM-390 spectrometer, ^{31}P n.m.r. spectra on Bruker 500-MHz and JOEL FZ 90Q FT multinuclear spectrometers.

NN'-Dimethylurea and *NN'*-diphenylurea (Fluka) were used after drying for about 4 h under vacuum. Freshly sublimed dimanganese decacarbonyl and dicobalt octacarbonyl (Strem chemicals, U.S.A.) were used. Methyl-lithium was prepared from CH_3I (John Baker & Co.) by treatment with *n*-butyl-lithium in hexane solution.[7]

Syntheses.—The starting materials (**1a**)—(**1c**) were prepared according to published methods.[8]

(*i*) *Pentacarbonyl* (1,3,5,7-*tetramethyl*-2,6-*dioxo*-1,3,5,7-*tetra-aza*-4λ^5-*phosphaspiro*[3.3]*hept*-4-*yl*)*manganese* (**3a**). The compound $[Mn_2(CO)_{10}]$ (2.58 g, 6 mmol) in tetrahydrofuran (thf) (60 cm^3) was treated with sodium metal (0.41 g, 12 mmol + 50% excess) in mercury (100 g).[9] The resulting $Na[Mn(CO)_5]$ solution was filtered and added dropwise to a solution of compound (**1a**) (2.94 g, 12 mmol) in thf at −78 °C with continuous stirring. The reaction mixture was allowed to warm slowly to ambient temperatures and filtered, yielding a yellow solution. After removal of thf, the crude product was dissolved by multiple washings with toluene on a filter frit. Finally toluene was removed yielding the pure product, as a pale yellow moisture-sensitive solid. Yield 2.1 g (40%), m.p. 105 °C (decomp.). Molar conductance in nitrobenzene 1.0 S cm^2 mol^{-1} (Found: C, 31.60; H, 2.95; Mn, 12.9; N, 13.75; P, 7.20. Calc. for $C_{11}H_{12}MnN_4O_7P$: C, 33.15; H, 3.00; Mn, 13.80; N, 14.05; P, 7.80%).

(*ii*) *Pentacarbonyl*(1,3,5,7-*tetraphenyl*-2,6-*dioxo*-1,3,5,7-*tetra-aza*-4λ^5-*phosphaspiro*[3.3]*hept*-4-*yl*)*manganese* (**3b**). This was prepared by a method similar to that for (**3a**). Yield 40%, m.p. 110 °C (decomp.). Molar conductance in nitrobenzene 2.99 S cm^2 mol^{-1}. Molecular weight in nitrobenzene: Found 615; Calc. 645.9. (Found: C, 56.95; H, 3.20; Mn, 7.90; N, 8.80; P, 4.60. Calc. for $C_{31}H_{20}MnN_4O_7P$: C, 57.60; H, 3.10; Mn, 8.50; N, 8.65; P, 4.80%).

(*iii*) *Pentacarbonyl*(1,3-*dimethyl*-5,7-*diphenyl*-2,6-*dioxo*-1,3,5,7-*tetra-aza*-4λ^5-*phosphaspiro*[3.3]*hept*-4-*yl*)*manganese* (**3c**). This was also prepared by a method similar to that for (**3a**). Yield 40%, m.p. 110 °C (decomp.). Molar conductance in nitrobenzene 3.30 S cm^2 mol^{-1}. Molecular weight in nitrobenzene: Found 519; Calc. 521.9. (Found: C, 47.65; H, 3.00; Mn, 9.90; N, 10.20; P, 5.40. Calc. for $C_{21}H_{16}MnN_4O_7P$: C, 48.30; H, 3.05; Mn, 10.50; N, 10.75; P, 5.95%).

(*iv*) *Reaction of Compound* (**1b**) *with Methyl-lithium to yield* 4-*Methyl*-1,3,5,7-*tetraphenyl*-1,3,5,7-*tetra-aza*-4λ^5-*phosphaspiro*-[3.3]*heptane*-2,6-*dione* (**4**). Methyl-lithium (3.0 cm^3, 2.37 mmol, 0.79N) was added by syringe to a solution of compound (**1b**) (1.15 g, 2.36 mmol) in thf at 0 °C with continuous stirring. The reaction mixture was slowly warmed to ambient temperature and stirring continued for 10 h. Filtration of LiCl and removal of solvent afforded a residue which was purified by recrystallization from chloroform to produce a light brown powder in 70% yield, m.p. 68 °C (decomp.). Molar conductance in nitrobenzene 11.33 S cm^2 mol^{-1} (Found: C, 69.20; H, 4.55; N, 11.85; P, 7.00. Calc. for $C_{27}H_{23}N_4O_2P$: C, 69.50; H, 4.95; N, 12.00; P, 6.65%).

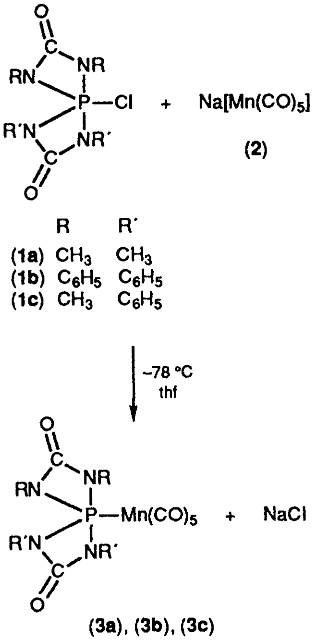
Results and Discussion

The reaction of compounds (**1a**)—(**1c**) with $Na[Mn(CO)_5]$ in a 1:1 molar ratio in thf solution at −78 °C leads to the

Table. N.m.r. data (δ)[a]

	(1a)	**(3a)**	**(1b)**	**(3b)**	**(1c)**	**(3c)**
^{1}H	3.30	3.60	6.90—7.40	7.30—7.60	3.20	3.55
	(12 H, 4NCH$_3$, s)		(20 H, 4NC$_6$H$_5$, m)		(6 H, 2NCH$_3$, s)	
					7.55—7.86	7.80—8.06
					(10 H, 2NC$_6$H$_5$, m)	
^{31}P	−56.60	−1.30 (br)	−1.49[b]	−12.30 (br)[b]	−62.40	−1.19 (br)

[a] ^{1}H in CDCl$_3$ referenced to SiMe$_4$, ^{31}P in acetonitrile referenced to 85% H$_3$PO$_4$. s = singlet, m = multiplet. [b] Referenced to trimethyl phosphate.



formation of transition-metal-bonded four-membered spirobicyclic phosphoranes (**3a**)—(**3c**).

Since nitrogen atoms bonded to phosphorus are in general not very nucleophilic,[10] the synthesis involves preferential nucleophilic substitution at five-co-ordinate phosphorus in (**1a**)—(**1c**) involving cleavage of the P–Cl bond. The compounds (**3a**)—(**3c**) are all pale yellow solids which decompose without melting, are soluble in polar solvents, and are covalent in nature as evidenced by the molar conductance of millimolar solutions in nitrobenzene,[11] thus ruling out the possibility of their existing as phosphonium salts in solution. This may be attributed due to the incorporation of a four-membered ring in the phosphorane structure.[1b] The compounds are all fairly stable at room temperature but undergo slow decomposition (as noted by their gradual colour change) when stored for longer times.

These compounds could be transferred into the gas phase to get good mass spectra. While (**3a**) and (**3c**) exhibit the parent molecular-ion signals of low intensity (1% of base peak) at *m*/*z* 397 (calc. 398) and 521 (calc. 522) respectively, (**3b**) does not show any signal corresponding to the parent molecular ion. This could be partly attributed to its being insufficiently volatile, however its fragmentation pattern was very similar to those of (**3a**) and (**3c**): all these compounds exhibited signals corresponding to sequential stepwise loss of carbon monoxide. The stepwise loss of carbon monoxide has been beautifully captured in a derivatogram while studying their thermal decomposition. The striking similarity in the mode of decomposition is that all three compounds lose five molecules of CO in more than one step. For example, (**3b**) shows a weight loss equivalent to two molecules of CO beween 45 and 100 °C in its first step of decomposition. It then loses the remaining three molecules of CO in a second step which is completed at 170 °C. The loss of CO in these two steps is evidenced by the differential thermal analysis (d.t.a.) curve corresponding to these steps which indicates an exothermic decomposition process. As soon as the loss of five molecules of CO is completed, the compound decomposes in a single step and the change in the direction of the curve near 300 °C conforms rather well with the formation of the slightly less stable MnHPO$_4$.[12] However, this is quantitatively converted into the more stable Mn$_2$P$_2$O$_7$ between 610 and 700 °C in the case of (**3a**) and (**3c**).

The Table reports the n.m.r. data of the starting materials (**1a**)—(**1c**) and their transition-metal derivatives (**3a**)—(**3c**). The single ^{31}P signals of (**3a**)—(**3c**) in the five-co-ordinate phosphorus region are quite broad. This is due, most likely, to the quadrupole and spin ($\frac{5}{2}$) of the manganese nucleus.[2,13]

The nucleophilic substitution at five-co-ordinate phosphorus is found to occur only by strong nucleophiles. Thus whereas the reactions of (**1a**)—(**1c**) with Na[Mn(CO)$_5$] result in the isolation of well characterized species, with Na[Co(CO)$_4$] under similar reaction conditions sticky materials with indefinite compositions are obtained. This may be due to [Co(CO)$_4$]$^-$ being a much weaker nucleophile[14] than [Mn(CO)$_5$]$^-$. It has been further observed that substitution reactions of compounds (**1a**)—(**1c**) are possible with moieties which are isolobal with Cl. Thus the reaction of (**1b**) with LiCH$_3$ in thf resulted in the isolation of its P-methylated derivative (**4**). Compound (**1b**) was chosen for this reaction for the expected simplicity of its ^{1}H n.m.r. spectrum in the methyl region. Although it has not been possible to grow good quality crystals of any of these compounds, on the basis of an *X*-ray analysis[8] it was shown that the chlorine atom in (**1c**) is in an equatorial position of a trigonal-bipyramidal configuration together with two nitrogen atoms. The same structure is adopted for (**3c**) and also by analogy for (**3a**) and (**3b**) with the Mn(CO)$_5$ group in an equatorial position.[15]

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