Synthesis and Spectroscopic Study of a Transition Metal-Substituted Phosphorane: 2-Pentacarbonylmanganese-2,2'-spirobi(1,3,2-benzodioxaphosphole)

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Received September 3, 1982

Introduction

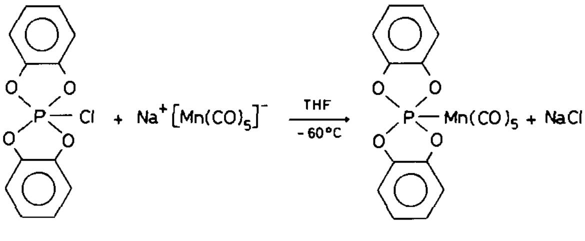
Phosphoranes are well-known examples of a class of compounds where the Lewis octet of the central atom is expanded. These 'hypervalent' [1] molecules have received considerable attention from both theoretical and experimental chemists [2]. However, until recently, the chemistry of these molecules has been limited to direct attachment of the hypervalent atom to main group elements only. A few examples of an RP (R = aryl, alkyl, OCH_3) [3] group bridging four metal atoms exist and, recently, Riess and coworkers [4] have prepared cyclic $\overline{M-P-O}$ and $\overline{M-P-N}$ (M = Mo, W) species where P is pentacoordinate. Riess' method involves proton abstraction from a bicyclic phosphine cationic complex and is very specific to the ligands.

The synthetic method described below illustrates a possible general route to obtaining transition metal-substituted phosphoranes. The idea behind the method is straightforward: nucleophilic substitution at pentacoordinate phosphorus involving cleavage of a P–X (X = halogen) bond is well documented [5]. For example, Me_3SiNMe_2 reacts with fluorophosphoranes [5] according to

$$(Me_2N)_nPF_{5-n} + Me_3SiNMe_2 \rightarrow (Me_2N)_{n+1}PF_{4-n} + Me_3SiF \quad (n = 0, 1, 2) \qquad (1)$$

A suitable scheme for synthesizing transition metal-substituted phosphoranes should involve a phosphorane with at least one P–X bond and the readily obtained transition metal anions [6]. Such a combination would be expected to yield a metal–phosphorus(V) bridge-free linkage.

2-Chloro-2,2'-spirobi(1,3,2-benzodioxaphosphole), I, reacts with $Na^+[Mn(CO)_5]^-$ to yield the title compound, II, according to



(I) (II)

II is the first example of a transition metal-substituted phosphorane, $R_4P{-}ML_n$, where only the phosphorus of the R_4P moiety is directly bonded to the transition metal.

Experimental

All procedures in the preparation of II are carried out in an inert atmosphere using dry and degassed solvents. In a typical preparation, 4.41 g (11.3 mmol) of freshly sublimed $Mn_2(CO)_{10}$ (Strem Chemical) is treated with 100 g of 1% Na/Hg in THF (60 ml) [6]. The resulting $Na^+[Mn(CO)_5]^-$ solution is filtered and added dropwise to a solution of 6.29 g (22.3 mmol) of I [7] in THF (60 ml) at –60 °C. The reaction mixture is allowed to slowly warm to ambient temperature and filtered, yielding a yellow-orange solution. After removal of the THF, the crude product is dissolved by myltiple washings with toluene on a filter frit. Finally, the toluene is removed, yielding the pure product, II, as a slightly yellow, moisture sensitive solid (9.20 g, 91%). *Anal.* Calc.: C, 46.18; H, 1.83; P, 7.00; Mn, 12.43. Found: C, 46.01; H, 2.16; P, 6.98; Mn, 11.90.

Results and Discussion

The mass spectrum of II, obtained at an inlet temperature of 40 °C, exhibits a significant molecular ion (6% of the base peak, $C_6H_4O_2P^+$). Sequential loss of CO is evident in the spectrum as well as significant peaks corresponding to $(C_6H_4O_2)_2PMn^+$ and $(C_6H_4O_2)_2P^+$ (23% and 29% of the base peak, respectively). Solution (THF) IR shows bands in the CO stretching region at 2133(m), 2075(w, sh), 2041 (vs), and 2003(m, sh).

NMR data are presented in Table I. A shift in the complex multiplet in the ^1H spectrum and a large downfield shift in the $^{31}P[^1H]$ spectrum is evident.

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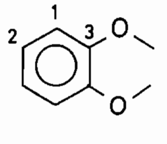
0020-1693/83/0000-0000/$03.00

TABLE I. NMR Data (ppm) for I and II.[a]

	I	II
^{1}H	7.15 (mult)	6.85 (mult)
^{31}P[^{1}H]	–12	67 (broad)
^{13}C[^{1}H]	111.8 (C_1)[b], J_{POCC} = 19.4 Hz	110.6 (C_1)[b], J_{POCC} = 6.8 Hz
	123.7 (C_2)[b]	121.4 (C_2)[b]
	143.4 (C_3)[b], J_{POC} = 7.6 Hz	147.0 (C_3)[b], J_{POC} = 4.2 Hz
		206 (CO, broad)

[a] All data obtained in THF. ^{1}H and ^{13}C data measured relative to solvent peaks (referenced to TMS). ^{31}P data referenced to external H_3PO_4.



[b] Assigned as in accordance with the assignments for catechol in reference 8.

The ^{31}P signal for II is quite broad (1100 Hz, width at half height) due, most likely, to the quadrupole and spin (5/2) of the Mn nucleus. Small, but significant, shifts in the ^{13}C[^{1}H] spectrum are also evident.

The frequencies of the CO stretches in the IR (*ca.* 2000–2150 cm^{-1}), as well as the ability to obtain a mass spectrum, eliminate the possibility of formation of an ionic species, *viz.* $(C_6H_4O_2)_2P^+$-$[Mn(CO)_5]^-$. Also, the very similar ^{13}C[^{1}H] NMR spectra for I and II preclude any ring opening.

Finally, mention should be made of the nature of the metal–phosphorus σ bond. Riess [4] has described the metal–phosphorus(V) bond in his system as a phosphoranide, R_4P^-, ligand donating a pair of electrons to the metal, a traditional ligand–metal bond. By referring to II as a substituted phosphorane, the opposite case is implied here, consistent with the synthesis. This is just a matter of electron count when looking at the final molecule; however, it should prove valuable for general syntheses of this class of compounds.

Acknowledgment

The authors are grateful to the Robert A. Welch Foundation for generous financial support. We thank Mr. T. Truong for obtaining the mass spectra. Also, helpful discussions with Professor M. H. Chisholm are gratefully acknowledged. B. N. Anand thanks Panjab University, Chandigarh, India, for granting a leave of absence.

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