Letters to the Editor

A reaction of 2,5-diphenylphosphacymantrene with diethylamine in the presence of water

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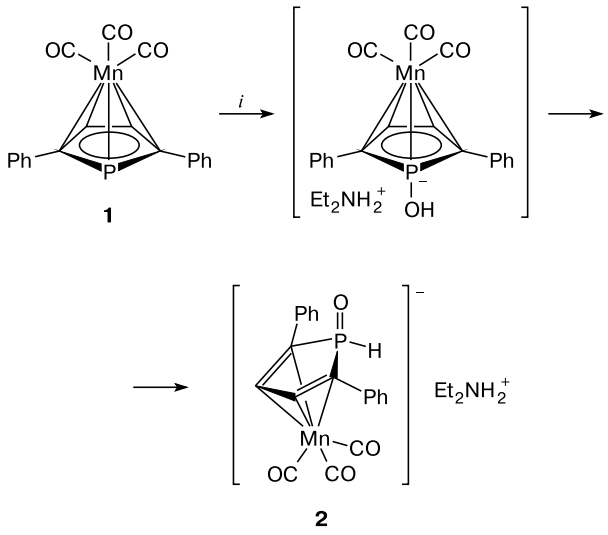
In our continued investigations of the chemistry of 2,5-diphenylphosphacymantrene (**1**),[1,2] we found that compound **1** does not react with Et_2NH in benzene or CH_2Cl_2. However, in the presence of small amounts of water (amine : water = ~(8—10) : 1), complex **2** forms slowly (Scheme 1). The transformation **1**→**2** results in the following spectral changes: in the ^{31}P NMR spectrum, the signal for the starting reagent **1** (s, δ −30.6) becomes less intense and a low-field doublet ($^1J_{P,H}$ = 549 Hz) characteristic of a P—H bond appears. Complex **2** is poorly soluble in C_6H_6 and CH_2Cl_2 and insoluble in pentane and hexane.

In the IR spectrum of complex **2**, both the bands ν(CO) are shifted to the lower wavenumbers, thus suggesting the formation of an anion. The ratio of the band widths characteristic of the fragment $Mn(CO)_3$ is retained: in CH_2Cl_2, ν(CO) 1950 (br) and 2025 cm^{-1} for **1** and 1900 (br) and 1990 cm^{-1} for **2**. The $^1H\{^{31}P\}$ NMR spectrum of complex **2** contains a broadened singlet at δ 7.83 for the P—H proton, which is absent from the spectrum of the starting compound **1**. According to preliminary X-ray diffraction data, complex **2** has an ionic structure consisting of the anion $[(CO)_3Mn\text{-}\eta\text{-}2,5\text{-}Ph_2H_2C_4P(=O)H]^-$ and the cation $Et_2NH_2^+$. It is known that such nucleophiles as OMe, OEt,[2] PhLi,[3] and Bu^tLi[4] can add to the P atom, which correlates with quantum-chemical calculations.[3,5] The formation of complex **2** can be explained as follows. Ap-

Scheme 1



i. Et_2NH, H_2O

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parently, the presence of a strong base (amine) leads to the equilibrium in solution

$$Et_2NH + H_2O \rightleftharpoons Et_2NH_2^+OH^-.$$

In a reaction of $Et_2NH_2^+OH^-$ with compound **1**, the nucleophile OH^- adds to the P atom to give an unstable intermediate anion containing a P—OH bond (see Scheme 1). Migration of the H atom from oxygen to phosphorus results in rapid transformation of the anion into complex salt **2** containing the phosphoryl fragment P(=O)H with the P—H bond in the anion.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance-400 instrument (400.16 (^{1}H) and 161.92 MHz (^{31}P)). Chemical shifts are referenced to $SiMe_4$ for ^{1}H and to H_3PO_4 for ^{31}P.

Complex 2. Two to three drops of water were added in an inert atmosphere to compound **1** (30 mg, 0.08 mmol) in a mixture of diethylamine (1 mL) and CH_2Cl_2 (3 mL). The reaction mixture was stirred and left in the dark at room temperature. After ~24 h, yellow crystals began to form. The solution was decanted and the crystals were washed with cold pentane two to three times and dried *in vacuo*. The yield of complex **2** was 22 mg (60%). Found (%): C, 59.13; H, 5.45; N, 3.16. $C_{23}H_{25}MnNO_4P$. Calculated (%): C, 59.36; H, 5.41; N, 3.01. ^{31}P NMR (CH_2Cl_2), δ: −8.70 (d, $^1J_{P,H}$ = 549.0 Hz; the chemical shift refers to the midpoint of the doublet). Either line of the doublet is split into a triplet with the constant $^3J_{P,H(3,4)}$ = 12.7 Hz. $^1H\{^{31}P\}$ NMR (DMSO-d_6), δ: 7.82 (br.s, 1 H, P—H); 7.30, 7.19, 7.00 (10 H each, *o*-, *m*-, and *p*-C_6H_5); 5.51 (d, 2 H, H(3), H(4), $^3J_{H(3,4),P}$ = = 12.7 Hz); 2.81 (br.q, 4 H, N—CH_2); 1.09 (t, 6 H, CH_3, $J_{H,H}$ = = 7 Hz). The coupling constant $^1J_{^1H,^{31}P}$ = 549.0 Hz obtained by comparing the ^{1}H and $^1H\{^{31}P\}$ NMR spectra is identical with that determined from the ^{31}P NMR spectrum.

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