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Synthesis and Reactions of Tris(tricarbonyl-η^5-cyclopentadienylmolybdyl)phosphine, μ^3-P[η^5-$C_5H_5Mo(CO)_3$]$_3$

VOLKER GROSSBRUCHHAUS and DIETER REHDER*

Institut für Anorganische Chemie der Universität,
Martin-Luther-King-Platz 6, D-2000 Hamburg 13, F.R.G.

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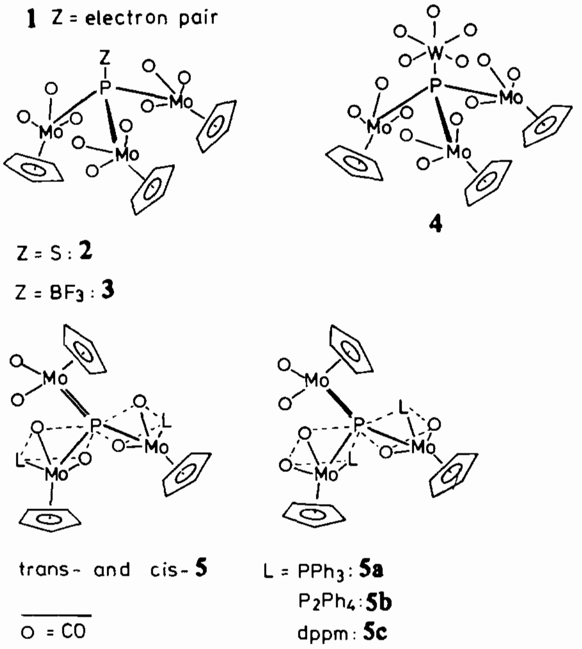

Scheme 1.

Organometallic derivatives of trivalent phosphorus and its heavier homologues are of interest as synthons for cluster compounds built up by metals and nonmetals or by main group and transition metals [1, 2]. Examples are the complexes $R_2E\{M\}$ (E = P, As; {M} is a carbonyl-cyclopentadienyl group 6 or group 8 fragment) and their secondary products generated by removal of one CO and containing a M=E double bond [3], RP{M'}$_2$ ({M'} e.g. = $Cr(CO)_5$, $Mn(CO)_2Cp$ [4]) and $\{(CO)_5Cr\}_2P{=}W(CO)_2Cp$ [5], again with the phosphorus in the sp^2 hybridized state. More recently, 'open clusters' of the composition Bi{M''}$_3$ ({M''} = $Co(CO)_4$ [6] and $Mn(CO)_5$ [7]) with sp^3 bismuth have been synthesized and structurally characterized. We report now on the comparable complex $P[Mo(CO)_3Cp]_3$ (**1**) and some of the reactions at the nucleophilic sp^3 phosphorus, which constitutes the centre of this cluster compound.

1 is obtained from the reaction between PCl_3 and $K[Mo(CO)_3Cp]$ (molar ratio 1/3) in highly purified THF under an inert gas atmosphere. Concentration of the red solution and chromatography on silica gel (Merck, 70-230 mesh ASTM) with THF/n-pentane 1/1 as the elutant yields a red fraction from which **1** is precipitated by addition of ether/$CHCl_3$ 1/1 as an analytically and spectroscopically pure, cherry-red powder. ^{1}H NMR [$\delta(C_5H_5)$ = 5.67(s) ppm], ^{31}P NMR [δ(P) = −40.2 ppm in $CDCl_3$] and IR data [ν(CO) = 2068s, 1965vs,br cm^{-1}, in THF] are in accord with the tentative formulation as given in Scheme 1, *i.e.* with the trigonal-pyramidal geometry of the PMo_3 moiety. The lacking ^{1}H(Cp)–^{31}P coupling conforms with the small (e.g. 1.6 Hz in $Ph_2PMo(CO)_3Cp$ [8]) or non-observed coupling interaction in phosphine and phosphide complexes containing the cyclopentadienylmetal fragment attached to phosphorus [9].

The comparatively high CO stretching frequencies of **1** indicate that there is substantial nucleophility left on the phosphorus function. Consequently, the reaction of **1** with S=PCl_3 or a CS_2 solution of sulfur leads to the phosphorane S=P[$Mo(CO)_3Cp$]$_3$ (**2**) [ν(CO) = 2060s and 1955vs, in THF], and reaction with $F_3B{\cdot}OEt_2$ yields the adduct F_3B–P[$Mo(CO)_3Cp$]$_3$ (**3**). In the ^{11}B NMR spectrum, **3** exhibits a singlet at −3.46 ppm in $CDCl_3$, relative to δ($F_3B{\cdot}OEt_2$) = 0; compare $\delta(BF_3)$ = +11.5 ppm [10]. With the solvent-stabilized, 16-electron fragments $M(CO)_5$ (M = Cr, Mo, W), no defined products have been obtained. However, $(CO)_5WP[Mo(CO)_3Cp]_3$ (**4**) can be synthesized via $(CO)_5WPCl_3$ [11] by salt metathesis with $K[Mo(CO)_3Cp]$. The composition of **4** (see Scheme 1) has been established by its spectral patterns [$\delta(C_5H_5)$ = 5.63 ppm in $CDCl_3$; ν(CO) = 2055w, 2018m, 1970sh, 1953s, 1910s cm^{-1}, in THF].

1 can also undergo CO substitution. Treatment of THF solutions of **1** in the presence of phosphines leads to complexes showing the common feature in the ν(CO) region (1960vs and 1878s cm^{-1} in THF) corresponding with $LMo(CO)_2Cp$. Since the ^{31}P resonance typical of the sp^3 phosphorus is no longer observed, one of the $Mo(CO)_2Cp$ moieties should be double-bonded to the phosphorus, hence $Cp(CO)_2Mo{=}P[Mo(CO)_2(L)Cp]_2$ [L = PPh_3 (**5a**), Ph_2P–PPh_2 (**5b**), $Ph_2PCH_2PPh_2$ (dppm) (**5c**)]. While, in the ^{31}P NMR spectrum of **5b**, there is one signal for coordinated P [+64.1(d) ppm, *J*(PP) = 87 Hz] and uncoordinated P [−9.5(d) ppm], two sets of signals are observed for **5a** and **5c** in the approximate intensity ratio 1/2 [**5a**: +57.8 and +49.8; **5c**: +40.6(d)/−26.7(d) ppm, *J*(PP) = 65 Hz, and +25.6(d)/−28.1(d) ppm, *J*(PP) = 45 Hz]. We tentatively assign these two sets to *cis* and *trans* isomers as shown in Scheme 1. The ^{31}P chemical shifts for sp^2 hybridized phosphorus in

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*Author to whom correspondence should be addressed.

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mono-, di- and trivalent species are 402 ppm [$(tBu)_2$-P=$W(CO)_2Cp$] [3], 1362 ppm [t-BuP$\{Cr(CO)_5\}_2$] [4] and 945 ppm [P$\{Cr(CO)_5\}_2W(CO)_2Cp$] [5], respectively, but have not been observed in our complexes.

An X-ray structure determination of **1** is in progress.

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