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## Stabilization of Hydroxy Tautomeric Form of Dimethyl Phosphite in the Coordination Sphere of Carbonyl Complexes of Group VI Metals

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**Abstract**—The interaction of dimethyl phosphite with hexacarbonyls of the chromium group metals in a nonpolar solvent has afforded metal(0)  $\sigma^4, \lambda^4$ -(dimethyl phosphite)pentacarbonyls containing a hydroxy tautomeric form of dimethyl phosphite in the coordination sphere. Hydrogen of the phosphite OH group in the metal(0)  $\sigma^4, \lambda^4$ -(dimethyl phosphite)pentacarbonyls exhibited a significant acidity, strongest for the chromium complexes. Due to the significant acidity of the phosphite hydroxyl, the metal(0)  $\sigma^4, \lambda^4$ -(dimethyl phosphite)pentacarbonyls are intermediates in the electrophilic version of the Pudovik reaction.

**Keywords:** outer sphere hydrophosphorylation, chromium group metals, phosphonates, phospho-organometallic compounds, metal(0)  $\sigma^4, \lambda^4$ -(dimethyl phosphite)pentacarbonyls, metal(0)  $\sigma^4, \lambda^5$ -(dimethyl phosphite)pentacarbonyls

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Organophosphorus compounds take an important part in organoelemental compounds chemistry owing to the applications in organic synthesis [1], pharmaceuticals [2], and material science [3], the compounds containing the C–P(=O) moiety being the most attractive in view of the practical application. Such compounds can be conventionally prepared from halogenated phosphorus derivatives like POCl<sub>3</sub> [4], R<sub>2</sub>PCl<sub>2</sub> [5], or R<sub>2</sub>POCl [6].

Over two recent decades, many studies appeared reporting the formation of the P–C bond via cross-coupling of alkenes or alkynes with the hydrophosphoryl compounds R<sub>2</sub>P(O)H [7], the key stage of the reaction being oxidative insertion of the metal in the P–H bond [8] yielding the R<sub>2</sub>P(O)ML<sub>x</sub> derivative. Nevertheless, it should be noted that the use of metal complexes for the stabilization of the hydroxy form of the hydrophosphoryl compound and involvement of the latter in the electrophilic version of the Pudovik reaction [9] have been underestimated.

Theoretical and experimental study of the interaction between dialkylphosphorous acids with homo-

ligand hexacarbonyl complexes of the chromium group metals [10] and participation of the formed products in the catalytic addition of dialkyl phosphites to the olefins not activated with any electron acceptor have been earlier reported. Basing on this, we have concluded on the feasibility of the participation in the addition reaction of the in situ formed metal hydride derivative of the chromium group metal. However, the formation of such reactive species demands high, almost 100%, concentration of the diethyl phosphite which cannot be realized for the catalytic cycle involving the activated olefin.

Here we describe in more details the synthesis, spectral parameters, and reactivity of the organophosphorus compounds, products of stabilization of the hydroxy tautomer of dimethyl phosphite by a chromium group transition metal, metal(0)  $\sigma^4, \lambda^4$ -(dimethylphosphite)pentacarbonyls, the formation of which was detected in dilute solutions containing metal(0) hexacarbonyl and dialkyl phosphite by means of <sup>31</sup>P NMR spectroscopy [11].

To obtain the comprehensive data, we performed the interaction of the dimethyl phosphite with a metal(0)