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Derivatization of Keggin-Type Polyoxometalates

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DERIVATIZATION OF KEGGIN-TYPE POLYOXOMETALATES

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Polyoxometalates (POMs) of the Keggin structure, $[XM_{12}O_{40}]^{n}$, are large metal-oxygen anions. They have shown significant antiviral activity, but failed in clinical trials due to their toxicity at the necessary dosages.¹ However, improving their bioselectivity through the attachment of appropriate ligands might decrease the required treatment levels and increase the POMs' therapeutic utility.

We have worked to attach organic ligands to lacunary Keggin ions $([XM_{11}O_{39}]^{n-})$, POMs in which a W-O group is missing, leaving a hole into which another metal atom may be inserted. From $[PW_{11}O_{39}]^{7-}$, we have successfully synthesized $[PW_{11}O_{39}RhCH_2COOH]^{5-}$, in which a rhodium atom bonded to a carboxylate group has entered the vacancy. Next, we modified the organic ligand by forming an amide bond to produce $[PW_{11}O_{39}RhCH_2CONPh]^{5-}$. Products have been characterized by ¹H and ³¹P NMR. We plan to extend this chemistry to include other, more biologically relevant amines.

¹J.T. Rhule, C.L. Hill, and D.A. Judd, "Polyoxometalates in Medicine," *Chem. Rev.* **1998**, 98, 327-357.