





plexes, which have only been observed for phosphorus<sup>6,16</sup> and antimony.<sup>17</sup> As such, **6b** and **10** define a new direction in the development of *catena*-phosphorus cations.<sup>18</sup>

In summary, dimethylthiophosphoryl chloride reacts with DMAP and Me<sub>3</sub>SiOTf to give a cationic adduct **9** represent-

ing a complex of the dimethylthiophosphonium cation. The quantitative ligand exchange of DMAP for Me<sub>3</sub>P gives **10**, demonstrating the coordinative nature of the N–P and P–P bonds. In the analogous exchange reaction with Me<sub>2</sub>PPMe<sub>2</sub>, a redox reaction is observed rather than the formation of a diphosphine–thiophosphonium complex.

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**Supporting Information Available:** X-ray crystallographic files in CIF format and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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