

OXIDATION OF 3d TRANSITION METALS BY MoF<sub>6</sub> AND WF<sub>6</sub> IN ACETONITRILE AND SOME REACTIONS OF THE SOLVATED CATION PRODUCTS

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One way of generating solvated metal cations in acetonitrile is to oxidize the metal with MoF<sub>6</sub> or WF<sub>6</sub>. In many cases these reactions are rapid and are thus good synthetic routes to the cations [M(NCMe)<sub>6</sub>]<sup>2+</sup>, M = Fe, Co, Cu and Zn. The oxidation of nickel is an exception however. Paradoxically, massive nickel (powder or wire 99.99%) reacts with WF<sub>6</sub> in MeCN at room temperature but not with MoF<sub>6</sub>, although the latter is the stronger oxidizing agent. MoF<sub>6</sub> does react when degassed nickel is evaporated in vacuo onto a Pyrex surface but under these conditions no reaction is observed using WF<sub>6</sub>. A possible explanation for these observations is that the oxide film on Ni passivates the metal to MoF<sub>6</sub> reaction, while it can be partially removed using the stronger Lewis acid WF<sub>6</sub>. The reduction products in these reactions are MoF<sub>6</sub><sup>-</sup> or mixtures of WF<sub>6</sub><sup>-</sup> and WF<sub>7</sub><sup>-</sup>; the oxidation product is [Ni(NCMe)<sub>6</sub>]<sup>2+</sup>. Generation of [M(NCMe)<sub>6</sub>]<sup>2+</sup> cations under strictly anhydrous conditions allows reactions to be performed which would be difficult or impossible with water present. [Fe(NCMe)<sub>6</sub>]<sup>2+</sup> forms high-spin [Fe(NCMe)<sub>5</sub>(NMe<sub>3</sub>)]<sup>2+</sup> with NMe<sub>3</sub> in MeCN. This undergoes stepwise substitution reactions with P(OMe)<sub>3</sub> giving, finally, low-spin [Fe(NMe<sub>3</sub>){P(OMe)<sub>3</sub>}]<sup>2+</sup>. Steric factors appear to be important, as the intermediate steps differ from those observed previously between [Fe(NCMe)<sub>6</sub>]<sup>2+</sup> and P(OMe)<sub>3</sub>. In contrast, NMe<sub>3</sub> is oxidized by [Cu(NCMe)<sub>6</sub>]<sup>2+</sup>, probably via an intermediate [Cu(NCMe)<sub>6-x</sub>(NMe<sub>3</sub>)<sub>x</sub>]<sup>2+</sup>, and similar behaviour is observed between [Cu(NCMe)<sub>6</sub>]<sup>2+</sup> and Me<sub>2</sub>S.

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