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ELECTROCHEMICAL REDUCTION MECHANISM OF TETRAFLUORO(TRIPHENYLPHOSPHINEIMINATO)TUNGSTEN(VI)

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The electrochemical reduction of tetrafluoro(triphenylphosphine-iminato)tungsten(VI) $[(\text{Ph}_3\text{P}=\text{N})_2\text{W}^{\text{VI}}\text{F}_4]$ in dichloromethane at 21 °C has been investigated using cyclic voltammetry and potentiostatic method. $\text{Ag}^+ - \text{Ag}^0$ was used as the reference electrode, the working and auxiliary electrodes were of Pt. The reaction products were analyzed by ^{19}F and ^{31}P n.m.r. spectroscopy.

The cyclic voltammogram of $(\text{Ph}_3\text{P}=\text{N})_2\text{W}^{\text{VI}}\text{F}_4$ in CH_2Cl_2 shows a one-electron reversible wave, $E_{1/2} = -1.45$ V vs. $\text{Ag}^+ - \text{Ag}^0$. A controlled potential reduction of $(\text{Ph}_3\text{P}=\text{N})_2\text{W}^{\text{VI}}\text{F}_4$ has also been carried out at -1.60 V (cathodic peak potential). The ^{19}F n.m.r. spectrum of the products from this electrochemical experiment showed two triplet signals centered at -83.6 and -100.8 ppm. It may be noted that these signals become broad in the course of time (24 h). The ^{31}P n.m.r. spectrum showed a broad resonance at 25.6 ppm and also indicated the formation of a small amount of $\text{Ph}_3\text{P}=\text{O}$.

These results are suggestive of the reduction of $(\text{Ph}_3\text{P}=\text{N})_2\text{W}^{\text{VI}}\text{F}_4$ to an unstable $[(\text{Ph}_3\text{P}=\text{N})_2\text{W}^{\text{V}}\text{F}_4]^-$ intermediate. This hydrolytically unstable intermediate presumably generates $\text{Ph}_3\text{P}=\text{O}$ as a minor reaction product and finally transforms autocatalytically into a stable paramagnetic tungsten(IV) species, $[(\text{Ph}_3\text{P}=\text{N})_2\text{W}^{\text{IV}}\text{F}_4]^{2-}$.