

SYNTHESIS AND REACTIVITY OF NEW NICKEL COMPLEXES. Anjaneyulu

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The reaction between $\text{Ni}(\text{COD})_2$, ${}^t\text{Bu}_3\text{SnH}$ and ${}^t\text{BuNC}$ (1:2:3 ratio) in hexane solution at 68 °C afforded the trigonal bipyramidal complex $\text{Ni}(\text{Sn}{}^t\text{Bu}_3)_2({}^t\text{BuNC})_3$, **1**. Compound **1** reacts with CO at room temperature and at higher temperatures (68 °C) to give $\text{Ni}(\text{Sn}{}^t\text{Bu}_3)_2({}^t\text{BuNC})_2(\text{CO})$, **2**, and $\text{Ni}(\text{Sn}{}^t\text{Bu}_3)_2({}^t\text{BuNC})(\text{CO})_2$, **3**, respectively. Compound **2** is a distorted trigonal bipyramidal structure due to steric repulsion between the bulky ${}^t\text{Bu}$ groups that are on both the equatorial and axial sites. Compounds **1**, **2** and **3** are all photoactive. When oxygen-free yellow hexane solutions of **2** is exposed to incandescent light, the purple colored complex $[\text{Ni}(\text{Sn}{}^t\text{Bu}_3)({}^t\text{BuNC})_2(\text{CO})]_2$, **4**, is obtained. Compound **4** is formed by the cleavage of a $\bullet\text{Sn}{}^t\text{Bu}_3$ radical from **2** and subsequent dimerization of $\bullet\text{Ni}(\text{Sn}{}^t\text{Bu}_3)({}^t\text{BuNC})_2(\text{CO})$ radical. Exposing hexane solutions of **2**, in the presence of TEMPO to incandescent light, gives brownish yellow $\text{Ni}(\eta^2\text{-N,O-TEMPO})(\text{Sn}{}^t\text{Bu}_3)({}^t\text{BuNC})$, **5**. $\text{Ni}(\text{COD})_2$ also reacts with TEMPO to give $16e^-$, $\text{Ni}(\eta^2\text{-N,O-TEMPO})_2$, **6**. The reactions of **6**, which are facilitated by the TEMPO ligand, will also be discussed.