Reactions of Co-ordinated Ligands: Amide Formation from Reactions of Isocyanates with β-Ketoimine Complexes

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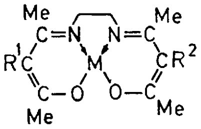
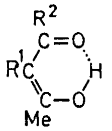
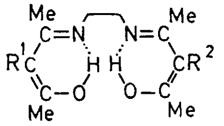
Summary Several organic isocyanates, R–N=C=O, have been found to undergo simple, quantitative, stepwise addition at the methine positions of Cu^{II} and Ni^{II} β-ketoimine complexes, to produce amides.

Although reactions of β-diketone complexes have been extensively studied,[1] only one reaction of β-ketoimine complexes has been reported.[2] We have recently discovered that compound (I; $R^1 = R^2 = H$, M = Cu, Ni) reacts quickly and quantitatively with isocyanates in dry benzene to form compounds (I; $R^1 = H$, $R^2 = CO{\cdot}NHR^3$) and (I; $R^1 = CO{\cdot}NHR^3$, $R^2 = CO{\cdot}NHR^3$). Production of either of these can be controlled by stoicheiometry and reaction time. There is no precedent for this type of reaction with isocyanates. The reaction rate is influenced both by the metal ion and by the nature of the organic group R^3. Cu^{II} complexes react at a much faster rate than Ni^{II} complexes and for both metals the rates decrease in the order R^3 = 1-naphthyl $\simeq$ Ph > Et $\simeq$ Me > Pr^i > Bu^t. Similar reactions also occur with bis-(2,4-pentanedionato)nickel(II) with the relative rates of reaction having the same R^3 dependence as noted above. No reaction occurs, however, over an extended period even at reflux with the 2,4-pentanedionates of Fe^{III}, Co^{III}, Al^{III}, Tl^{I}, Cu^{II}, or V^{IV}. Reactions between the free en(acac)$_2$ or 2,4-pentanedione and isocyanates do occur, but not in the same fashion as with the complexes and the rates are greatly reduced.


(I)


(III)


(II)

The ligands can be liberated from the metal ions by treatment with H_2S in benzene for (II; R^1 = H, R^2 =CO·NHR^3) and (II; R^1 = CO·NHR^3, R^2 = CO·NHR^3) or H_2SO_4 in methanol for (III; R^1 = H, R^2 = NHR^3). Treatment of the products derived from Ni(acac)$_2$ with H_2SO_4 in benzene, acid: complex (2: 1), produced (III; R^1 = CO·NHR^3, R^2 = Me) or, acid: complex (4: 1), produced (III; R^1 = H, R^2 = NHR^3). The ligands have been characterized by m.p. and elemental analyses, and by i.r., n.m.r., and mass spectrometry. Those compounds for which literature data are available[3] have also been identified by preparing their 2,4-dinitrophenylhydrazone derivatives. The complexes have been characterized by elemental analyses, m.p.s, electronic, i.r., and, where applicable, n.m.r. spectroscopy.

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[1] J. R. Collman, *Angew. Chem. Internat. Edn.*, 1965, **4**, 132.
[2] R. W. Kluiber, *J. Amer. Chem. Soc.*, 1960, **82**, 4839.
[3] Z. Bukac and J. Sebenda, *Coll. Czech. Chem. Comm.*, 1966, **31**, 3315.