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SUMMARY

The $M(CO)_5(CNC_6H_5)$ and $cis-M(CO)_4(CNC_6H_5)_2$ ($M = Mo$ and W) complexes have been successfully synthesized by photochemical route. The compounds are quite stable and readily soluble in several organic solvents. Infrared data show that the arylisonitrile is a better π -acceptor than an alkylisonitrile, when coordinate with a metal. Their electronic spectra exhibit high absorption bands some of which are due to charge transfer transitions.

Luminescence from the complexes could not be detected, but they undergo photosubstitution very well except $cis-Mo(CO)_4(CNC_6H_5)_2$. Using pyridine or piperidine as an incoming ligand (L) in the 364 nm irradiation of $M(CO)_5(CNC_6H_5)$ it is suggested that the photoproduct be $cis-M(CO)_4(CNC_6H_5)L$. This result is different from that of $M(CO)_5(CNR)$ ($R = \text{alkyl}$) where the photoproduct is $M(CO)_5L$. Furthermore, irradiation of $cis-W(CO)_4(CNC_6H_5)_2$ with 2,2'-bipyridyl reveals that CO, not CNR, is replaced. The photoreactivity of both types of complexes $M(CO)_5(CNC_6H_5)$ and $cis-M(CO)_4(CNC_6H_5)_2$ suggests that the strength of M-CNR bonding is higher than the M-CO one according to the first LF state of the complexes. The lack of photosubstitution in $cis-Mo(CO)_4(CNC_6H_5)_2$ should be due to the presence of a charge transfer state as its lowest energy excited state. The results of this work have been interpreted according to the model proposed by Wrighton, Gray and Hammond.