

Thermodynamic and Spectroscopic Studies of Some Metal Dimers

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There has been a great deal of interest over the years concerning the structure and reactivity of multi-metal systems. [1] Some of the most intensely studied of these have been the carboxylate bridged metal dimers having the classical copper acetate structure in which four acetates bridge two metal atoms. These dimers have been investigated theoretically, structurally, thermodynamically, and spectroscopically by a host of researchers. While much has been learned about the metal carboxylates, there are still some important questions regarding the nature of adduct formation between these dimers and axial bases.

Earlier published work from this laboratory has dealt with the Lewis acid-base reactivity of rhodium trifluoroacetate, [2] rhodium butyrate, [3] rhodium heptafluorobutyrate, [4] and molybdenum heptafluorobutyrate. [4] Several conclusions have been drawn from the thermodynamic and spectroscopic results concerning the contributions which the metal core, the bridging ligands, and the axial bases make to adduct formation. Using an "E and C" type interpretation of the Lewis acid-base reactions, it has been shown that the relative electrostatic and covalent contributions to the interaction are dependent upon the electron withdrawing properties of the bridging ligands and the formal bond order of the metal-metal core. In certain instances, the results are consistent with a back donation of π^* -electron density from the metal to the axial ligand. The extent of this π -stabilization to the adduct bond again depends on the metal core and on the bridging ligands, as well as the ability of the axial base to act as a π -acceptor.

More recently, thermodynamic studies of ruthenium butyrate have given further support for the interpretation of the reactivity of the metal dimers in terms of the E and C correlation. The ruthenium dimer appears to undergo π -bonding interactions with certain bases, as was the case for the rhodium dimers. The difference between the formal positive charge of the ruthenium core (+5) and that of the rhodium or molybdenum cores (+4) is reflected in the electrostatic contributions to the enthalpies of adduct formation for each. The relative importance of the covalent and electrostatic contributions is again seen to depend upon the formal bond order.

EPR studies of the adducts of $\text{Rh}_2(\text{OCR})_4$ and phosphine or phosphite bases by Kawamura, et al., [5] led to some interesting results and conclusions concerning the interaction between the metal atoms and the axial ligands. Most importantly, they concluded that the axial bond between the metal and base was " σ -only" in nature and that there was no need to invoke π -stabilization in interpreting their epr spectra, in contrast to the conclusions drawn from Drago and coworkers from their work on metal carboxylates. An extension of the epr investigation of rhodium butyrate to include other bases and conditions

has subsequently shown that the epr spectra obtained appear to be a function of the strength of the acid-base interaction rather than the type of bonding involved.

References

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