

Transition Metal Complexes of Imido Ligands:  
Structure and Reactivity

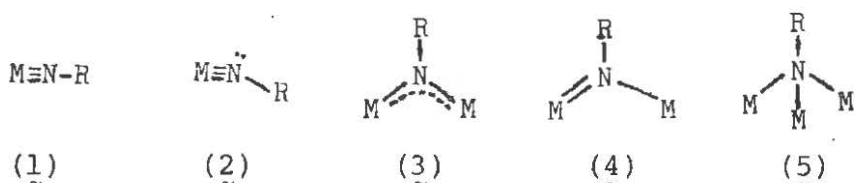
Yun Chi

Literature Seminar

December 9, 1983

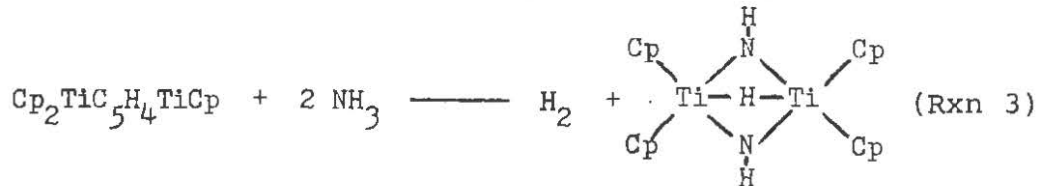
Transition metal complexes containing ligands in which there is M-N multiple bonding are currently the focus of considerable research activity [1,2]. Interest in complexes of imido (NR) ligands reflects growing recognition of their potential role in several areas, i.e., as synthetic reagents in organic chemistry [3,5], as intermediates in catalytic processes [6] and as analogs of oxo complexes [7,8].

In general, imido ligands are bound to transition metals in five different modes: terminal linear (1); terminal bent (2); symmetric doubly bridging (3); asymmetric doubly bridging (4) and triply bridging (5).

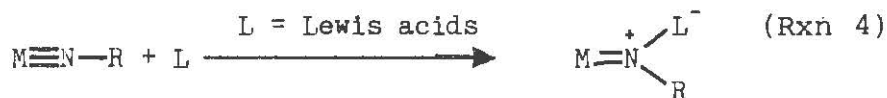


Doubly bridging imido ligands are symmetrically bound (3) for group IV transition metal dimers, e.g.,  $[(\text{Me}_2\text{N})\text{M}]_2[\mu^{\text{t}}\text{BuN}]_2$ ,  $\text{M} = \text{Ti}, \text{Hf}, \text{Zr}$ , and unsymmetrically bound (4) for group VI metal dimers, e.g.,  $[(^{\text{t}}\text{BuN})\text{Me}_2\text{M}]_2[\mu^{\text{t}}\text{BuN}]_2$ ,  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$  [9]. The asymmetry of the bridging imido ligands in the later case, may be caused by second order Jahn-Teller effects. Triply bridging complexes (5) are symmetrically bound in trimetallic complexes, e.g.,  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{NCH}_3)$  [10].

Sharpless and coworkers have shown that the transition metal imido complexes,  $[\text{Os}(\text{O})_n(\text{NR})_{4-n}]$ ;  $n = 1, 2, 3$ , react stoichiometrically in vicinal hydroamination [3,4] (Rxn 1) and diamination reactions [5] (Rxn 2). An imido complex has been prepared directly from ammonia (Rxn 3) and has been found to be an olefin hydrogenation catalyst [11].



Terminal imido ligands have been shown to react with Lewis acids and bases. Lewis acids interact with the imido group through the nitrogen atom to form a zwitterionic adduct [12] (Rxn 4). However, bases react with the  $\alpha$ -hydrogen atom to produce alkylidene imido complexes [13] (Rxn 5). Schrock and coworkers have shown that terminal imido-alkylidene and imido-alkylidyne complexes are more stable than their oxo- analogs. Intermediates which are unstable in oxo-alkylidene chemistry can be isolated from the analogous imido complexes [13,14]. Thus, the imido ligand offer an opportunity to further the understanding of the alkylidene and alkylidyne chemistry.



## References

1. Nugent, W. A. Coord. Chem. Rev. 1980, 31, 123.
2. Dehnicke, K.; Strahle, J. Angew. Chem. Int. Ed. Eng. 1981, 20, 413.
3. Sharpless, K. B.; Hori, T. J. Org. Chem. 1976, 41, 177.
4. Chong, A. O.; Oshima, K.; Sharpless, K. B. J. Am. Chem. Soc. 1977, 99, 3420.
5. Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. J. Org. Chem. 1978, 43, 2628.
6. Levering, D. R. U.S. Patent 3,152,184.
7. Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. Organometallics 1982, 1, 1332.
8. Wengrovius, J. H.; Schrock, R. R. Organometallics 1982, 1, 148.
9. Thorn, D. J.; Nugent, W. A.; Harlow, R. L. J. Am. Chem. Soc. 1981, 103, 357.
10. Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. J. Organomet. Chem. 1981, 213, C41.
11. Armor, J. N. Inorg. Chem. 1978, 17, 213.

12. Kress, J.; Wesolek, M.; Osborn, J. A. Chem. Commun. 1981, 1039.
13. Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. J. Chem. Soc., Dalton Trans. 1976, 2435.
14. Pederson, S. F.; Schrock, R. R. J. Am. Chem. Soc. 1982, 104, 7483.
15. Edwards, D. S.; Schrock, R. R. J. Am. Chem. Soc. 1982, 104, 6806.
16. Nugent, W. A.; Harlow, R. L.; McKinney, R. J. J. Am. Chem. Soc. 1979, 101, 7265.
17. Haymore, B. L.; Matta, E. A.; Wentworth, R. A. D. J. Am. Chem. Soc. 1979, 101, 2063.
18. Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. J. Am. Chem. Soc. 1981, 103, 965.
19. Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. Chem. Lett. 1978, 525.