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Preliminary communication

LEWIS-SALT TYPE ADDUCTS OF HALONITROSYL AND HALOCARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN AS INTERMEDIATES IN THE FORMATION OF HOMOGENEOUS OLEFIN DISPROPORTIONATION CATALYSTS

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Summary

Highly reactive Lewis salt type adducts of halocarbonyl and halonitrosyl complexes of molybdenum and tungsten with $AlCl_3$ and $AlEtCl_2$ have been shown to be present in homogeneous olefin disproportionation catalyst mixtures.

Several adducts are known in which Lewis acids attach to coordinated halogen, carbonyl or dinitrogen groups of transition metal complexes [1—3]. Such interactions were observed and the formation of such adducts was suggested in the reductive nitrosation of molybdenum and tungsten chlorides in the presence of $EtAlCl_2$ [4] as well as in homogeneous catalytic systems based on tungsten halocarbonyl [5, 6] or molybdenum halonitrosyl compounds [7].

$W(CO)_3(PPh_3)_2Cl_2$ and an excess of $EtAlCl_2$ yield a homogeneous olefin disproportionation catalyst [5]. $W(CO)_3(PPh_3)_2Cl_2$ alone is insoluble in chlorobenzene, but dissolves rapidly in the presence of $EtAlCl_2$, and at the same time ν(CO) absorption peaks appear in the IR spectrum of the solution (1978s, 1999vs, 2038s, 2104vw). This absorption spectrum is stable in an atmosphere of CO and is similar to that of $W(CO)_3(PPh_3)_2Cl_2$ measured in chlorobenzene suspension but with the carbonyl absorptions at somewhat higher (20—80 cm^{-1}) frequencies. Similar results were observed using $AlCl_3$ instead of $EtAlCl_2$, but the spectrum showed a more significant change in this case (ν(CO) 1962vs, 1972w, 2045s, 2055m, 2110vw).

The electron-withdrawing effect of the aluminium compounds, shown by the higher ν(CO) frequencies, results in a weakening of the M—CO bonds, and as expected, the adducts spontaneously lose CO forming dicarbonyl derivatives. If the CO is vented off the decomposition continues through an unidentified monocarbonyl derivative to derivatives containing no carbonyl.

The light green $Mo(NO)_2Cl_2(PPh_3)_2 \cdot 2AlCl_3$ (ν(CO) 1703s, 1815s, in Nujol) and the yellow $W(CO)_3Cl_2(AsPh_3)_2 \cdot 2AlCl_3$ (ν(CO) 1880vw, 1968s, 1952s, in CH_2Cl_2) are stable in argon and are isolated as crystalline products; the crystallization of the latter needed several weeks at —5°C, however. Satisfactory Cl, Al, Mo and W analyses were obtained for these compounds.

The adducts are very sensitive to air and moisture, and conductivity measurements reveal some ionic character. Stronger bases (B:), such as PPh_3, ethanol or water, attack the Lewis salt type adducts to displace the weaker bases, the transition metal complexes.

$$W(CO)_3Cl_2(PPh_3)_2 \cdot 2AlEtCl_2 + 2B: \rightarrow W(CO)_3Cl_2(PPh_3)_2 + 2[B:AlEtCl_2]$$

These base displacement reactions may explain the contradictory observations on the poisoning effect of phosphines [8, 9], water and alcohol in the homogeneous olefin disproportionation catalytic systems, since the effective amount of base should be proportional to the amount of cocatalyst not to that of the transition metal present. On the other hand, we have observed that in Lewis acid-catalysed reactions like Friedel—Crafts reactions, the catalytic activity of $AlCl_3$ may be diminished by such transition metal carbonyl or nitrosyl complexes.

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References

1 J. Chatt, J.R. Dilworth, G.J. Leigh and R.L. Richards, Chem. Commun., (1970) 955.
2 A.E. Crease and P. Legzdins, Chem. Commun., (1972) 268.
3 M. Pankowski, B. Demerseman, G. Bouquet and M. Bigorgne, J. Organometal. Chem., 35 (1972) 155.
4 L. Bencze, J. Organometal. Chem., 56 (1973) 303.
5 L. Bencze and L. Markó, J. Organometal. Chem., 38 (1971) 271.
6 L. Bencze, G. Pályi and L. Markó, Vth Intern. Conf. Organometal. Chem., Moscow, 1971, Vol. 2, p. 194.
7 W.B. Hughes, Organometal. Chem. Synt., 1 (1972) 341.
8 L. Bencze, A. Rédey and L. Markó, Hung. J. Ind. Chem., 1 (1973) 453.
9 V.M. Kothari and J.J. Tazuma, J. Org. Chem., 36 (1971) 2951.