Orbital Symmetry and the Thermolysis of Metallacycles

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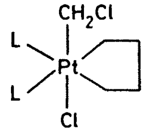
Summary Unexpected supporting ligand effects in metallacycle thermolysis are predictable consequences of frontier orbital symmetry.

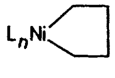
It has recently become clear that the preferred thermolysis pathway for a late transition metallacycle is sensitive to the supporting ligands. For instance, (Ia) decomposes to give cyclobutane as well as C-5 open chain species, but the former is absent from the thermolysis products of (Ib).[1] Species assigned as (IIa,b) decompose to give cyclobutane and (co-ordinated) ethylene respectively as major products;



(I)

a; L = PBu$_3$

b; L$_2$ = Me$_2$PCH$_2$CH$_2$PMe$_2$



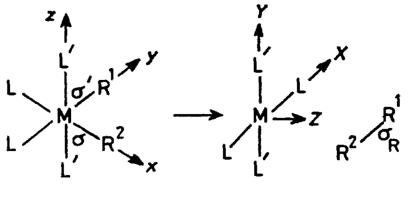
(II)

a; n = 2, L$_2$ = (PPh$_3$)$_2$, [P(C$_6$H$_{11}$)$_3$]$_2$, or Ph$_2$PCH$_2$CH$_2$PPh$_2$

b; n = 3, L = PPh$_3$, or P(C$_6$H$_{11}$)$_3$

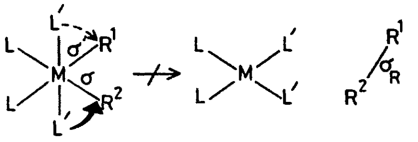
this last result is particularly surprising since increasing co-ordination number has led to the formation of more ligands,[2a] which are initially retained in the co-ordination sphere.[2b]

Both these results are foreseeable consequences of orbital symmetry correlations of the type proposed some time ago[3] for reductive elimination. For example, Scheme 1



Scheme 1

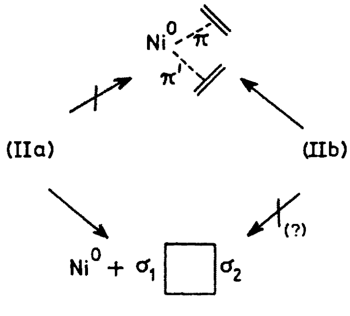
represents an allowed process, being of type $(\sigma+\sigma')^2$-$(\sigma-\sigma')^2d(x^2-y^2)^0d(z^2)^0 \rightarrow (\sigma\mathrm{R})^2[d(x^2-y^2) \equiv d(XZ)]^2[d(X^2-Y^2)]^0$, which is $(a_1)^2(b_1)^2(a_1)^0 \rightarrow (a_1)^2(b_1)^2(a_1)^0$ in C_{2v}, and $a^2b^2a^0 \rightarrow a^2b^2a^0$ in C_2 symmetry. The opening of the LML angle is not a symmetry requirement but must happen if $d(XZ)$ is not to be raised in energy. The conceivable alternative of Scheme 2 is forbidden, being of type $(\sigma+\sigma')^2$-



Scheme 2

$\sigma-\sigma')^2d(x^2-y^2)^0d(z^2)^0 \rightarrow (\sigma_\mathrm{R})^2d(x^2-y^2)^0d(z^2)^2$ which is $a^2b^2 \rightarrow a^2a^2$; $(\sigma-\sigma')$ can only correlate with high energy product orbitals such as $d(x^2-y^2)$ or $\sigma^*{}_\mathrm{R}$.[†] Thus reductive elimination in (Ia) can occur with bond formation between the two ring C_α atoms, or between one ring C_α and the chloromethyl group, but only the latter type of process is energetically feasible in (Ib).

Easy reductive eliminations from d^8 systems occur even when the LML angle is constrained by chelation.[2,4] This is not totally surprising, since d^{10} systems impose no directionality. In Scheme 3, conversion of (IIa) [or of the square-pyramidal isomer of (IIb)] into Ni^0 + cyclobutane is an allowed process; $(\sigma_2)^2(\sigma+\sigma')^2(\sigma-\sigma')^2d(z^2)^2d(x^2-y^2)^0 \rightarrow (\sigma_2)^2(\sigma_1)^2d(z^2)^2d(x^2-y^2)^2$ [where Oz is the approximate 4-fold axis and the $(x+y)$ axis bisects the ring] is of type $a^2a^2b^2a^2 \rightarrow a^2a^2a^2b^2$. Likewise, conversion of the (e,e) trigonal-bipyramidal isomer of (IIb) into Ni^0 + 2 ethylene is allowed, being (with Oz as 3-fold axis) $(\sigma_2)^2(\sigma+\sigma')^2(\sigma-\sigma')^2$-$d(z^2)^0d(x^2-y^2)^2 \rightarrow \sigma_2{}^0(\pi+\pi')^2(\pi-\pi')^2d(z^2)^2d(x^2y^2)^2$ or $a^2a^2b^2b^2 \rightarrow a^2b^2a^2b^2$, and the ethylene being retained in the co-ordination sphere. However, the production of ethylene from (IIa), or of cyclobutane from the (e,e) trigonal-bipyramidal isomer of (IIb), is forbidden.



Scheme 3

The symmetry restrictions described for the nickel system depend on either $d(x^2-y^2)$ or $d(z^2)$ being occupied. Less electron-rich systems are allowed to show both processes in a single species provided the empty acceptor orbitals are not ligand field repelled. The implications for catalyst design are obvious, although other factors are also important. For instance, ethylene evolution took place from the titanacyle $(\eta^5\text{-}C_5H_5)_2Ti[CH_2]_4$ but reductive elimination was observed only after carbonylation.[5] It is also significant that the ground state forbidden production of ethylene from $I_2\overline{Pt[CH_2]_3CH_2}(PMe_2Ph)_2$ occurs on photolysis.[6]

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[†] Transition states may [and sometimes must (J. N. Murrell, *J.C.S. Chem. Comm.*, 1972, 1044)] deviate from ideal symmetry, and configuration interaction can, in the transition state, cause mixing of a^2 and b^2 states. However, what most matters on the one-electron argument is connectivity, which is insensitive to detailed geometry (see *e.g.*, M. J. S. Dewar and R. C. Dougherty, 'The P.M.O. Theory of Organic Chemistry,' Plenum Press, New York and London, 1975, Ch. 5) and the matrix element linking $d(x^2-y^2)^2$ and $d(z^2)^2$ is 4B + C (this result follows from the coupling constants and term energies given by J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, 1961, Tables A20 and A28), far less than the one-electron energy separations involved.

[1] G. B. Young and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1978, **100**, 5808.
[2] (a) R. H. Grubbs, A. Miyashita, M.-I. M. Liu, and P. L. Burk, *J. Amer. Chem. Soc.*, 1977, **99**, 3863; (*b*) R. H. Grubbs and A. Miyashita, *ibid.*, 1978, **100**, 1300.
[3] P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.
[4] P. S. Braterman, R. J. Cross, and G. B. Young, *J.C.S. Dalton*, 1976, 1306; *ibid.*, 1977, 1892.
[5] J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1976, **98**, 6529.
[6] D. L. Perkins, R. J. Puddephatt, and C. F. H. Tipper, *J. Organometallic Chem.*, 1978, **154**, C16.