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THE THERMAL FORMATION OF BIALKYLS FROM ALKYLMETALS

IV *. THE SYMMETRY REQUIREMENTS FOR REDUCTIVE ELIMINATION FROM DIALKYLMETALS

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Summary

A general symmetry analysis of reductive elimination from transition metal alkyls has been carried out. It shows that concerted reaction is permitted for various complexes with the configurations d^1—d^8. Concerted reaction is not permitted for any d^0, d^9 and d^{10} systems. For the d^1—d^8 systems the auxiliary ligands are important since they determine the coordination numbers and the spin states of the various complexes. The theoretical predictions agree fairly well with experimental results.

Introduction

A recent ab initio SCF-MO study on dimethylnickel suggests that both symmetry and electron distribution are important for the aptitude for reductive elimination from nickel(II)alkyls [1]. It seems probable that this has general validity for transition metal alkyls. In the present paper the symmetry aspect is examined in more detail for transition metal alkyls R_2ML_n, (Figs. 1—8), where configuration of M spans the entire d^{10}—d^0 series and n varies from 1—4.

The intermediate R_2ML_n is assumed, as is usual, to have a *cis* configuration. This seems reasonable since good carbon—carbon overlap is then possible. For comparison, one *trans* geometry is also examined.

According to the simple theory of concerted reactions [2] the requirements for reductive elimination are that the d_{xz} orbital is empty in the ground state reactant complex and filled in the ground state product complex (cf. Fig. 2). There will then be a correlation between the antisymmetric carbon—metal

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* For Part III see ref. 4b.

(Continued on p. 63)

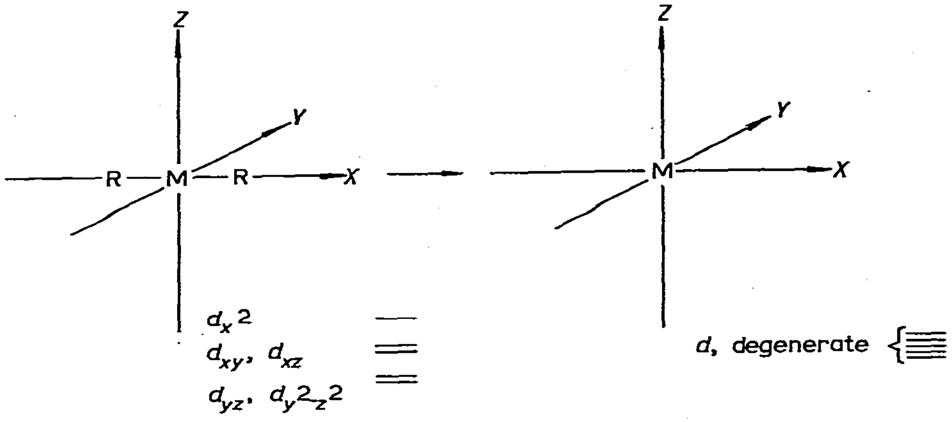


Fig. 1. *trans*-2-coordinate.

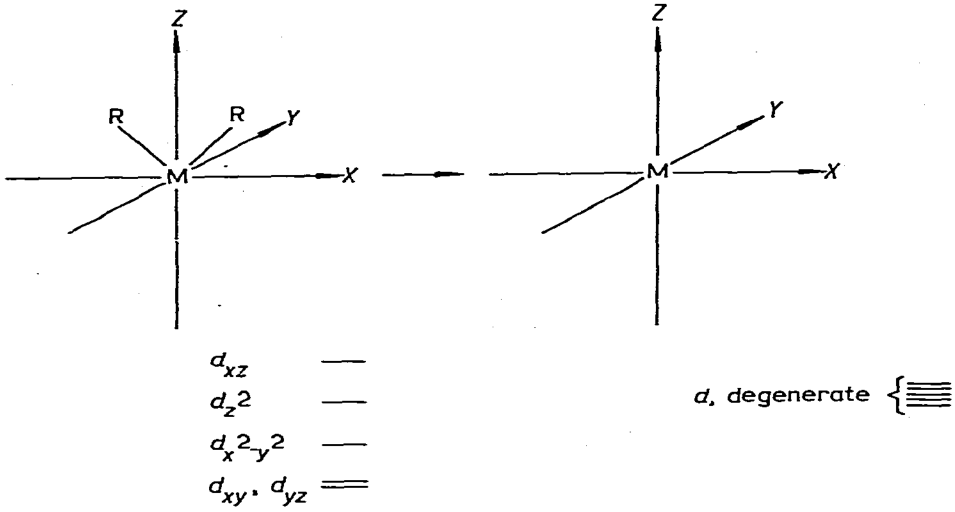


Fig. 2. *cis*-2-coordinate.

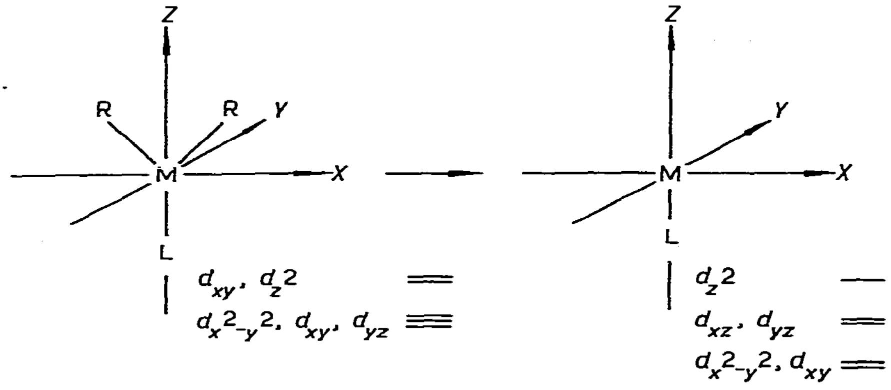


Fig. 3. 3-coordinate trigonal.

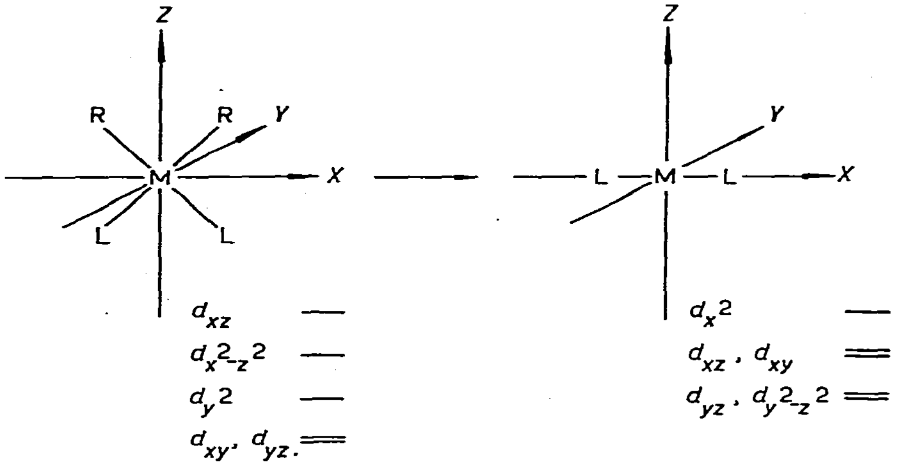


Fig. 4. 4-coordinate square planar.

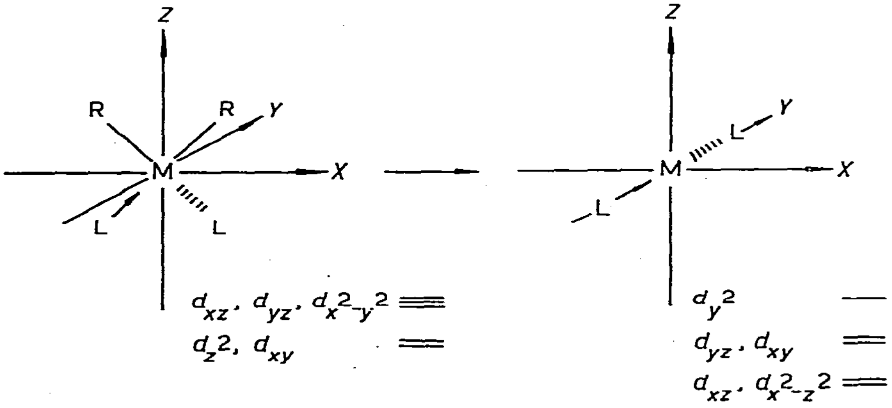


Fig. 5. 4-coordinate tetrahedral.

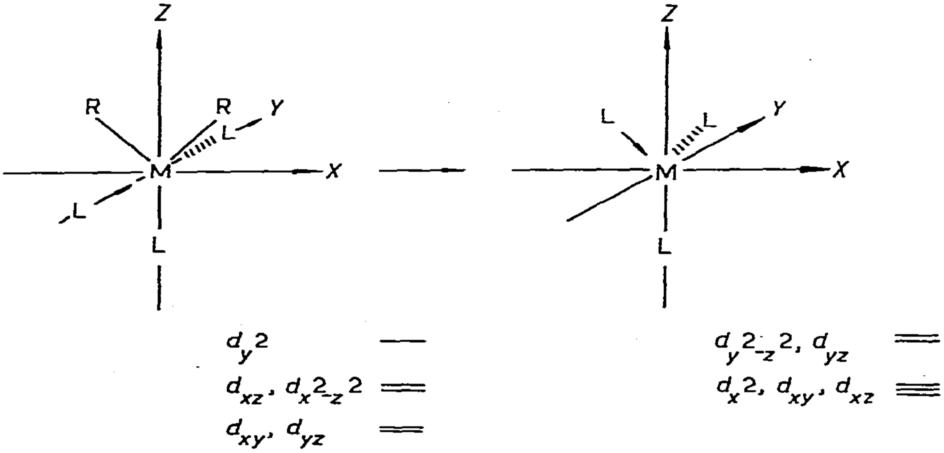


Fig. 6. 5-coordinate trigonal bipyramid.

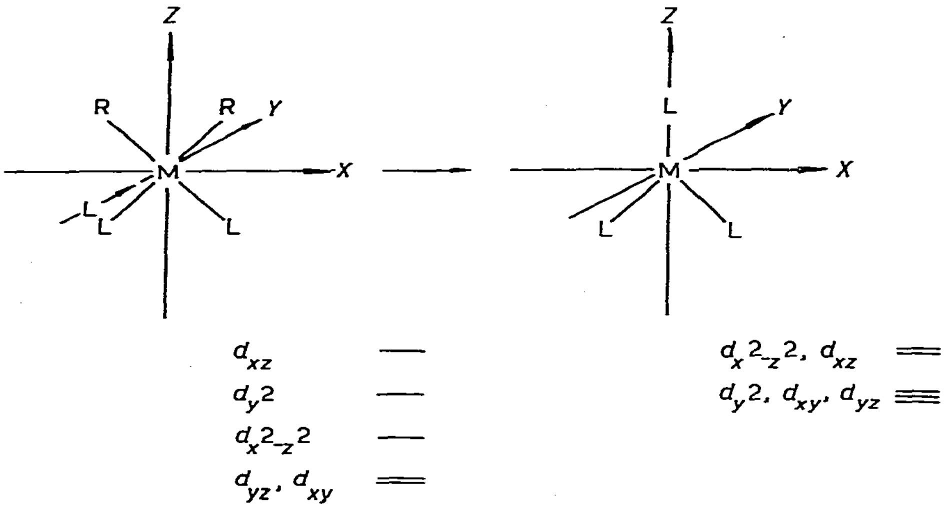


Fig. 7. 5-coordinate square pyramid.

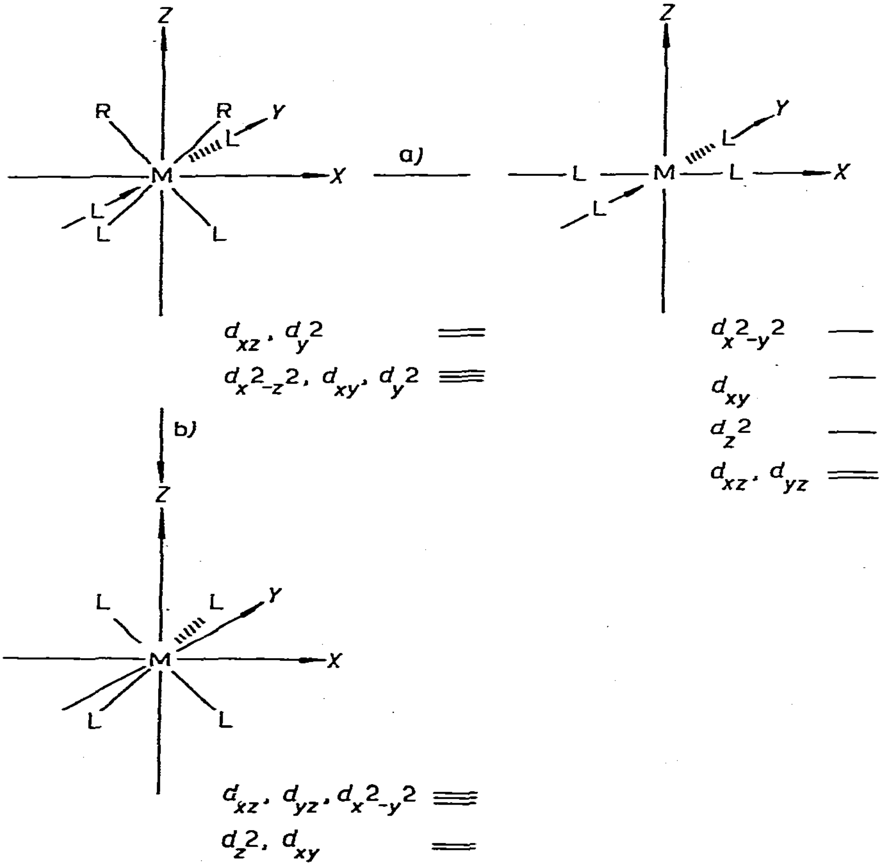


Fig. 8. 6-coordinate octahedral.

orbital in the reactant and d_{xz} orbital in the product. As it turns out, this is not necessarily sufficient, since ground state correlation may not be obtained between the other occupied d-orbitals in reactant and product. The purpose of the present paper is to examine this question in some detail. The valence orbitals are classified according to the symmetry groups of C_{2v} symmetry which is the symmetry retained during the reductive elimination. The sum of the electrons in each symmetry is determined before and after reaction. The results can be presented conveniently in tabular form (Tables 1—10). If the total symmetry is retained, the reaction is symmetry allowed. Of the valence orbitals in the hydrocarbon moiety, only the carbon—metal bonds are included since the others are unaltered during the reaction.

An alternative to the presentation as tables is of course the construction of correlation diagrams but this is less concise. Also, the inclusion of unpaired electrons is very simple when the tabular form is used.

Results

The valence shell of the d^{10}-system R_2ML_n has the configuration $(R—M)^2_{a_1}$-$(R—M)^2_{b_1}d^{10}$, which in C_{2v} symmetry is $(a_1)^6(a_2)^2(b_1)^4(b_2)^2$. After reductive elimination to give alkane and the reduced metal complex, the "added configuration" of the system is $(a_1)^8(a_2)^2(b_1)^2(b_2)^2$. According to our symmetry treatment the reaction is consequently forbidden. This is also true for the d^9 system (Table 1).

In principle, the concerted formation of an alkyl radical pair and the reduced metal complex is also possible. For the d^{10} system, this would require a configuration $(d_{xz})^1d^8s^1$ for the reactant, which is probably not the ground state (Table 1). In contrast, the ground state configuration of the *cis*-d^9-complex does

TABLES 1—9

SUMMATION OF THE VALENCE ELECTRONS, CLASSIFIED ACCORDING TO THE SYMMETRIES OF THE ORBITALS THEY OCCUPY, FOR THE COMPLEXES R_2ML_n AND THEIR DECOMPOSITION PRODUCTS

Only the electrons of the R—M and R—R bonds and the metal d-electrons (d^{10}—d^0) are included.

TABLE 1

d^{10}, d^9

Structure	Metal-d-electron configuration	Number of electrons in orbitals of symmetry			
		a_1	a_2	b_1	b_2
R_2ML_n	d^{10}	6	2	4	2
	$(d_{xz})^1d^8s^1$	7	2	3	2
	$(d_{xz})^0d^8s^2$	8	2	2	2
$R_2 + ML_n$	$d^{10}s^2$	8	2	2	2
$2 R + ML_n$	$d^{10}s^2$	7	2	3	2
R_2ML_n *trans* (Fig. 1)	$(d_{x^2})^1d^8$	5	2	4	2
cis (Fig. 2)	$(d_{xz})^1d^8$	5	2	3	2
	$(d_{xz})^0d^8s^1$	7	2	2	2
$R_2 + ML_n$	$d^{10}s^1$	7	2	2	2
$2 R + ML_n$	$d^{10}s^1$	6	2	3	2

TABLE 2. d^8

Structure R_2ML_n n	Metal d-electron configuration	Number of electrons in orbitals of symmetry			
		a_1	a_2	b_1	b_2
0, *trans*	$(d_x2)^0d^8$	4	2	4	2
0, *cis*	$(d_{xz})^0d^8$	6	2	2	2
0, *cis*, high spin	$(d_{z^2})^1(d_{xz})^1d^6$	5	2	3	2
1 (Fig. 3)	$(d_{z^2})^1(d_{xz})^1d^6$	5	2	3	2
2, SPL (Fig. 4)	$(d_{xz})^0d^8$	6	2	2	2
2, T, (Fig. 5)	$(d_{x^2-y^2})^1(d_{xz})^1d^6$	5	2	3	2
3, TBP (Fig. 6)	$(d_{y^2})^0d^8$	4	2	4	2
3, SPY (Fig. 7)	$(d_{xz})^0d^8$	6	2	2	2
4, O (Fig. 8)	$(d_{y^2})^1(d_{xz})^1d^6$	5	2	3	2
$R_2 + ML_n$ $n = 0$—4	d^{10}	6	2	2	2
$2\,R + ML_n$ $n = 0$—4	d^{10}	5	2	3	2

correlate with that of the product radical pair (Table 1). In fact, this type of correlation may be obtained for most of the d^n- configurations, e.g. for d^8, Table 2. In these configurations, the electronic structure of the alkyl radical pair will resemble that of $\sigma \rightarrow \sigma^*$ excited alkane. The species formed will thus have a high energy and may be unimportant despite the expected low energy barrier to the transition state. Nonetheless, states of this type may contribute to homolytic cleavage by interaction in the transition state. For the d^{10} and d^9 states of R_2ML_n there are excited state configurations, $(d_{xz})^0d^8s^2$ and $(d_{xz})^0d^8s^1$, respectively, which lead to symmetry allowed reductive elimination.

TABLE 3. d^7

Reactant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal d-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{xz})^0(d_{z^2})^1d^6$	5	2	2	2
—	1	$(d_{z^2})^1d^8$	5	2	2	2
2, SPL	—	$(d_{xz})^0(d_{x^2-z^2})^1d^6$	5	2	2	2
—	2	$(d_{x}2)^1d^8$	5	2	2	2
2, T	—	$(d_{xz})^1(d_{yz})^1(d_{x2-y2})^1d^4$	5	2	3	1
—	2	$(d_{y}2)^1d^8$	5	2	2	2
3, TBP	—	$(d_{y}2)^0(d_{xz})^1d^6$	4	2	3	2
—	3	$(d_{y2-z2})^1d^8$	5	2	2	2
3, SPY	—	$(d_{xz})^0(d_{y}2)^1d^6$	5	2	2	2
—	3	$(d_{x2-z2})^1d^8$	5	2	2	2
4, O	—	$(d_{xz})^0(d_{y}2)^1d^8$	5	2	2	2
—	4, SPL (Fig. 8a)	$(d_{x2-y2})^1d^8$	5	2	2	2
—	4, T (Fig. 8b)	$(d_{x2-y2})^1d^8$	5	2	2	2

TABLE 4. d^6

Reactant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal d-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{xz})^0(d_{z^2})^0d^6$	4	2	2	2
—	1	$(d_{z^2})^0d^8$	4	2	2	2
2, SPL	—	$(d_{xz})^0(d_{x^2-z^2})^0d^6$	4	2	2	2
—	2	$(d_{x^2})^0d^8$	4	2	2	2
2, T	—	$(d_{xz})^0(d_{yz})^1(d_{x^2-y^2})^1d^4$	5	2	2	1
—	2	$(d_{y^2})^0d^8$	4	2	2	2
3, TBP	—	$(d_{y^2})^0(d_{xz})^1(d_{x^2-z^2})^1d^4$	3	2	3	2
—	3	$(d_{x^2-y^2})^1(d_{yz})^1d^6$	5	2	2	1
3, SPY	—	$(d_{y^2})^0(d_{xz})^0d^6$	4	2	2	2
—	3	$(d_{x^2-z^2})^1(d_{xz})^1d^6$	5	2	1	2
4, O	—	$(d_{y^2})^0(d_{xz})^0d^6$	4	2	2	2
—	4, SPL	$(d_{x^2-y^2})^0d^8$	4	2	2	2
—	4, T	$(d_{x^2})^1(d_{xz})^1d^6$	5	2	1	2

For the d^8-configuration, symmetry-allowed reductive elimination is possible for several different coordination numbers, 2-coordinate *cis*, 4-coordinate square planar (SPL) and 5-coordinate square pyramid (SPY) (Table 2). For a number of other structures, 4-coordinate tetrahedral (T), 5-coordinate trigonal bipyramid (TBP) and 6-coordinate octahedral (O) concerted formation of two alkyl radicals is in principle possible. This is also true for high spin configurations of the 2-coordinate *cis* and *trans*, the SPL and the SPY complexes. It is interesting to note that for the *trans* low spin complexes, as represented by the 2-coordinate complex, neither reductive elimination nor radical formation is symmetry allowed.

TABLE 5. d^5

Reactant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal d-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{yz})^1(d_{x^2-y^2})^2(d_{xy})^2$	4	2	2	1
—	1	$(d_{z^2})^1(d_{yz})^1d^6$	4	2	2	1
2, SPL	—	$(d_{y^2})^1(d_{xy})^2(d_{yz})^2$	3	2	2	2
—	2	$(d_{x^2})^0(d_{xy})^1d^6$	4	1	2	2
2, T	—	$(d_{yz})^1(d_{xy})^2(d_{z^2})^2$	4	2	2	1
—	2	$(d_{y^2})^0(d_{yz})^1d^6$	4	2	2	1
3, TBP	—	$(d_{x^2-z^2})^1(d_{xy})^2(d_{yz})^2$	3	2	2	2
—	3	$(d_{y^2-z^2})^0(d_{yz})^1d^6$	4	2	2	1
3, SPY	—	$(d_{x^2-z^2})^1(d_{yz})^2(d_{xy})^2$	3	2	2	2
—	3	$(d_{x^2-z^2})^0(d_{xz})^1d^6$	4	2	1	2
4, O	—	$(d_{xy})^1(d_{x^2-z^2})^2(d_{yz})^2$	4	1	2	2
—	4, SPL	$(d_{x^2-y^2})^0(d_{xy})^1d^6$	4	1	2	2
—	4, T	$(d_{xz})^1(d_{yz})^1(d_{x^2-y^2})^1d^4$	5	2	1	1

TABLE 6. d^4

Reactant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal *d*-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{x^2-y^2})^1(d_{yz})^1(d_{xy})^2$	3	2	2	1
—	1	$(d_{xz})^1(d_{yz})^1(d_{x^2-y^2})^2(d_{xy})^2$	4	2	1	1
2, SPL	—	$(d_{y^2})^1(d_{xy})^1(d_{yz})^2$	3	1	2	2
—	2	$(d_{y^2-z^2})^2(d_{xz})^2(d_{yz})^2$	4	0	2	2
2, T	—	$(d_{z^2})^2(d_{xy})^2$	4	2	2	0
—	2	$(d_{xy})^1(d_{yz})^1(d_{xz})^2(d_{x^2-z^2})^2$	4	1	2	1
3, TBP	—	$(d_{xy})^2(d_{yz})^2$	2	2	2	2
—	3	$(d_{x^2})^2(d_{xy})^2(d_{xz})^2$	4	2	2	0
3, SPY	—	$(d_{xy})^2(d_{yz})^2$	2	2	2	2
—	3	$(d_{y^2})^2(d_{xy})^2(d_{yz})^2$	4	2	0	2
4, O	—	$(d_{x^2-z^2})^1(d_{xy})^1(d_{yz})^2$	3	1	2	2
—	4, SPL	$(d_{z^2})^2(d_{xz})^2(d_{yz})^2$	4	0	2	2
	4, SPL, high spin	$(d_{xy})^1(d_{z^2})^1(d_{xz})^2(d_{yz})^2$	3	1	2	2
	4, T	$(d_{xz})^1(d_{yz})^1(d_{z^2})^2(d_{xy})^2$	4	2	1	1

Charge transfer may be important, especially for metals in high formal oxidation states. This may be exemplified by the results in Table 10. For the d^8-system, the unsymmetric charge transfer states $(d_{xz})^1d^8(\text{R—M})^2_{a1}(\text{R—M})^1_{b1}$ and $d^{10}(\text{R—M})^2_{a1}(\text{R—M})^0_{b1}$ both lead to concerted reductive elimination. Similar states, from which concerted reductive elimination is possible, exist also for the d^{10} and d^9 configurations.

Charge transfer interaction can also yield states that correlate with formation of a radical pair, e.g. the symmetric state $d^{10}s^1(\text{R—M})^1_{a1}(\text{R—M})^1_{b1}$ for the d^9 system.

TABLE 7. d^3

Reactant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal *d*-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{yz})^1(d_{xy})^1(d_{x^2-y^2})^1$	3	1	2	1
—	1	$(d_{xz})^1(d_{x^2-y^2})^2(d_{xy})^2$	4	2	1	0
2, SPL	—	$(d_{y^2})^1(d_{xy})^1(d_{yz})^1$	3	1	2	1
—	2	$(d_{xz})^1(d_{yz})^2(d_{y^2-z^2})^2$	4	0	1	2
2, T	—	$(d_{xy})^1(d_{z^2})^2$	4	1	2	0
—	2	$(d_{xy})^1(d_{xz})^2(d_{x^2-z^2})^2$	4	1	2	0
3, TBP	—	$(d_{yz})^1(d_{xy})^2$	2	2	2	1
—	3	$(d_{x^2})^1(d_{xy})^2(d_{xz})^2$	3	2	2	0
3 SPY	—	$(d_{xy})^1(d_{yz})^2$	2	1	2	2
—	3	$(d_{y^2})^1(d_{xy})^2(d_{yz})^2$	3	2	0	2
4, O	—	$(d_{x^2-z^2})^1(d_{xy})^1(d_{yz})^1$	3	1	2	1
—	4 SPL (high spin)	$(d_{z^2})^1(d_{xy})^1(d_{yz})^1(d_{xz})^2$	3	1	2	1
	4 SPL (low spin)	$(d_{z^2})^1(d_{xz})^2(d_{yz})^2$	3	0	2	2
	4, T	$(d_{xz})^1(d_{z^2})^2(d_{xy})^2$	4	2	1	0

TABLE 8. d^2

Reatant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal d-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{x^2-y^2})^1(d_{xy})^1$	3	1	2	0
—	2	$(d_{x^2-y^2})^2(d_{xy})^2$	4	2	0	0
2, SPL	—	$(d_{xy})^1(d_{yz})^1$	2	1	2	1
—	2	$(d_{yz})^2(d_{y^2-z^2})^2$	4	0	0	2
2, T	—	$(d_{xy})^1(d_{z^2})^1$	3	1	2	0
—	2	$(d_{xz})^2(d_{x^2-z^2})^2$	4	0	2	0
—	2	$(d_{xy})^1(d_{x^2-z^2})^1(d_{xz})^2$	3	1	2	0
3, TBP	—	$(d_{xy})^1(d_{yz})^1$	2	1	2	1
—	3	$(d_{x^2})^1(d_{xy})^1(d_{xz})^2$	3	1	2	0
3, SPY	—	$(d_{xy})^1(d_{yz})^1$	2	1	2	1
—	3	$(d_{y^2})^1(d_{xy})^1(d_{yz})^2$	3	1	0	2
4, O	—	$(d_{x^2-z^2})^1(d_{yz})^1$	3	0	2	1
	4, SPL	$(d_{z^2})^1(d_{yz})^1(d_{xz})^2$	3	0	2	1
	4, SPL (high spin)	$(d_{z^2})^1(d_{yz})^1(d_{xz})^1(d_{xy})^1$	3	1	1	1
	4, T	$(d_{z^2})^2(d_{xy})^2$	4	2	0	0

TABLE 9. d^1, d^0

Reactant: R_2ML_n n	Products: $R_2 + ML_n$ n	Metal d-electron configuration	Number of electrons in orbitals of symmetry			
			a_1	a_2	b_1	b_2
1	—	$(d_{xy})^1$	2	1	2	0
—	1	$(d_{xy})^1(d_{x^2-y^2})^2$	4	1	0	0
2, SPL	—	$(d_{yz})^1$	2	0	2	1
—	2	$(d_{yz})^1(d_{y^2-z^2})^2$	4	0	0	1
2, T	—	$(d_{z^2})^1$	3	0	2	0
—	2	$(d_{x^2-z^2})^1(d_{xz})^2$	3	0	2	0
3, TBP	—	$(d_{xy})^1$	2	1	2	0
—	3	$(d_{x^2})^1(d_{xy})^1(d_{xz})^1$	3	1	1	0
3, SPY	—	$(d_{xy})^1$	2	1	2	0
—	3	$(d_{y^2})^1(d_{xy})^1(d_{yz})^1$	3	1	0	1
4, O	—	$(d_{yz})^1$	2	0	2	1
—	4, SPL	$(d_{yz})^1(d_{xz})^2$	2	0	2	1
—	4, SPL high spin	$(d_{z^2})^1(d_{xz})^1(d_{yz})^1$	3	0	1	1
—	4, T	$(d_{z^2})^1(d_{xy})^2$	3	2	0	0
2, T	—	d^0	2	0	2	0
—	2	$(d_{x^2-z^2})^1(d_{xz})^1$	3	0	1	0
4, O	—	d^0	2	0	2	0
—	4, SPL	$(d_{xz})^1(d_{yz})^1$	2	0	1	1
—	4, SPL, low spin	$(d_{xz})^2$	2	0	2	0

L is auxiliary ligand, M metal, SPL square planar, T tetrahedral, TBP tetragonal bipyrdamid, SPY square pyramid, and O octahedral. The orbital symmetries (C_{2v}) are d_{z^2}, $d_{x^2-y^2}$: a_1, d_{yx} : a_2, d_{xz} : b_1, and d_{yz} : b_2.

From the symmetry point of view, the d^7 configuration is the most favourable for reductive elimination. The reaction is symmetry allowed for the low spin 3-coordinate trigonal, 4-coordinate SPL, 5-coordinate SPY and 6-coordinate O complexes. All the usual coordination numbers are thus represented. As is the case for the d^8 configuration, reductive elimination is permitted only from the low spin configurations.

The d^6-system is another example of this. Symmetry-allowed reductive elimination is possible from the low spin 3-coordinate, 4-coordinate SPL and 6-coordinate O complexes (Table 4).

For the d^5-configuration also, concerted reductive elimination is permitted from three configurations, the 3-coordinate, the 4-coordinate T and the 6-coordinate O (Table 5).

In contrast, reductive elimination is permitted only for one d^4-complex, the 6-coordinate O (Table 6). In this case, the formation of the product in a high spin state is necessary.

Concerted reductive elimination is permitted for two d^3-structures, the 4-coordinate T and the 6-coordinate O. In the latter case, the product must end up in a high spin configuration (Table 7).

Reaction is possible from the same structures, 4-coordinate T and 6-coordinate O in the d^2 series (Table 8), but in this case the product from the T-com-

TABLE 10
CHARGE TRANSFER CONFIGURATIONS INVOLVING THE CARBON—METAL BONDS AND THE OUTER METAL ELECTRONS OF COMPLEXES R_2ML_n

Formal *d*-configuration	Electron configuration	Number of electrons in orbitals of symmetry			
		a_1	a_2	b_1	b_2
d^{10}	$d^{10}s^1(R—M)^2_{a_1}(R—M)^1_{b_1}$	7	2	3	2
	$d^{10}s^1(R—M)^1_{a_1}(R—M)^2_{b_1}$	6	2	4	2
	$d^{10}s^2(R—M)^2_{a_1}(R—M)^0_{b_1}$	8	2	2	2
	$d^{10}s^2(R—M)^1_{a_1}(R—M)^1_{b_1}$	7	2	3	2
d^9	$d^{10}(R—M)^2_{a_1}(R—M)^1_{b_1}$	6	2	3	2
	$d^{10}(R—M)^1_{a_1}(R—M)^2_{b_1}$	5	2	4	2
	$d^{10}s^1(R—M)^2_{a_1}(R—M)^0_{b_1}$	7	2	2	2
	$d^{10}s^1(R—M)^1_{a_1}(R—M)^1_{b_1}$	6	2	3	2
d^8	$(d_{xz})^1d^8(R—M)^2_{a_1}(R—M)^1_{b_1}$	6	2	2	2
	$(d_{z^2})^1d^8(R—M)^1_{a_1}(R—M)^2_{b_1}$	4	2	4	2
	$d^{10}(R—M)^2_{a_1}(R—M)^0_{b_1}$	6	2	2	2
	$d^{10}(R—M)^1_{a_1}(R—M)^1_{b_1}$	5	2	3	2
d^7	$(d_y2)^1(d_{xz})^1d^6(R—M)^2_{a_1}(R—M)^1_{b_1}$	5	2	2	2
d^6, $n = 3$, TBP	$(d_y2)^0(d_{xz})^1d^6(R—M)^2_{a_1}(R—M)^1_{b_1}$	4	2	2	2
d^6, $n = 3$, SPY	$(d_{xz})^0(d_y2)^1d^6(R—M)^2_{a_1}(R—M)^1_{b_1}$	5	2	1	2
d^0	$(d_z2)^1d^8(R—M)^2_{a_1}(R—M)^1_{b_1}$	3	0	1	0

plex must be in a high spin state and that from the O complex in a low spin state (Table 8).

The d^1T and O-complexes should also undergo concerted reductive elimination (Table 9). In both cased the products must be low spin.

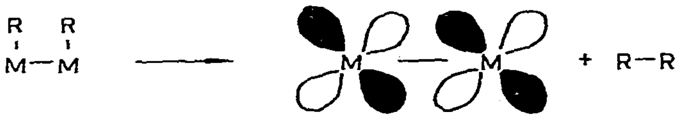
Finally, for the d^0 configuration, there are no symmetry-allowed pathways for reductive elimination. Charge transfer may be important, the state $(d_{z^2})^1$-$(\text{R—M})^2_{a1}(\text{R—M})^1_{b1}$, for instance, correlates with the product ground state for the T complex (Tables 9, 10).

Discussion

Since concerted reductive elimination is symmetry forbidden for the d^{10} configuration, such systems would be expected to yield radicals on thermolysis. This is verified by results from thermal decomposition of dialkylzinc(II) [3] which may be regarded as a d^{10} system although it is uncertain if the d-orbitals may really be included in the zinc(II) valence shell. Neophyl and similar derivatives of copper(I) and silver(I) also seem to yield radicals on thermolysis [4] but there are results which indicate concerted reductive elimination from some alkyls of copper(I), silver(I) and gold(I) [5]. The reason for this ambiguity may be competition between concerted and radical pathways. The concerted element could be derived from charge transfer or low lying excited states. As seen from Table 1, there is an excited state for the d^{10} system with the configuration $(d_{xz})^0d^8s^2$, from which concerted reductive elimination is permitted. There is also an excited state, $(d_{xz})^1d^8s^1$, from which concerted formation of two methyl radicals is possible. Again, the importance of this state is difficult to predict but it may contribute to radical formation. Examination of the charge transfer states (Table 10) shows that similar principles apply here. A charge transfer state with the configuration $d^{10}s^2(\text{R—M})^2_{a1}(\text{CH}_3\text{—M})^0_{b1}$ must have an electron distribution very similar to that of the products and should therefore strongly promote reductive elimination. For copper(I) this state should have a fairly high energy since it would in principle give copper(—I). Its importance is therefore questionable. On the other hand, a related configuration with less pronounced charge transfer, $d^{10}s^1(\text{CH}_3\text{—M})^2_{a1}(\text{CH}_3\text{—M})^1_{b1}$, is more probable and should contribute to radical formation. In general, charge transfer should be particularly important for high formal oxidation states.

The importance of these different exited and charge transfer states is a question of relative energies. It can be settled only by accurate calculations and clearly indicates the importance of such calculations in the transition metal series. Another factor, which could promote reductive elimination is cluster formation. According to the simple symmetry model [2], concerted reaction from a binuclear cluster I is orbital symmetry forbidden since the two electrons, which are added to the metal in the reaction, must occupy a metal—metal antibonding orbital as in II. However, particularly in a large cluster, this formally antibonding orbital may have a sufficiently low energy to make concerted reductive elimination possible (cf. ref. [4b]). This is naturally not restricted to d^{10} systems but applies generally.

Finally, there is the possibility that electron transfer reactions may precede reductive elimination. It is well known that oxidation of copper(I) alkyls will induce decomposition [5f]. For e.g. methylcopper, alkyl transfer within a binuclear complex should be facile, and give a copper(I) cuprate III in which the copper atoms might be expected to have different redox potentials. This could result in electron transfer to give a mixed copper(0)—copper(II) complex IV



I II

$$\overset{\oplus}{Cu}{}^{I}\overset{\ominus}{Cu}{}^{I}R_2 \longrightarrow Cu^{0}Cu^{II}R_2$$

$R = CH_3$ $R = CH_3$

III IV

$CpPt(CH_3)_3$ $CpCo(PR_3)(CH_3)_2$

V VI

Cp = cyclopentadienyl

which would rapidly decompose. The decomposition from a d^9 system is symmetry forbidden and should thus yield radicals. However, both charge transfer (Table 10) and thermal excitation (Table 1) will give states from which concerted reductive elimination is symmetry allowed. Perhaps then, the conflicting evidence from the reactions of the copper(I) groups alkyls could also be due to transient formation of divalent species, in which e.g. charge transfer interaction would be more important than in the monovalent complexes. In fact, the similarity in the product patterns from the decomposition of neophylcopper(I) species [4b] supports the idea of a common copper(II) intermediate.

Alkyls and aryls of the divalent nickel group metals (d^8) appear to react essentially as predicted by symmetry arguments (Table 2). Reductive elimination is favoured from 4- and 5-coordinate nickel(II) and platinum(II) complexes [6]. For palladium, reductive elimination is facile even for formally 2-coordinate species [6d] but here the solvent may well participate as ligand.

The reductive elimination is only permitted from the low spin state (Table 2). Spin restrictions will in fact be important for the whole d^n series for $8 \geqslant n \geqslant 1$. For $n \leqslant 6$ these restrictions will of course also apply to the product complexes. Since the spin properties are partly determined by the auxiliary ligands, these will be very important.

Unfortunately, the spin question is more complex than indicated by qualitative theory and the orbital composition [7c], and phenomena such as recoupling [1] confuse the picture and call for quantitative calculations. In the nickel(II) series, at least, the qualitative conclusions are nonetheless useful, and reductive elimination apparently takes place from low spin states as predicted.

Alkyls of copper(III) have not been isolated, but gold(III) alkyls have been studied in some detail. The complexes are generally 4-coordinate but appear to undergo reductive elimination only after dissociation of an auxiliary ligand [7]. Reductive elimination from a trigonal, 3-coordinate species is symmetry forbidden (Table 2), but the solvent may participate. T-shaped intermediates are also possible [7c]. An alternative explanation is the operation of charge transfer which should be important since the metal is in a high formal oxidation state. Reductive elimination from the charge transfer states $(d_{xz})^1 d^8(\text{R—M})^2_{a1}$-$(\text{R—M})^1_{b1}$ and $d^{10}(\text{R—M})^2_{a1}(\text{R—M})^0_{b1}$ should be facile (Table 10, 2). Both these states seem unlikely as ground states, but Extended Hückel calculations predict that even the second state may become the ground state for trimethylgold(III) [7c]. This may also be true for copper(III) alkyls and aryls, which have been postulated as intermediates in a number of copper-promoted coupling reactions [8].

The d^7 systems are particularly interesting since symmetry allowed reductive elimination is possible for all coordination numbers between 3 and 6 (Table 3). In accord with this, nickel(III) species prepared by electrolytic oxidation undergo very facile reductive elimination [9]. This reaction is possibly also promoted by charge transfer, since even moderate unsymmetrical charge transfer will yield a state with the correct symmetry for reductive elimination (Table 10). In accordance with the symmetry predictions, concerted reductive elimination occurs from cobalt(II) alkyl—vinyl systems [5b]. With simple alkyls, coupling is also observed, but other reactions predominate [10,5d]. However, a recent study of neophylcobalt(II) shows that efficient reductive elimination takes place in the presence of phosphine ligands [4b].

The interpretation of the experimental evidence for the d^6 system is not entirely straightforward. Symmetry allowed reductive elimination is only permitted when low spin d^6-complexes give low spin d^8 complexes (Table 4). Part of the problem may therefore be involvement of high spin states.

6-Coordinate platinum(IV) alkyls undergo facile reductive elimination [11] as would be expected from symmetry consideration. However, for phosphine complexes it has been shown that added phosphine strongly retards reductive elimination [11d]. This is not in accord with the symmetry rules, since it seems to imply that a 5-coordinate intermediate is involved (Table 4). One possible explanation is that the rate of reaction is considerably increased by exchange of a phosphine ligand for a solvent molecule. Some support for this explanation is provided by the fact that reductive elimination from a diphosphinoethane complex is fairly slow but unaffected by added phosphine [11d].

Similar retardation by added phosphine ligands has been observed for cobalt(III) complexes [12], and again an intermediate containing a solvent molecule in place of phosphine is possible. A second possible explanation which also applies to the platinum(IV) complexes, is that charge transfer is important. From Tables 10 and 4 it is seen that moderate charge transfer from the b_1 metal—alkyl orbitals results in symmetry allowed reductive elimination from the SPY 5-coordinate species. It is reasonable to assume that loss of a phosphine ligand would result in an increased charge transfer from the metal—alkyl bond and more facile reductive elimination, in accord with experimental results.

The cyclopentadienyl complexes V [13a] and VI [13b] are exceptionally stable and give methane on decomposition instead of ethane. Since they are probably tetrahedral, this is in accordance with the symmetry rules (Table 4).

Finally, for iron(II) alkyls other reactions than reductive elimination predominate [4b,14]. In this case, the reason may be secondary reactions initiated by iron(0) rather than low reactivity of the iron alkyls. Iron hydrides, formed e.g. by the reaction of iron(0) and the solvent, might be expected to yield mixed alkyl-hydrides, which should eliminate alkane very readily.

According to the symmetry predictions for the d^5 systems, reductive elimination from the 4-coordinate T and 6-coordinate O complexes should be symmetry allowed (Table 5). In agreement, 6-coordinate iron(II) and cobalt(III) complexes undergo very facile reductive elimination on 1-electron oxidation [9b]. In general, reductive elimination is fairly efficient with iron(III) complexes [4b,5e] but their structures are uncertain.

For manganese(II), reactions other than reductive elimination dominate. Again, the structures of the intermediates are not known [5e,15].

The experimental results for d^n systems where $n \leqslant 4$ [16] are somewhat confusing. For the d^4 system reductive elimination should be symmetry allowed only for the 6-coordinate O structure (Table 6). The suggested iron(IV) intermediate in the facile reductive elimination from neophyliron(III)chloride [4b] could well be 6-coordinate in agreement with symmetry predictions. Reductive elimination should be forbidden for a tetrahedral d^4 system and that may be one reason for the stability of tetrabornyliron(IV) [17]. Steric factors are also probably important. It may be noted that for a high energy intermediate like iron(IV) reductive elimination may be possible also for coordination numbers other than 6. This may be exemplified for the d^4 system. Reductive elimination is symmetry allowed for most d^4 coordination numbers according to the simplest model for orbital control [2] which requires only that d_{xz} is empty in the reactant and filled in the product (Table 6). The energy required to rearrange the other d-electrons to comply with the symmetry restrictions suggested here (Tables 1—9) may be quite small. The symmetry related barrier imposed on a highly reactive system like iron(IV) may therefore be negligible and facile reaction is possible. These effects are of course not restricted to the d^4 system but are also found for other systems.

6-Coordinate anionic chromium(II) complexes [18] and a 6-coordinate diphenylchromium(II) complex are quite stable [19]. Since strongly coordinating auxiliary ligands such as bipyridine are involved, a possible explanation is that the product d^6-complexes have low spin structures. Reductive elimination becomes forbidden, although the barrier may be moderate.

For the d^3 system, reductive elimination should be permitted from the 4-coordinate T and possibly the 6-coordinate O systems (Table 7). In the octahedral case, where the product must have a high spin configuration, a low spin arrangement may be favoured when the ligands are strongly coordinating. The reaction then becomes symmetry forbidden. In fact, chromium(III) species are fairly stable in THF, where 6-coordinate complexes are probably formed [20]. The products are alkane and alkene formed via α and β-elimination [20d]. In THF solution also neophylchromium(III) fails to yield products from reductive elimination [4b]. The phenyl derivatives give biphenyl but the reaction is not necessarily simple reductive elimination [20b,c].

The stability of tetrabornylmanganese(IV) [17], which probably has a tetrahedral structure and which should thus be able to undergo symmetry allowed reductive elimination, again indicates that steric factors may be important for bornyl systems.

Tetraneopentylchromium(IV) and a number of related d^2 systems have been prepared [21]. The compounds are fairly stable and decomposition of e.g. tetraneopentylchromium(IV) gives little of the product from reductive elimination [21b,d]. This is contrary to the predictions of the symmetry rules and may be due to steric hindrance to coupling of the bulky alkyl groups. It could also be a question of spin states, since the product must be high spin. Tetramethylchromium(IV), which should have a higher coordination number than 4, decomposes fairly readily but the products have not been analysed [21b,c]. According to the symmetry predictions, reductive elimination from a 6-coordinate O structure, which is the most likely, should be permitted if a medium spin square planar product is obtained. Since the product is probably high spin, the barrier may be sufficient to result in other products than alkyl dimer.

The chemical properties of d^1-alkyls are not well known. A few different vanadium(IV) [21] and titanium(III) [22] alkyls have been studied but the products from decomposition have generally not been determined. An exception is neophyltitanium(III) which was shown to give only monomer, that is t-butylbenzene [4b]. This is surprising since reductive elimination from a 6-coordinate complex, which is the probable structure of the intermediate, should be symmetry allowed. Perhaps, 5-coordination is preferred due to the steric requirements of the neophyl group. Another possibility is that the product ends up in a high spin configuration which is against the symmetry rules (Table 9).

For the d^0 system, finally, concerted reductive elimination is symmetry forbidden since the ground state product can never have a d^2 low spin configuration. If the energy difference between the ground state and the low spin state is small, reductive elimination might be possible anyway, especially if charge transfer is involved (Table 10).

The studies of d^0-alkyls, e.g. hexamethyltungsten [23], pentamethyltantalum [24] and tetramethyltitanium [22,25] indicate that reductive elimination is disfavoured for these systems, as suggested by the symmetry treatment.

Some early evidence claims that methyltitanium(IV)trichloride gives methyl radicals on decomposition [22a,26], in accordance with the symmetry predictions. More recent evidence seems to refute this suggestion [27] and neophyltitanium(IV)trichloride gives bineophyl containing none of the rearranged dimers, which would be expected from a radical reaction [4b]. Methyltitanium(IV)trichloride also gives considerable amounts of dimer, that is ethane, in contrast to dimethyltitanium(IV)dichloride [27b]. Coupling is thus especially favoured when only one alkyl group is attached to the metal. This is contrary to our model for reductive elimination. An attractive explanation is that metal clusters are involved specifically for the monoalkyl derivatives [4b].

Finally, it is interesting to note that the oxidation of alkanes with chromium trioxide and potassium permanganate often is assumed to have a radical character. Since d^0 metal alkyls may well be intermediates in these reactions [28], this is in accordance with the symmetry rules (Table 9).

Conclusion

The predictive power of the present symmetry treatment depends on several factors. The assignments of ground states may be inaccurate since they are based on ligand field theory. In particular, the choice between a low and a high spin state can be difficult and this choice is often essential as indicated by the discussion above. Furthermore, when the ligands and the metal *d*-orbitals interact strongly, that is when the energy separation between the different *d*-states and probably also the symmetry related reaction barriers are high, simple ligand theory will often fail. More accurate estimates, based on calculations, will therefore be required, but the symmetry properties will still be important in suggesting relevant states for the calculations.

When the ligand—metal *d*-interactions are small, ligand field theory will probably be more accurate but the energy differences between the states leading to symmetry allowed and those leading to forbidden reductive elimination will be small. The difference between the activation energies for allowed and forbidden reactions may also be small. However, for transition metal alkyls several reactions with similar activation energies but different symmetry requirements will compete with reductive elimination, e.g. α- and β-elimination, and perhaps radical cleavage. This balance is clearly indicated for Cu^{I} and Cu^{II} and Ni^{II}.

Even small, symmetry related, reaction barriers will therefore have considerable influence on the product pattern. This may be the basis for the surprisingly good agreement between theoretical predictions and experimental results, such as the radical character of the reactions involving d^{10} and d^9 copper alkyls, the facile reductive elimination from 4- and 5-coordinate d^8 nickel alkyls and the remarkable stability of the d^6-complexes V and VI. There are of course also failures, e.g. the facile reductive elimination from monoalkyltitanium(IV)(d^0). However, even then the symmetry model is useful, since it suggests a mechanism for bialkyl formation, other than simple reductive elimination, e.g. formation of a metal cluster.

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