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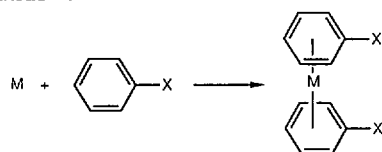
Electronic Configuration and Reactivity: First Semi-Quantitative Assessment of Relative Reactivities for the 3d Transition Metal Vapors Toward *p*-Bromotoluene in a Methylcyclohexane Solution

Jean-Claude Négrel*, Robert W. Zoellner, and Michel Chanon

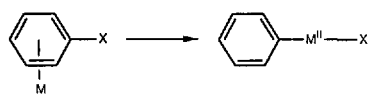
Abstract: A specifically designed metal vapor synthesis apparatus makes possible the semi-quantitative assessment of the reactivities for the elements of the first transition series toward *p*-bromotoluene kept in a -118°C solution of methylcyclohexane. In all cases, the two main processes are coupling and reduction of the substrate. The intrinsic reactivity of the substrate displays a behavior highly dependent upon the metal electronic configuration, suggesting a direct importance of the 18e rule in ruling these phenomena. Zn and Mn are the less reactive of the studied metals. In a way reminiscent of Rieke coupling of haloaromatics by metal powders, Ni vapor displays the highest ability in mediating the coupling of the substrate.

Metal vapor chemistry^[1], initiated in the sixties, has mainly been used to obtain new organometallic structures. Meanwhile, far less information in the direction of quantitative reactivity has been gathered^[2]. The present contribution aims at bringing new data in this second direction.

Vapors of V, Cr, Mo, W react by co-condensation at -196°C with aryl halides to yield bis(arene)metal coordination compounds^[3]:



Vapors of metal belonging to the nickel triad react at the same temperature to give π -arene metal complexes; when the temperature rises, these complexes evolve to yield the oxidative addition products^[4]:



In order to obtain significant quantitative measurements, we have utilized a rotary solution reactor^[5]. The metal vapors,

generated in the center of a flask maintained under high vacuum, react with a film of *p*-bromotoluene solubilized in methylcyclohexane (conc. $\approx 2\%$) and maintained by the cold and rotation on the walls of the flask. The reactor being returned to atmospheric conditions at the end of the reaction, we therefore study the organic products (coupling and reduction from *p*-bromotoluene) resulting from the reaction of the firstly formed organometallics. The quantitative measurement of organic products, combined with the knowledge of the quantity of vaporized metal, allows a quantitative assessment of the relative reactivity of various metals toward *p*-bromotoluene (PBT).

Experimental

Our home-made rotary apparatus, derived from the Green reactor^[6], is a large-sized prototype with several improvements^[7].

Metals are vaporized by a 30–120 A current heating tungsten alumina-coated crucibles. The solution is carefully degassed by three freeze-thaw cycles. It contains ≈ 20 mmol of *p*-bromotoluene in 200 mL of methylcyclohexane which constitute a film on the walls of the rotating (20 rpm) 6 liters flask, kept at $-118 \pm 1.5^{\circ}\text{C}$ by a bath of liquid methylcyclohexane cooled by liquid nitrogen. It takes 30 min to 1 h to vaporize 0.1 g to 1 g of metal under the pressure of 10^{-4} Torr. When this vaporization is finished, the vacuum is switched off and the flask is gently allowed to return at room temperature. The products are quantitatively recovered; a filtration under pressure eliminates metal halides and the unreacted particles of metal. The filtrate is diluted to a standard volume of 500 mL by addition of methylcyclohexane. The quantitative determination of organic products is performed by GC and HPLC with standard products. Coupled GC-MS analysis allows the identification of secondary products. One must

stress that a quantitative evaluation of metal vapor reactivities is made difficult for several reasons:

a) one must know the exact quantities of reactive substrate; this is particularly difficult in co-condensation studies performed in rigid matrix. Under our conditions (rotating flask, liquid solution), the actual concentration of substrate is known with the minimum of uncertainty;

b) the exact measurement of vaporized metal is made possible by the design of our apparatus, where the major part of the metal deposited (i.e., not reaching the solution) may easily be weighted. The cylindrical surface of the cabinet-tubing system allows an easy recovery of the small complementary amount of metal deposited;

c) the quantitative recovery of the reaction products. A bakeout procedure of the liquid nitrogen cooled trap under static vacuum allows the return to the reaction flask, kept cold, of any possible trap condensate. A specially designed «solvent sweeper» device is fitted on the flask at the end of the reaction, for the quantitative recovery of the reaction mixture;

d) the difficulty of obtaining a comparable rate of vaporization for various metals. We have checked that this parameter has no consequence on the studied reactivity parameters, within a range of rates of one to twice. – In contrast with a relative insensibility of r (see Discussion for definition of r) to the rate of metal vaporization, we have checked that the relative quantity of substrate versus that of vaporized metal plays a non-negligible role. For example, the reactivity drops from 78.4% when 2.1 mmol of chromium are vaporized with 26.5 mmol of *p*-bromotoluene (PBT) solubilized in 200 mL of methylcyclohexane (MCH), to 35.9% with 15 mmol of Cr and 23.4 mmol of PBT; this represents a variation of the ligand/metal ratio by a factor of 8. However, for titanium, the relative variation for r is 10%, when the ligand/metal ratio varies by a factor of 2.3. For nickel, the r variation falls to 3.4% for a variation of the ligand/metal ratio by a factor of 1.2. In contrast to the case of iron, with reactivities of 40% and 40.1% for the same ligand/metal ratio, we observed a 9.5% variation for cobalt when the ligand/metal ratio varies only by a factor of 1.1. So, despite all the efforts made to ensure reproducibility, we consider our results as a semi-quantitative evaluation with about 10% of relative error;

e) the uniformity for the reaction mixture warming procedure. This is probably far less important for these solution reactions than for co-condensation experiments. In any case, this factor has been kept invariable in our experiments;

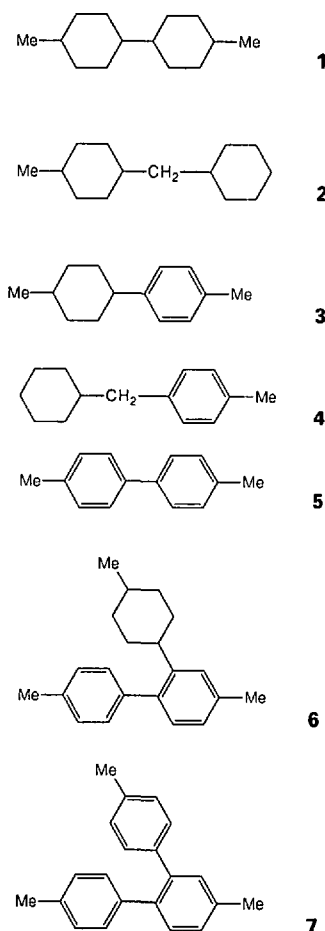
f) the effect of radiant heat. The vaporizing source is equipped in five directions with a water cooled shielding. A continuous monitoring of the temperature of the substrate solution shows a good constancy on the reacting temperature while vaporizing the metal. Furthermore, the secondary vacuum gauge, located before the trap, never displays the vacuum variations that should occur in the case of liquid film local warming.

The uniformity of all the other experimental conditions allows us a comparison of reactivities.

The products have been identified by GC-MS analysis: 4,4'-dimethyl-1,1'-bicyclohexyl (1), m/z : 194, 112, 97, 81, 69, 55, 41; cyclohexyl-4-methylcyclohexylmethane (2), m/z : 194, 111, 97, 69, 55, 43; *p*-(4-methylcyclohexyl)toluene (3), m/z : 188, 173, 131, 118, 106, 105, 97, 91, 77, 55, 41; cyclohexyl-*p*-tolylmethane (4), m/z : 188, 173, 159, 145, 132, 119, 105, 97, 91, 55, 41; 4,4'-dimethyl-1,1'-biphenyl (5), m/z : 182, 167, 152, 91

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(for Ti, V, Cr, we observed several isomers of this «normal» coupling product 5);
2-(4'-methylcyclohexyl)-4,4'-dimethyl-1,1'-biphenyl (6), m/z : 278, 264, 173, 159, 131, 105, 91, 77, 55;
2-(*p*-tolyl)-4,4'-dimethyl-1,1'-biphenyl (7), m/z : 272, 257, 242.



For the last two products, the position of the methylcyclohexyl and tolyl substituents is uncertain: either 2 or 3.

Results and Discussion

The results of our experiments are summarized in Fig. 1. The «intrinsic» reactivity

of a given metal is measured by the ratio r (in %):

$$r = \frac{\text{total quantity of PBT transformed}}{\text{total quantity of vaporized metal}}$$

The parameter s displayed in the dotted curve of Fig. 1 stands for:

$$s = \frac{\text{quantity of coupled aromatics}}{\text{quantity of reduced aromatics}}$$

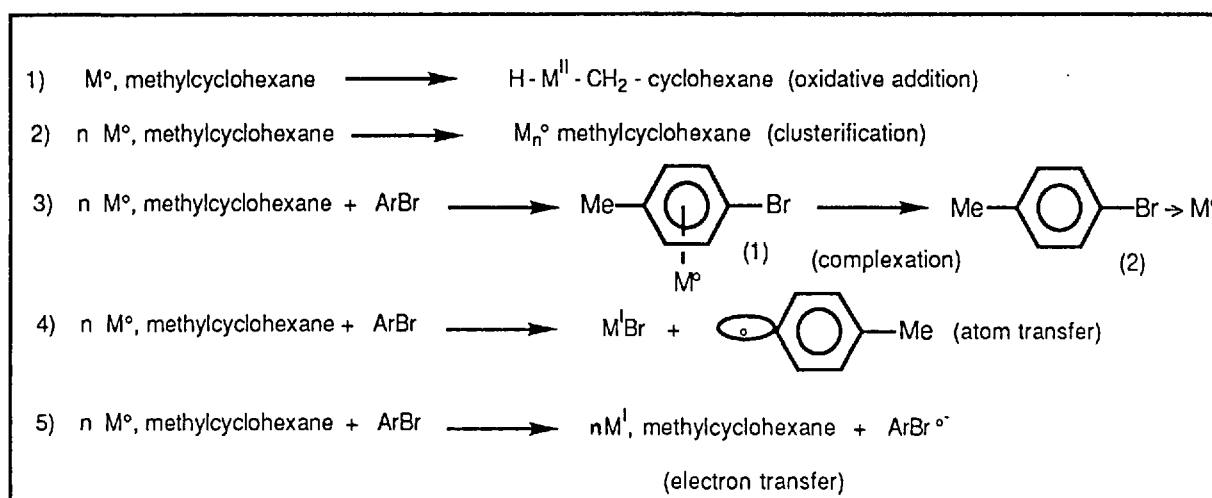
Fig. 1 shows that r varies widely when different metals are considered.

Table I gathers some physical data on the vaporized metals which could be relevant to the experimental measurements of r . When the atoms reach the solution of substrate kept at -118°C , different fates wait for them. Being totally naked, they probably get solvated by any solvent molecule that they encounter. The various studies on the activation of C-H bonds^[8] suggest that a loose solvation^[9] may occur, even with methylcyclohexane as solvent. It is currently believed that prior π -complexation is the best way to reduce the extent of metal aggregation (in the co-condensation conditions)^[10]. Even with alkyl halides, *Timms*^[11] and *Klabunde*^[12] have shown a metal atom complexation by the halogen. From this point, five virtual possibilities may be thought (Scheme 1).

We implicitly discard the possibility that, on the way to clusters, Equation (2), highly reactive di- or trinuclear metal species react more rapidly than naked atoms toward organic species. We must recognize that this assumption, which follows a kind of Occam's razor philosophy, is not completely safe: *Klabunde* has indeed suggested that small clusters of Mg may be more reactive than naked atom counterparts^[13]. But with the relative high temperature and the experimental conditions of our solution reactions, the formation of such small clusters is in severe competition with the metal atom-solvent-substrate interaction^[14].

The valence-orbital ionization potential of the most electropositive metal (Table I) is still far higher than that of Na (5.2 eV). When this alkali metal is added to a methylcyclohexane solution of *p*-bromotoluene, the coloration obtained (light yellow) is quite different from the one observed during our metal vapor experiments with Ti and V. Therefore, we discard Equation (5) as significant in the possible fates of metallic vapors. Equations (1)–(4) allow a rationalization of the most typical points in Fig. 1. Equation (2) is the main responsible for the denominator of r . The highest value for r , obtained for Cr, suggests that, at least for this element, Equation (3₁) plays an important role. Everything goes as if the formation of a 18-electron (NVE) sandwich complex for this case was providing a strong driving force for Equation (3₁). In the order of stability, 16 e NVE organometallic transition metal centered species follow the saturated (18 e) stable organometallics: this could explain the good reactivity measured for titanium. The low value of r for vanadium could be due to a high tendency toward cluster formation, under its metallic form; this element indeed displays the highest $\Delta H_{\text{vaporization}}$ (Table 1). This high $\Delta H_{\text{vaporization}}$ hints at a high metal-metal bond strength, providing a good driving force for Equation (2). Our results for vanadium converge with previous reports signaling a low reactivity of this element^[15]. The type of argument set forth for V does not seem to be involved to explain the low reactivity of manganese and zinc toward organic substrates: data shown in Table I indeed, hint a low metal-metal bond strength for these elements. One rather thinks of a type of enhanced stability (and therefore decreased reactivity) for the configurations corresponding to half-filling^[16] and filling of these valence orbitals. The similarity of these two elements is greater than only their common small reactivity measured by r : in contrast with all the other metals studied in this report, both elements dis-

Scheme 1 (Ar = *p*-MeC₆H₄)



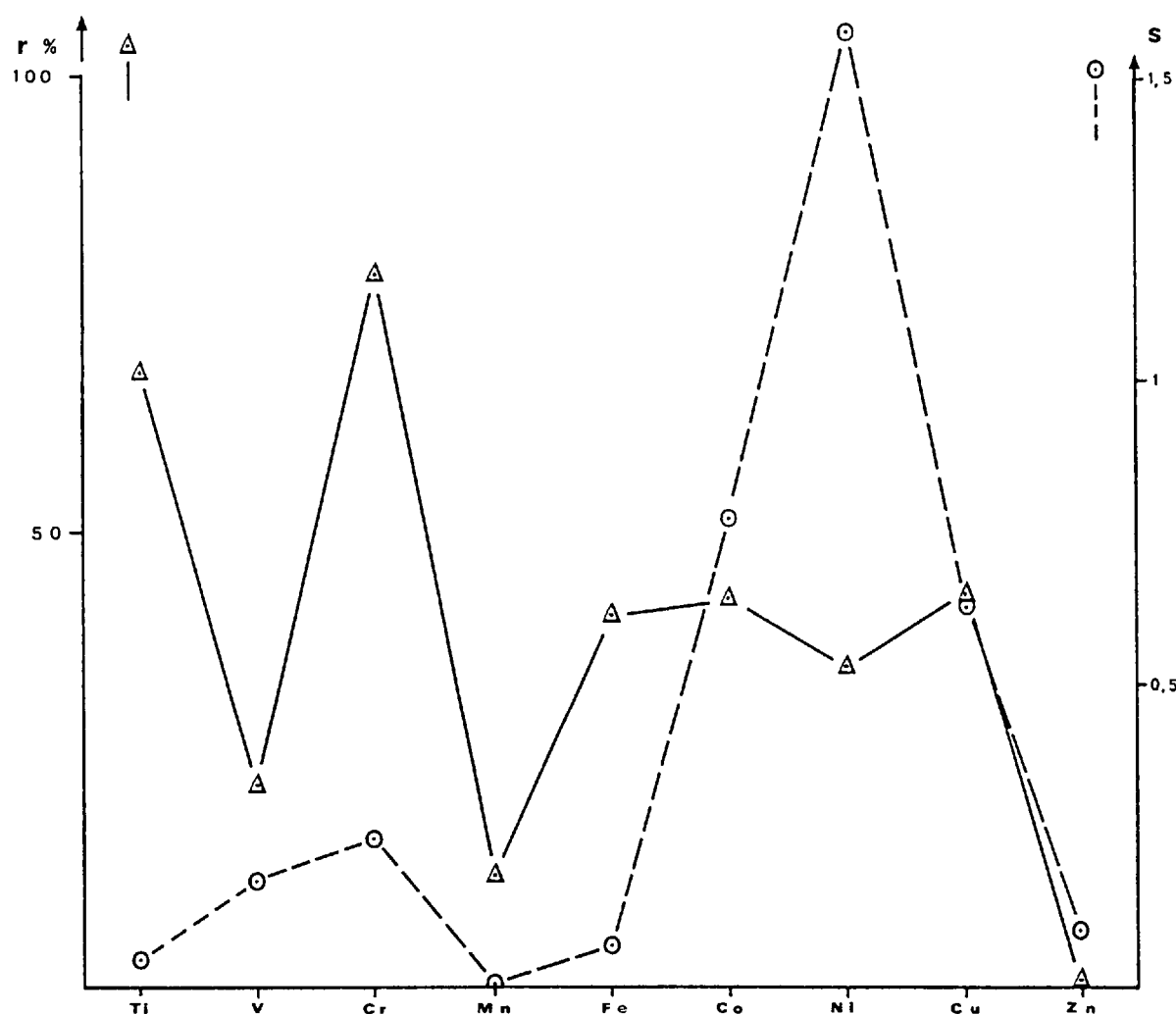


Fig. 1. Reactivity parameters r and s (cf. text) for elements of the first transition series.

Table 1. Selected properties of the studied metals.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic Configuration	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Valence-Orbital Ionization Potentials [eV] ¹⁾	s 6.1 d 5.6	d 6.3 s 6.3	d 7.2 s 6.6	d 7.9 s 6.8	d 8.7 s 7.1	d 9.4 s 7.3	d 10 s 7.6	d 10.7 s 7.7	s 9.4
$\Delta H_{\text{vaporization}}$ [kJ mol ⁻¹] ²⁾	425	460	342	221	340	382	375	307	114
Temperature of Evaporation under 10^{-5} Torr [°C] ³⁾	1546	1888	1205	980	1447	1649	1510	1273	343

¹⁾ From W.W. Porterfield: *Concepts of Chemistry*, Norton, New York (1972).

²⁾ *Natl. Bur. Stand. (US) Circ. 500*, February (1952).

³⁾ L. Holland: *Vacuum Deposition of Thin Films*, Chapman, London (1956).

play an absence of coloration when the metal meets the solution of the substrate in methylcyclohexane. The medium «reactivity» of atoms Fe, Co, Ni, Cu could be due to the impossibility, for these atoms, to reach the sandwich disposition (EAN rule). These atoms would therefore reach a half-sandwich only disposition, better prone to equilibrium return to methylcyclohexane solvated form and therefore, better chances for clusterification, Equation (2). However, for iron, the η^6, η^4 -bis(arene) complex could exhibit some stability under our experimental conditions^[17]. For copper, the half-sandwich disposition is known^[18,19]. However, among these four last metals, the higher reactivity of copper could have to do with high efficiency of copper atoms for the direct abstraction of halogens^[20].

Two main kinds of organic products are formed by the reaction of metal atoms with *p*-bromotoluene: (i) coupling at the position originally occupied by the bromine, (ii) reduction at this position. Besides these main products, one also identifies small amounts of the by-products 6 and 7. The observation of coupled methylcyclohexane (cf. 1-4 and 6) strongly suggests that the solvent, methylcyclohexane, provides the H necessary for the reduction of the substrate. With the presently available experimental data, it is difficult to decide if this reduction is the consequence of a radical pathway (phenyl radicals formed by reaction (4) abstracting H from methylcyclohexane), or the consequence of an initial insertion of metal atoms or clusters adding oxidatively to the C-H bond of methylcyclohexane and forming a metal hydride

able to reduce *p*-bromotoluene. Such a type of insertion has been reported in some experiments on C-H activation^[21a]. On the other hand, Jones' recent work^[21b] suggests that, when Rh centered complexes insert in C-H bonds, the reverse elementary step (reductive elimination) dominates at temperature above -20°C . The dichotomy of pattern for r opposing the early transition metals to the late ones (Fig. 1), joined to the observation of several isomers for the normal coupling product (5) for the most electropositive metals could even suggest different mechanisms for these two groups of metals. This remark applies also to the important formation of coupling products for Co, Ni, and Cu. The outstanding reactivity of nickel atoms in promoting the coupling of *p*-bromotoluene, is highly reminiscent of the results with Ni⁰ powders and

complexes, reported by Rieke et al.^[22] on one hand and Kochi et al.^[23] on the other. But it doesn't seem that the mechanistic considerations developed by Kochi could apply here: in our experimental conditions, we have never seen the strong development of coloration characteristic of the formation of an organometallic compound by oxidative addition^[10,24] either for nickel or for any of the metals studied in this report.

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Löschbare optische Fluoreszenz-Datenspeicher**

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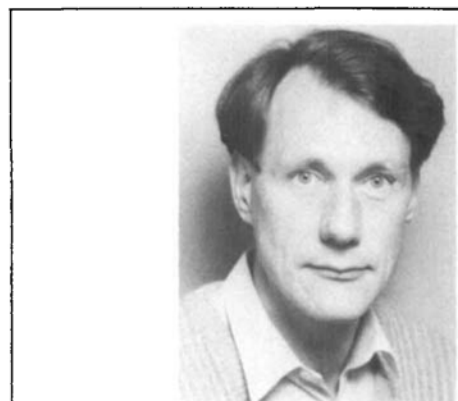
In the past, dye chemistry has chiefly been oriented towards traditional areas such as the development of textile dyes. However modern applications, for example reproduction and information technologies, call for new developments in this line. The storage of information might become a domain of dye chemistry.

1. Einleitung

Die bereits weit verbreitete und immer noch schnell expandierende Datenverarbeitung hat einen grossen Bedarf an Massenspeichern. Mit den für Computer bisher überwiegend verwendeten magnetischen

Speichermaterialien können nur schwierig noch wesentlich höhere Speicherdichten erreicht werden. Ausserdem sind diese Materialien in bezug auf die Langzeitstabilität problematisch, was sich besonders bei grossen Datenmengen bemerkbar macht. Und schliesslich stört auch ihre Anfälligkeit gegen magnetische Felder.

Optische Datenspeicher sollten aber sehr hohe Speicherdichten und Langzeitstabilitäten zulassen und darüber hinaus unempfindlich gegen Magnetfelder sein. Wichtig wären Systeme, die beschrieben und auch wieder – selbst wenn nur wenige Male – gelöscht werden können. Benötigt werden für hohe Lesegeschwindigkeit ge-



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eignete Speicher; die Geschwindigkeit des Schreib- oder Löschvorgangs darf vergleichsweise niedriger sein.

2. Optische Speicher

Die zuvor genannten Anforderungen werden zum Teil von den bereits entwickelten optischen Datenspeichern^[1a] erfüllt, von denen das bekannteste System die CD-Laserdisk für Audiosignale ist. In letzte-

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