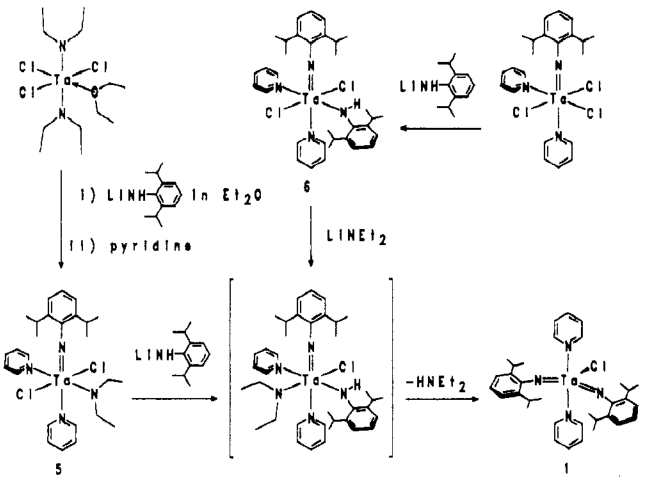
**Scheme I**



π interaction) only if the imido ligand is bent.[22]

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**Supplementary Material Available:** Text containing analytical and spectroscopic data for compounds **1–8** and tables of crystal data and data collection parameters, atomic positional and thermal parameters, bond distances, and bond angles for Ta(=NAr)$_2$Cl(py)$_2$ (Ar = 2,6-diisopropylphenyl) (7 pages). Ordering information is given on any current masthead page.

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[22] Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

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## Is There an Effective Atomic Number Rule for Adsorption on Surfaces?

The effective atomic number rule has long provided a useful tool with which to understand the stability of molecules. The 8- and 18-electron rules provide the basis for the organization of organic and organometallic chemistry. Along with geometry-dependent modifications (such as the square-planar 16-electron rule and the amendations for hypervalent molecules) and Wade's rules for clusters, these electron-counting processes allow access to much of chemistry.[1] Is there a similar rule that controls the stoichiometry of adsorbed molecules on metal surfaces? Such surface species include hydrogen, CO, NO, and unsaturated organic molecules, and thus the surface with its adsorbed molecules is, in principle, just a very large organometallic molecule.

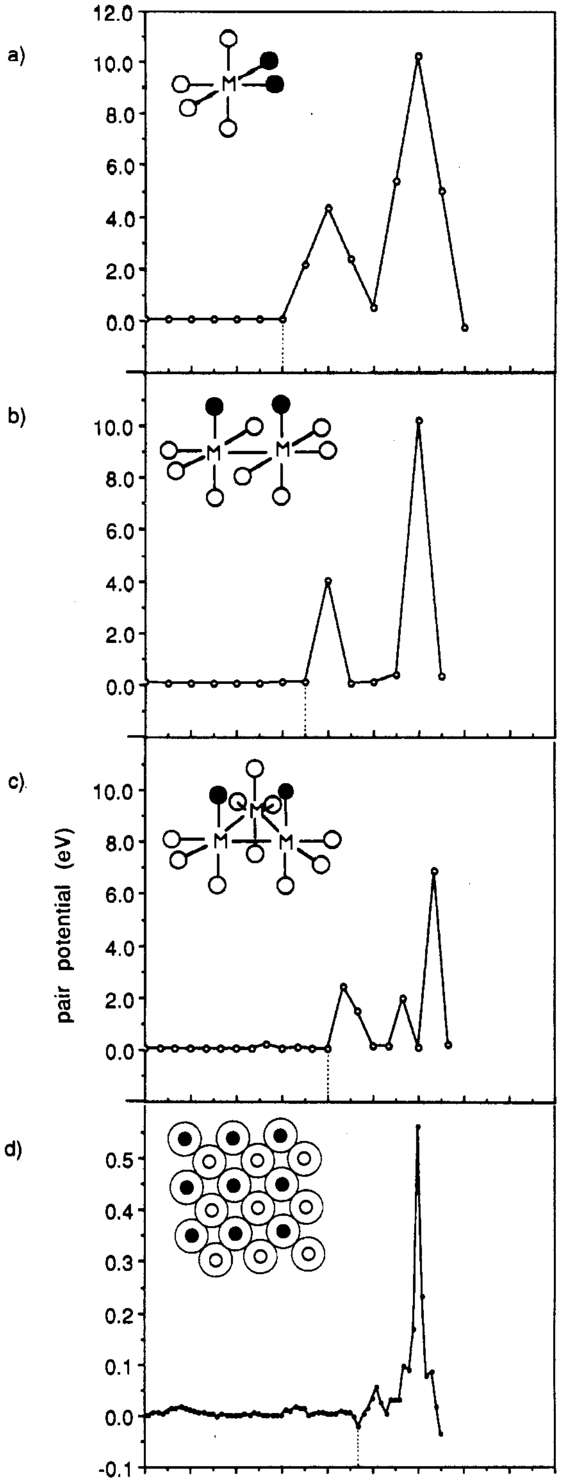

**Figure 1.** Calculated L–L pair potentials (between the ligands drawn as shaded circles) for the species (a) ML$_6$, (b) M$_2$L$_{10}$, (c) M$_3$L$_{12}$, and (d) a completely covered (100) fcc metal surface with L on the top sites. (The values given refer to the potential between one pair of ligands.)

The atom–atom, or fragment–fragment, pair potentials describing the interaction between two units is a common concept for surfaces[2-4] but is one that has not been generally used in molecular chemistry outside of the molecular modeling area. Their signs and magnitudes crucially control the ordering patterns of adsorbed species. The potential describes how two atoms or fragments "see" each other through direct interactions and electronically through the atoms that make up a surface or through the central atom in a mononuclear coordination compound or the atoms of a cluster. It represents the difference between the sum

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[1] See, for example: Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.

[2] Einstein, T. L. In *Chemistry and Physics of Solid Surfaces*; Vanselow, R., Ed.; CRC Press: Boca Raton, FL, 1979.

[3] Einstein, T. L. *Crit. Rev. Solid State Sci.* **1978**, *7*, 261.

[4] See also: White, J. M.; Akhter, S. *Crit. Rev. Solid State Sci.* **1988**, *14*, 131. Christmann, K. *Surf. Sci. Rep.* **1988**, *9*, 1.

0020-1669/90/1329-4594$02.50/0

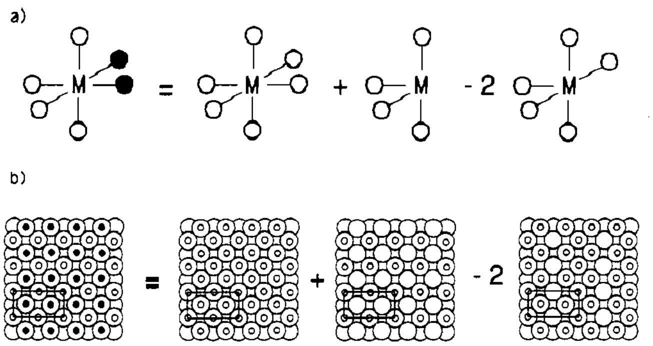

**Figure 2.** Definition of the pair potential used in Figure 1 in symbols.

of the individual bond energies of the two atoms or fragments and the total bond energy when the two fragments are coordinated at the same time. For an $ML_6$ species it is simply the energy($ML_6$) + energy($ML_4$) − 2 × energy($ML_5$). Positive and negative pair potentials represent respectively a repulsion and attraction between the two fragments. For the systems we will discuss here, the pair potential will thus be directly calculated rather than coming from some empirical model. Although the bond energy from such calculations is not reliable, the pair potential obtained via this isodesmic (same number of linkages) process should be well approximated.

Figure 1 shows the pair potential calculated (using the extended Hückel model[5]) between two L groups in several geometries, as a function of central atom or bulk atom electron count (L for our purposes is a hydrogen atom, but similar results are found for other ligands). In all cases of Figure 1 the pair potential is calculated between the shaded ligands as described in Figure 2 for the $O_h$ $ML_6$ complex and the (100) surface of a fcc metal.

Notice the two large peaks in the plot of Figure 1a that represent the pair potential in an octahedral transition-metal complex $ML_6$. The first rises steeply past six electrons and the second past ten electrons. The amplitude of these peaks are very large, larger indeed than the metal–ligand bond energy. Thus for the hypothetical species ($d^8$) $Fe(CO)_6$ the pair potential is so repulsive that one of the CO groups is ejected to give $Fe(CO)_5$. A 20-electron molecule is thus converted into an 18-electron one by ligand loss. For ($d^6$) $Cr(CO)_6$ the pair potential is negligibly small and no ligand is ejected. $Fe(CO)_5$ and $Cr(CO)_6$ are both stable molecules. The foot of the second peak of Figure 1a occurs at the filled d shell. A molecule with this electronic configuration is $SF_6$ ($SeF_6$), a stable octahedral species. With two extra electrons, the pair potential is repulsive and the hypothetical molecule $IF_6^-$ loses a ligand to give stable square pyramidal $IF_5$.[6]

Similar considerations apply to the pair potential (Figures 1b,c) calculated for two L atoms in the molecules $M_2L_{10}$ and $M_3L_{12}$. The d electronic configuration corresponding to the foot of the first peak is $d^7$ and $d^8$ per metal atom respectively, appropriate for the stable isoelectronic molecules $Mn_2(CO)_{10}$ and $Fe_3(CO)_{12}$. The electronic configuration at the foot of the second peak in Figure 1b is for an atom with a filled d-shell, plus a pair of central atom s/p electrons per molecule, an electron count appropriate for the species $S_2F_{10}$. The extra pair of electrons is associated with the S–S bond. For $M_3L_{12}$ the foot of the large peak at 12 electrons corresponds to the filling of all three M–M bonding orbitals. The small peak at 11.33 electrons represents the Jahn–Teller instability associated with the half-filling of the e′ orbitals of this set. The result we get from here is that the pair potential is small as long as we do not put the $(n + 1)$th pair in an orbital which is separated by a large gap from that holding the $n$th pair or half-fill degenerate levels. This represents therefore the rule that stable geometries occur in general with large HOMO–LUMO gaps.

In all of these molecular examples, the location of the peaks in a plot of pair potential versus electron count delineate those areas where traditional electron-counting considerations predict that species with the given stoichiometry are unlikely to exist. Elsewhere, we describe[7] other aspects of this new molecular parameter. Another set of calculations for the square-planar geometry shows stability for 16 electrons; one for a $B_6H_6$ cluster, stability for seven skeletal electron pairs. Molecules with less than the magic number of electrons are expected to be stable *with respect to ligand loss*. Thus both ($d^6$) $Cr(CO)_6$ and ($d^5$) $V(CO)_6$ are known. The pair potential arguments make no statement as to stability with respect to ligand gain for these molecules.

As the number of metal atoms increases the foot of the d-region peak moves to a higher electron count, $d^6$ for $ML_6$, $d^7$ for $M_2L_{10}$, and $d^8$ for $M_3L_{12}$. Also the amplitude of the potential decreases with the number of metal atoms.

The form of the pair potential plot for two L atoms adsorbed on a (100) surface of a fcc metal (Figures 1d and 2b) is then readily appreciated. The foot of the peak in the pair potential has moved to around $d^{9.2}$ and its amplitude is now below the metal–ligand bond energy. The result for the hypothetical pattern chosen here (Figure 2) tells us that there are no repulsive forces between second nearest neighbors within a 1 × 1 pattern of a fcc metal (100) surface up to $d^{10}$ but that repulsion occurs after $d^{10}$. Thus the surface analogue of the *molecular* effective atomic number rule controls the magnitude of the adatom–adatom pair potentials that set the form of the adsorption patterns and phase diagram for adsorption. There is no fierce electronic destabilization of a surface structure that contains "too many" adsorbed L units as there is in molecules, although the usual steric constraints will apply.

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[5] For all calculations, the extended Hückel method was used. For the molecular case, the usual Cr parameters and for the tight-binding computatation of a five-layer slab of a fcc metal (both sides covered with hydrogen atoms in on-top position) the usual Ni–metal parameters were used. All M–H and M–M distances were fixed to 1.8 and 2.49 Å, respectively.

[6] With two extra electrons, $XeF_6$, though stable as a six-coordinate molecule, is not octahedral.

[7] Burdett, J. K.; Fässler, T. F. Submitted for publication.

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## *d,l*- and *meso*-Bis(α-mercaptobenzyl)dimethylsilane: New Hindered Bidentate Ligands and a Novel Binuclear Molybdenum Complex Formed Therefrom

Silicon has been shown to be a useful structural element in thiolate ligands by allowing regulation of steric hindrance and solubility in complexes involving silylated methanethiols,[1] benzenethiols,[2] and pyridine-2-thiols[3] and by functioning as a con-

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[1] Block, E.; Aslam, M. *Tetrahedron Lett.* **1985**, *26*, 2259. Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Siegel, G. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1674. Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1985**, *107*, 6729. Tank, K.; Aslam, M.; Block, E.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 488. Koo, B.-K.; Block, E.; Liu, S.; Zubieta, J. *Polyhedron* **1988**, *7*, 1397.