$Ph_4P_2N_4S_2Me_2$ has been prepared from $Me_2S(NH)_2$ via a three-step process involving the use of the explosive reagent $Me_2S(NBr)_2$.[12]

In order to confirm the cyclic structure of the sulphur-containing products, an X-ray structural analysis of **2a** was carried out.[13] The molecular geometry and atomic numbering scheme are illustrated in Figure 1. The molecule is an eight-membered chair with the sulfur atoms displaced by 0.938 (5) Å on either side of the least-squares plane through $P_2N_4$. The exocyclic phenyl groups attached to the sulfur atoms occupy axial position with respect to their NSN planes [the angle between the S–C bond and NSN plane is 72.5 (3)°] but equatorial positions with respect to the $P_2N_4$ plane [the angle between the S–C bond and $P_2N_4$ plane is 11.8 (2) Å]. Similar ring conformations have been observed for 1,5-$Ph_4P_2N_4S_2Br_2$[14] and 1,5-$Ph_4P_2N_4Se_2Me_2$.[10] The S–N and P–N bond lengths in **2a** are equal within experimental error, and the average values are 1.622 (3) and 1.617 (4) Å, respectively, compared to 1.527 (6) and 1.621 (8) Å for the corresponding bonds in 1,5-$Ph_4P_2N_4S_2Br_2$.[14b] Thus, the replacement of Br by a Ph group results in a substantial lengthening of the S–N bond.

In view of the ready accessibility of both main-group and transition-metal reagents of the type $AN(SiMe_3)_2$,[15] the application of the organosulfur/selenium methodology represented by eq 2 is potentially capable of extension to a range of nitrogen-containing heterocycles wider than those from the condensation reaction (eq 1). The mild reaction conditions and the fact that the diaryl dichalcogenides can be recycled (after reaction with $SO_2Cl_2$) are attractive features of the new route to inorganic heterocycles exemplified by eq 3. The formation of eight-membered rings is in marked contrast to the reaction of $PhCN_2(SiMe_3)_3$ with 3 equiv of PhECl (E = S, Se), which produces the intensely colored azo compounds *trans*-PhENC(Ph)N=NC(Ph)NEPh[16a] via the resonance-stabilized radicals $PhC(NEPh)_2^{\bullet}$.[16b] The mechanistic implications of eq 3 are under investigation.

**Acknowledgment.** Financial support from the NSERC (Canada) is gratefully acknowledged.

**Supplementary Material Available:** Tables listing crystallographic parameters, atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances, bond angles, and torsion angles (7 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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(13) Colorless crystals of **2a** were obtained by recrystallization from $CHCl_3$–pentane. Crystal data: $C_{36}H_{30}N_4P_2S_2$, **2a**, $M = 644.73$, monoclinic, $P2_1/n$, at 295 K, $a = 10.563$ (2) Å, $b = 11.534$ (1) Å, $c = 13.031$ (3) Å, $\beta = 92.941$ (9)°, $V = 1585.5$ (5) Å$^3$, $Z = 2$, $D_c = 1.350$ g cm$^{-3}$, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0.71073$ Å, $\mu = 2.9$ cm$^{-1}$, $F(000) = 672$. Intensity data were collected on an Enraf-Nonius CAD-4F diffractometer operating in the $\omega-2\theta$ mode and interfaced to a Microvax 2000 computer. Crystal dimensions were 0.13 × 0.13 × 0.38 mm. The crystal structure was solved by standard Patterson methods and subsequent partial structure expansion and difference Fourier techniques. Anisotropic full-matrix least-squares refinement with 1873 observed reflections ($I \geq 2.5\sigma(I)$) (number of unique reflections 3105) and 259 parameters converged at $R_F = 0.057$.

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# Bis(phenylimido) Complexes of Niobium and Tantalum Prepared by α-Hydrogen Abstraction Reactions

Transition-metal organoimido complexes[1] are involved in a number of industrial processes and synthetic methodologies in which the imido moiety is transferred to an organic substrate,[2] such as the ammoxidation of propylene[3] and the amination[4] and aziridination[5] of olefins. Imido ligands have also proven useful as ancillary groups in olefin and acetylene metathesis,[6] alkane activation,[7] and ring-opening metathesis polymerization[8] systems. Single metal sites coordinated by *more* than one imido ligand are presently restricted to the group 6–8 metals.[1] By analogy to the known bis(alkylidenes) $L_nM(=CHR)_2$ of niobium and tantalum,[9] we have sought to synthesize their related bis(imido) $L_nM(=NR)_2$ complexes. Herein, we demonstrate this analogy through the α-hydrogen abstraction preparation of bis(imides) of group 5 and verify a structural parallel to their bis(alkylidene) congeners.

Upon reaction of $Ta(NEt_2)_2Cl_3(OEt_2)$[10] with 2 equiv of LiNHAr in THF (room temperature, 36 h, Ar = 2,6-diisopropylphenyl), a yellow complex forms in high yield but is isolated only as an oily solid. By addition of pyridine to the THF reaction solution, yellow-orange crystals of compound **1** can be obtained in ca. 60% yield. The absence of a ν(N–H) mode in the IR spectrum of **1**, the lack of N*H* or ethyl resonances in its $^1$H NMR spectrum, and its elemental analysis all support the formulation of **1** as the bis(imido) complex $Ta(=NAr)_2Cl(py)_2$.[11] The analogous complex of niobium, orange $Nb(=NAr)_2Cl(py)_2$ (**2**), is prepared from $[Nb(NEt_2)_2Cl_3]_2$[10] by a parallel procedure. Examining solutions of the initial yellow compound (which has not yet been induced to crystallize) led us to formulate this species as the THF adduct $Ta(=NAr)_2Cl(THF)_2$. $^1$H and $^{13}$C NMR measurements of **1** and **2** reveal that each compound's phenylimido ligands lie in a molecular plane of symmetry and are equivalent, thereby requiring a $C_{2v}$ molecule. Thus, both imido ligands must be either situated in the equatorial plane of a TBP or occuping its axial sites, with the chloride ligand necessarily equatorial in either case (although fluxionality could lead to a $C_{2v}$ structure

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(11) Analytical data for $Ta(=NAr)_2Cl(py)_2$ (**1**) are as follows. $^1$H NMR ($C_6D_6$): δ 9.23 (m, 4 H, $H_o$, py), 7.24 (d, 4 H, $H_m$, NAr), 6.96 (t, 2 H, $H_p$, NAr), 6.65 (m, 2 H, $H_p$, py), 6.28 (m, 4 H, $H_m$, py), 3.74 (spt, 4 H, C*H*Me$_2$), 1.04 (d, 24 H, CH*Me*$_2$). $^{13}$C NMR ($C_6D_6$): δ 153.7 ($C_o$, py), 153.6 ($C_{ipso}$, NAr), 142.8 ($C_o$, NAr), 138.8 ($C_p$, py), 124.4, 122.3, and 121.9 ($C_m$ and $C_p$, NAr; $C_m$, py), 28.0 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for $C_{34}H_{44}ClN_4Ta$: C, 56.32; H, 6.12; N, 7.73. Found: C, 56.39; H, 6.15; N, 7.78. Complex **2** ($Nb(=NAr)_2Cl(py)_2$) exhibits similar spectroscopic data.

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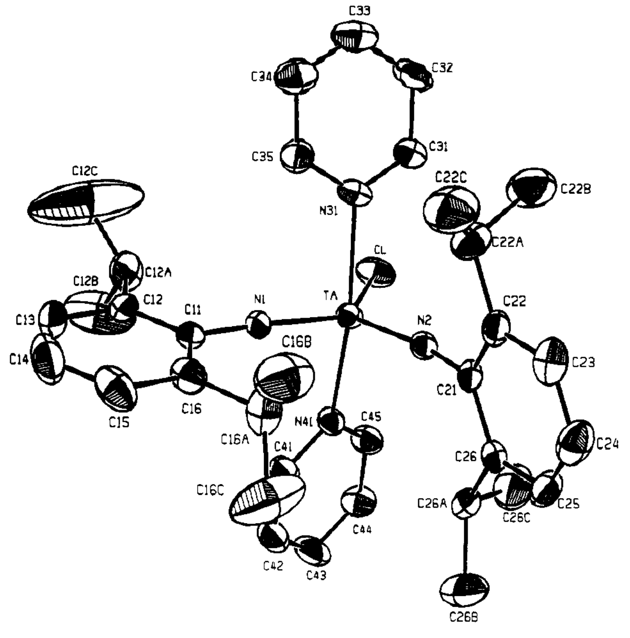

**Figure 1.** Molecular structure of Ta(=NAr)$_2$Cl(py)$_2$ (Ar = 2,6-diisopropylphenyl), with atoms shown as 30% probability ellipsoids.

on average). Proposed upon the precedence provided by d$^0$ TBP complexes with two $\pi$-donor ligands[12] and confirmed by X-ray crystallography, **1** is characterized by equatorial imido groups.

The molecular structure of Ta(=NAr)$_2$Cl(py)$_2$ (**1**) is presented in Figure 1.[13,14] Although the *average*[14] L$_{eq}$–Ta–L$_{eq}$ and L$_{ax}$–Ta–L$_{eq}$ angles are 120.0 (4) and 90.3 (5)°, respectively, it is clear that the pyridine ligands are bent away from the bulky diisopropylphenylimido ligands as N(31)–Ta–N(41) = 161.5 (2)°. Both tantalum–imido bonds are equivalent (Ta–N(1) = 1.812 (6) Å and Ta–N(2) = 1.809 (6) Å), and the Ta–N–C$_{ipso}$ angles are Ta–N(1)–C(11) = 170.9 (5)° and Ta–N(2)–C(21) = 165.4 (5)°. If both imides are donating their lone pair of electrons to the metal, **1** is *formally* an 18-electron complex, although it is clear that molecular orbital considerations do not always permit equating a linear imido ligand with a 4-electron donor (neutral sense).[15] One phenylimido ligand lies within the equatorial plane, while the other lies approximately perpendicular to that plane (dihedral angles 9.00 ± 0.29 and 82.89 ± 0.23°, respectively), which probably reflects the minimization of weak intramolecular or intermolecular packing forces,[15] since these ligands are equivalent in solution.

In more firmly establishing how compounds **1** and **2** might arise, we note the results of the following experiments. (i) When the reaction of Ta(NEt$_2$)$_2$Cl$_3$(OEt$_2$) with LiNHAr in THF-$d_8$ is monitored (over 41 h), 2 equiv of HNEt$_2$ are produced per 1 equiv of Ta(NEt$_2$)$_2$Cl$_3$(OEt$_2$) consumed ($^1$H NMR). (ii) Upon reaction of Ta(NEt$_2$)$_2$Cl$_3$(OEt$_2$) with LiNHAr in a weakly coordinating solvent (viz. Et$_2$O), a high yield of [Ta(=NAr)(NEt$_2$)(NHEt$_2$)Cl$_2$]$_2$ (**3**) is isolated.[16] Thus, the N*H* resonance at $\delta$ 2.37 (C$_6$D$_6$) in the $^1$H NMR spectrum of **3** (rather than near 8 ppm) requires an *amine* rather than *amido* proton environment.[17] Compound **3** is presumably dimeric (and six-coordinate) on the basis of related structures[18] and since **3** reacts with THF and with pyridine to afford monomeric Ta(=NAr)(NEt$_2$)Cl$_2$(THF)$_2$ (**4**) and Ta(=NAr)(NEt$_2$)Cl$_2$(py)$_2$ (**5**) quantitatively.[16,17] (iii) Nascent "Ta(=NAr)(NEt$_2$)(NHAr)Cl(py)$_2$" is accessible through either (a) the reaction of **5** with 1 equiv of LiNHAr or (b) the reaction of Ta(=NAr)(NHAr)Cl$_2$(py)$_2$ (**6**)[19] with 1 equiv of LiNEt$_2$ (both in THF) (Scheme I). However, the product isolated in high yield from *both* reactions is Ta(=NAr)$_2$Cl(py)$_2$ (**1**). On the basis of these experiments, **1** and **2** are proposed to arise through a two-step, $\alpha$-hydrogen abstraction sequence, formally analogous to the generation of the bis(neopentylidene) complex Ta(=CHCMe$_3$)$_2$Cl(PMe$_3$)$_2$ from the reaction of thermally unstable Ta(CH$_2$CMe$_3$)$_4$Cl with PMe$_3$ (Scheme I).[12a]

Complexes **1** and **2** provide useful entries into group 5 bis(imido) chemistry. Thus, the chloride ligand in Ta(=NAr)$_2$Cl(py)$_2$ (**1**) is readily metathesized in toluene/Et$_2$O by using LiDMP·THF (DMP = 2,6-dimethylphenoxide) to afford yellow needles of Ta(=NAr)$_2$(DMP)(py)$_2$ (**7**) in high yield.[20] Equivalent imido and pyridine ligands in **7** ($^1$H and $^{13}$C NMR) require that the phenoxide occupy an equatorial position of a TBP. Similarly, Nb(=NAr)$_2$Cl(py)$_2$ (**2**) reacts with NaCp in toluene/Et$_2$O to provide, after appropriate workup, red crystals of ($\eta^5$-C$_5$H$_5$)Nb(=NAr)$_2$(py) (**8**).[20]

The use of highly basic, dialkylamido ligands in a "sacrificial" role in the preparation of **1** and **2** suggests that sequential $\alpha$-hydrogen abstraction processes will prove useful in preparing other early-metal complexes containing more than one imido ligand.[21] Species such as ($\eta^5$-C$_5$H$_5$)Nb(=NAr)$_2$(py) (**8**), in which a bis(alkylidene) analogue ($\eta^5$-C$_5$H$_5$)Ta(=CHCMe$_3$)$_2$(PMe$_3$) is known,[12a] may prove central in testing the formal analogy between L$_n$M=CHR and L$_n$M=NR complexes. Of special interest are the differences that will arise in their structures and reactivities on the basis of the fact that [CHR]$^{2-}$ and [NR]$^{2-}$ ligands are *rigorously* isoelectronic (bonding to the metal with one $\sigma$ and one

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(13) A yellow-orange rectangular crystal of Ta(=NAr)$_2$Cl(py)$_2$ (**1**) (approximate dimensions 0.30 × 0.55 × 0.75 mm) crystallized (Et$_2$O, −30 °C) in the monoclinic space group $P2_1/c$ (No. 14) with $a$ = 14.514 (4) Å, $b$ = 13.487 (4) Å, $c$ = 17.466 (4) Å, $\beta$ = 101.32 (2)°, and $V$ = 3352.4 Å$^3$, with $Z$ = 4 ($\rho_{calcd}$ = 1.44 g cm$^{-3}$) and $\mu$ = 33.5 cm$^{-1}$. Data were collected on a Syntex P2$_1$ diffractometer at 23 ± 1 °C with Mo K$\alpha$ radiation and a graphite monochromator ($\lambda$ = 0.71073 Å). A total of 6522 reflections were collected in the $+h$, $+k$, $\pm l$ octants (5953 unique) in the range $2° \leq \theta \leq 50°$, with the 3598 reflections having $I \geq 3\sigma I$ used in the refinements. The structure was solved by the Patterson heavy-atom method and refined in full-matrix least squares for a final $R$ = 0.038 and $R_w$ = 0.042. The largest peak in the final difference Fourier map had a height of 0.96 e/Å. Lorentz and polarization corrections were applied to the data, and an empirical absorption correction based on a series of $\psi$ scans was applied to the data. Relative transmission coefficients ranged from 0.444 to 1.000 with an average value of 0.799.

(14) Selected interatomic distances (Å): Ta–Cl = 2.466 (2), Ta–N(1) = 1.812 (6), Ta–N(2) = 1.809 (6), Ta–N(31) = 2.270 (5), Ta–N(41) = 2.272 (5). Selected bond angles (deg): Cl–Ta–N(2) = 120.2 (2), Cl–Ta–N(31) = 80.7 (2), Cl–Ta–N(41) = 83.4 (2), N(1)–Ta–N(2) = 113.2 (3), N(1)–Ta–N(31) = 92.6 (2), N(1)–Ta–N(41) = 89.2 (2), N(2)–Ta–N(31) = 97.4 (2), N(2)–Ta–N(41) = 98.8 (2), N(31)–Ta–N(41) = 161.5 (2), Ta–N(1)–C(11) = 170.9 (5), Ta–N(2)–C(21) = 165.4, (5). The uncertainties in the *average* angles are calculated as $[\sum\sigma^2]^{1/2}$.

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(16) Analytical and spectroscopic data for compounds **1**–**8** are available as supplementary material.

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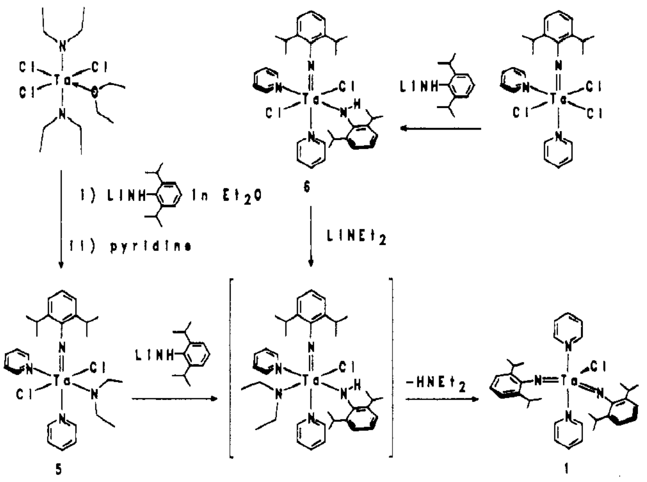
(18) Compare dimeric [Ta(=NCMe$_3$)(NHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$]$_2$: Jones, T. C.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1984**, 205.

(19) Ta(=NAr)(NHAr)Cl$_2$(py)$_2$ (**6**) is readily prepared from the reaction of Ta(=NAr)Cl$_3$(py)$_2$[17] with LiNHAr in THF solvent (Scheme I).

(20) Analytical data for Ta(=NAr)$_2$(DMP)(py)$_2$ (**7**) are as follows. $^1$H NMR (C$_6$D$_6$): $\delta$ 8.93 (m, 4 H, H$_o$, py), 7.30–6.80 (overlapping A$_2$B mult, 9 H, H$_{aryl}$, NAr and DMP), 6.58 (m, 2 H, H$_p$, py), 6.18 (m, 4 H, H$_m$, py), 3.84 (spt, 4 H, C*H*Me$_2$), 2.45 (s, 3 H, Me, DMP), 1.09 (d, 24 H, CH*Me*$_2$). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 154.4 (C$_{ipso}$, NAr), 152.5 (C$_o$, py), 142.0 (C$_o$, NAr), 138.7 (C$_p$, py), 129.0 (C$_m$, DMP), 126.7 (C$_o$, DMP), 124.5, 122.2, 120.4, and 118.9 (C$_m$ and C$_p$, NAr; C$_p$, DMP; C$_m$, py), 27.9 (*C*HMe$_2$), 24.0 (CH*Me*$_2$), 17.5 (Me, DMP). The C$_{ipso}$ resonance of the DMP ligand was not located. Anal. Calcd for C$_{42}$H$_{53}$N$_4$OTa: C, 62.21; H, 6.59; N, 6.91. Found: C, 62.07; H, 6.74; N, 6.63. Analytical data for ($\eta^5$-C$_5$H$_5$)Nb(=NAr)$_2$(py) (**8**) are as follows. $^1$H NMR (C$_6$D$_6$): $\delta$ 8.41 (m, 2 H, H$_o$, py), 7.16–6.89 (A$_2$B mult, 6 H, H$_{aryl}$, NAr), 6.65 (m, 1 H, H$_p$, py), 6.36 (s, 5 H, C$_5$H$_5$), 6.24 (m, 2 H, H$_m$, py), 3.79 (spt, 4 H, C*H*Me$_2$), 1.19 (br d, 24 H, CH*Me*$_2$). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 154.4 (C$_o$, py), 139.4 (C$_p$, py), 139.0 (C$_o$, NAr), 124.4 (C$_m$, py), 122.3 (C$_m$, NAr), 120.5 (C$_p$, NAr), 109.2 (C$_5$H$_5$), 28.1 (*C*HMe$_2$), 24.2 and 24.1 (CH*Me*$_2$). One resonance (C$_{ipso}$, NAr) was not located.

(21) Mono(imido) complexes of group 5 prepared by this method: Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965.

**Scheme I**



$\pi$ 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 $Ta(=NAr)_2Cl(py)_2$ (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.

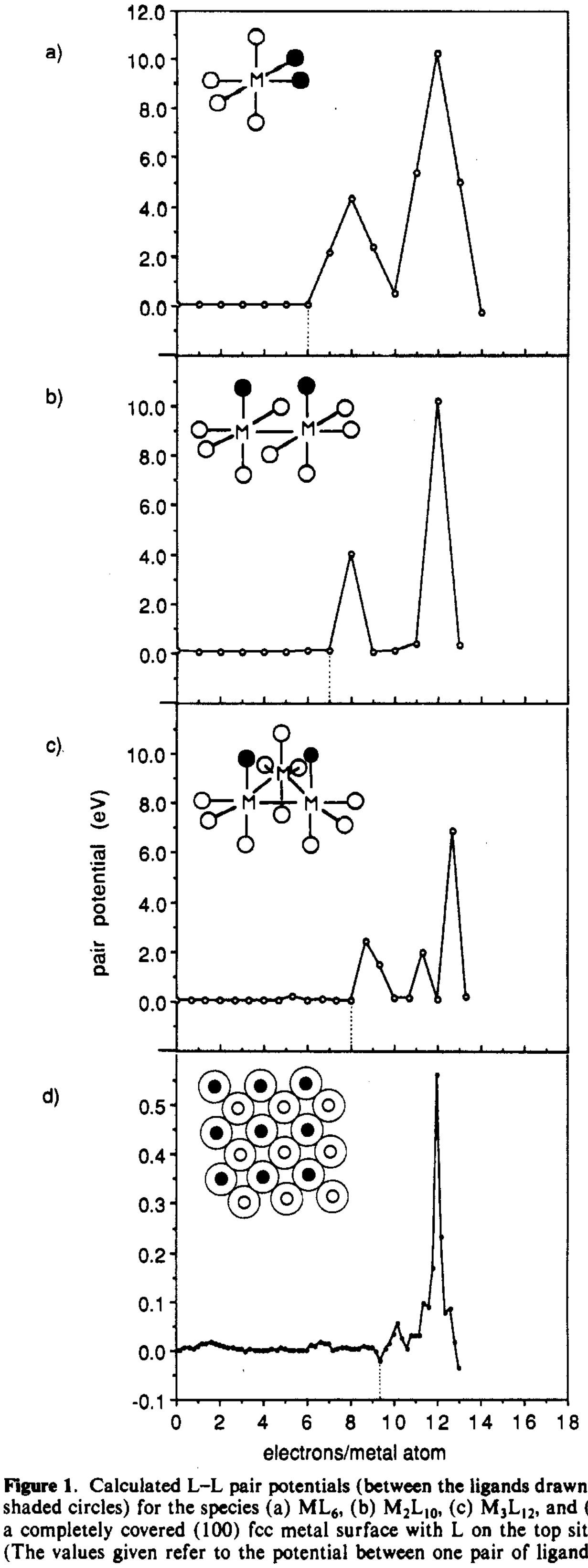

**Figure 1.** Calculated L–L pair potentials (between the ligands drawn as shaded circles) for the species (a) $ML_6$, (b) $M_2L_{10}$, (c) $M_3L_{12}$, and (d) a completely covered (100) fcc metal surface with L on the top sites. (The values given refer to the potential between one pair of ligands.)

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.

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