Electrophilic *vs.* Nucleophilic Reactivity in Complexes Containing Multiply-bonded (Alkylidene, Imido or Oxo) Ligands. A Conceptual Model

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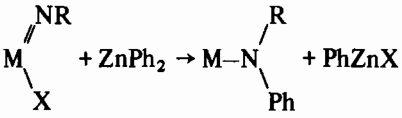
Received April 15, 1982

In some complexes, organoimido (NR) ligands [1] exhibit electrophilic reactivity as exemplified [2] by eqn. 1, while in other complexes the same ligands exhibit nucleophilic reactivity as exemplified [3] by eqn. 2. This dichotomy of reactivity modes appears to be characteristic of multiply-bonded (alkylidene [4], imido [5], oxo [6]) ligands in general. Recently we studied [7, 8] the reactivity of a series of d^0 organoimido complexes of the early transition metals. For the metals in this study, we found that there is a marked shift from nucleophilic to electrophilic reactivity as one proceeds upward and to the right across the periodic table.



$$\mathrm{M({=}NR)X + ZnPh_2 \rightarrow M{-}N(R)Ph + PhZnX}$$

(1)

$$\mathrm{M{=}NR + PhCHO \rightarrow M{=}O + PhCHNR} \qquad (2)$$

In order to assess the electronic factors underlying this effect, we have carried out *ab initio* calculations on appropriate model compounds using the extended muffin tin orbital technique [9]. The geometries utilized for the hypothetical methylimido complexes in Table I were based on X-ray crystal structures of related compounds [1, 7]. Once again, a simple trend was observed: The charge on the imido nitrogen atom was found to decrease on proceeding upward and to the right on the periodic table.

Table II summarizes ^{13}C nmr chemical shifts for a series of homologous d^0 tert-butylimido derivatives. Decreasing electron density on the imido nitrogen atom causes a downfield shift in the α-carbon resonance and an upfield shift in the β-carbon resonance. The difference [10] between these two chemical shifts, $\Delta = \delta(\alpha) - \delta(\beta)$, can thus be used as an experimental probe of electron density on the nitrogen atom. The complexes in this study were structurally diverse [7]; the series includes mono-, di-, and triimido compounds, bent and linear terminal imido ligands, symmetrically and unsymmetrically bridging imido ligands. Despite this structural diversity, a periodic trend analogous to those above is observed. For instance Δ increases along the series Hf < Ta < W < Re < Os and W < Mo < Cr.

TABLE I. Calculated Electronic Charge[a] on the Imido Nitrogen Atom to r = 0.66 Å.

Model Compound	Metal	Bond Distances (Å)[b]		
		M–N	M–O	Q
$(CH_3O)_3M(NCH_3)$	V	1.61	1.76	4.02
$(CH_3O)_3M(NCH_3)$	Nb	1.75	1.90	4.21
$(CH_3O)_3M(NCH_3)$	Ta	1.76	1.91	4.30
$(CH_3O)_2M(NCH_3)_2$	Cr	1.64	1.72	3.88
$(CH_3O)_2M(NCH_3)_2$	Mo	1.78	1.86	4.04
$(CH_3O)_2M(NCH_3)_2$	W	1.79	1.87	4.20

[a] Valence electrons only; the 1s core electrons are excluded.
[b] Other structural assumptions were N–C = 1.45 Å, O–C = 1.43 Å, C–H = 1.10 Å, <M–O–C = 150°. For group 5 complexes <M–N–C = 180°; for group 6 complexes < M–N–C = 155°.

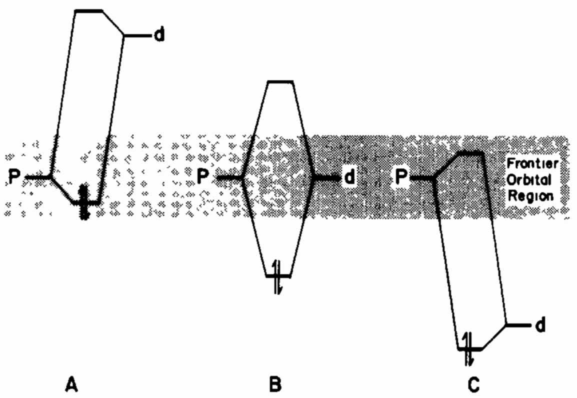


Fig. 1. Changes in ligand-p to metal-d π interaction as the relative energies of the atomic orbitals are changed.

In order to understand these results, we propose the extension of a conceptual model for alkylidene reactivity by Goddard, Hoffmann, and Jemmis [11]. Situation *A* in Fig. 1 serves as a model for π-bonding between a nitrogen p orbital and a diffuse (high energy) d orbital. Such a situation would be observed in an imido complex of, for instance, tantalum. The imido ligand will behave as a nucleophile since the high-lying HOMO is heavily nitrogen p in character. As one proceeds upward and to the

TABLE II. ^{13}C Chemical Shift Data for the *tert*-Butyl Groups in some *tert*-Butylimido Complexes.[a]

Complex[b]	Ref.	r(atomic)[c]	δ, C(α)	δ, C(β)	Δ[d]
$(Me_3SiO)_2Cr(NR)_2$	7e	1.30	77.79	31.32	46
$(Me_3SiO)_2CrO(NR)$	8	1.30	84.10	29.31	55
$(Me_3SiO)_3V(NR)$	7b	1.34	–[e]	30.74	–
$OOs(NR)_3$	5b	1.35	71.42	30.09	41
$O_2Os(NR)_2$	5b, 7f	1.35	75.13	29.64	46
$O_3Os(NR)$	5b, 7f	1.35	82.73	27.49	55
$(Me_3SiO)Re(NR)_3$	7c	1.37	67.33	31.91	35
$(Me_3SiO)_2Mo(NR)_2$	7e	1.39	68.76	32.24	37
$[Me_2Mo(\mu\text{-}NR)(NR)]_2$	2	1.39	67.26	32.17	35
$(Ph_3SiO)_2W(NR)_2$	7e	1.41	66.55	33.34	33
$(RO)_2W(NR)_2$	7e	1.41	65.58	33.79	32
$(RNH)_2W(NR)_2$	7e	1.41	66.09	33.86	32
$[Me_2W(\mu\text{-}NR)(NR)]_2$	7g	1.41	66.29	32.50[f]	34
$(Me_2N)_3Nb(NR)$	7a	1.46	68.63[f]	33.47	35
$(dtc)_3Nb(NR)$	7a	1.46	66.74	30.80	36
$[(Me_2N)_2Ti(\mu\text{-}NR)]_2$[g]	15, 7d	1.47	69.67	34.57	35
$(Me_2N)_3Ta(NR)$	7a	1.49	66.68	34.57	32
$(dtc)_3Ta(NR)$	7a	1.49	63.76	33.01	31
$[(Me_2N)_2Zr(\mu\text{-}NR)]_2$	7d	1.60	63.17	35.74	27
$[(Me_2N)_2Hf(\mu\text{-}NR)]_2$	7d	1.67	61.42	36.59	25

[a] In toluene-d_8 *vs.* internal standard TMS. All solutions 0.5 *M* except where otherwise noted. [b] Abbreviations are: dmc = dimethylcarbamate ligand; Ph = phenyl; R = *tert*-butyl, Me = methyl. [c] Atomic radius (Å) of the transition metals from ref. 13. [d] Chemical shift difference (ppm) for C(α) and C(β). [e] Not observed. [f] Resonance broadened. [g] Solution was 0.1 *M*

right among the early transition metals, the d orbitals become less diffuse as indicated by the decreasing radii of the free metal atoms [12]. The result, in a homologous series of imido compounds, is a systematic shift of electron density from the ligand to the metal resulting in a situation better represented as *B*. In *B*, the nucleophilic character of the imido ligand will be greatly diminished, the energy of the filled bonding orbital having fallen below the frontier orbital region. Significantly, the orbital occupancies summarized in Table I do *not* support the occurrence of the nd_M–$2p_N$ crossing which would be required to reach situation *C* [13]. However, this fact is not inconsistent with the observation of *formally* electrophilic reactions such as eqn. 1. Equation 1 probably involves initial replacement of the group X on the transition metal by the phenyl group, followed by a subsequent reductive elimination. Such a pathway is consistent with the mechanistic proposals of Sharpless [6] and also with our experimental observations on this system [2].

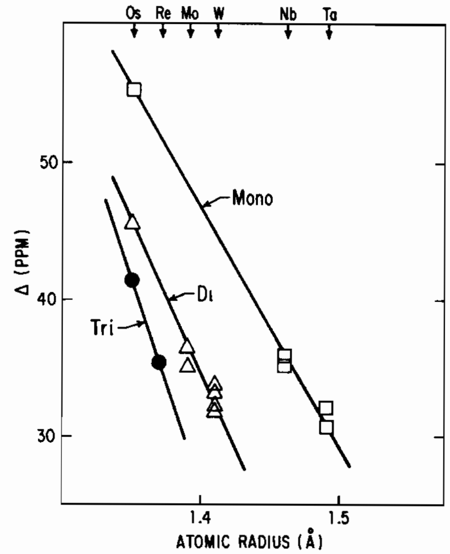


Fig. 2. Relationship between Δ-values and atomic radius for terminal imido derivatives of the 2nd and 3rd row transition metals.

Figure 2 shows the relationship between Δ and the atomic radius of the metal in the terminal imido derivatives of the 2nd and 3rd transition series. A simple correlation might be expected in Fig. 2 since, for such a limited series of compounds, the atomic radius serves as an indirect measure of the diffuseness of the d-orbitals. Instead, three separate correlations are observed, corresponding to the mono-, di-, and triimido complexes in this study. This demonstrates the importance of the metal–nitrogen bond order as an additional determinant of electron distribution in these complexes. The linear metal–nitrogen–carbon arrangement observed in monoimido compounds [1] indicates triple bond character in the metal–nitrogen bond, allowing effective nitrogen to metal π-donation. However, perturbation molecular orbital theory has been used to demonstrate that the total number of π-bonds in which a transition metal can participate is restricted; for tetrahedral coordination, the limiting π bond order is three [14]. Consequently, a lower bond order, a bent M–N–C arrangement* and less effective π-donation occurs in the di- and triimido species in Fig. 2. Consistent with this explanation, the electron density on the imido nitrogen atom is seen to increase along the series mono- $<$ di- $<$ triimido complexes.

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*Typically, in the solid state in diimido compounds one bent and one nearly linear imido ligand is observed [1]. However, these rapidly interconvert on the nmr time scale in solution.