The d^2-$M(NR)_2$ Fragment, High Valent and Low Valent Organometallic Equivalents, and an Unusual Mode of Ethylene Complexation

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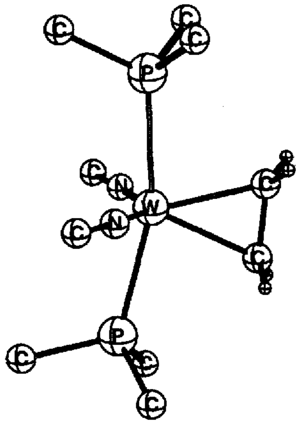
We report approximate molecular orbital calculations on models of the ethylene complex $W(NMes)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$ **1**. The ethylene unit in **1** is oriented perpendicular to the equatorial plane – an unusual orientation for trigonal bipyramidal $L_4M\text{-}(\eta^2\text{-}C_2H_4)$ complexes. In order to understand the bonding in **1**, the tungsten fragment $W(NR)_2L_2$ is discussed in some detail and we compare the "high valent" ethylene complex **1** and the "low valent" olefin complex $Fe(CO)_4(\eta^2\text{-}C_2H_4)$. An analysis of π-bonding shows that the metal nitrogen bond in the *cis*-$[M(NR)_2]$ unit is less than a triple bond, and the d^2-$[M(NR)L_2]$ fragment is more like a 16 than an 18 valence electron fragment. The nature of the occupied d-orbital explains the opening of the angle E–M–E in trigonal bipyramidal complexes d^2-*cis*-$M(E)_2L_3$. Both C_{2v} fragments d^2-$W(NR)_2L_2$ and d^8-$Fe(CO)_4$ have characteristic frontier orbitals, qualitatively similar to the frontier orbitals of CH_2. These orbitals guide the ethylene ligand into or out of the equatorial plane. The general analysis leads to the conclusion that d^n ($n > 0$) "high valent" complex fragments are actually better back-bonding donors for π-acidic ligands. For **1**, we detect also another minimum on the energy surface – the olefin ligand is now oriented parallel to the equatorial plane. This raises the fascinating possibilities of the existence of multiple conformational minima for some transition metal ethylene complexes.

Introduction

The impetus for this theoretical study is two-fold: first to understand the bonding in a recently synthesized olefin complex $W(NMes)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$[1] (**1**) and second, to set a theoretical foundation for comparing organoimido (NR) and cyclopentadienyl ($\eta^5\text{-}C_5R_5$) ligands.



1

The structure of **1** (only the *ipso* carbon atoms of the mesityl rings are shown) immediately impresses one with the fact that the olefin ligand is *not* oriented in the exquatorial plane of the approximate trigonal bipyramid around tungsten. In five-coordinate $L_4M(\eta^2\text{-}C_2H_4)$ complexes, exemplified by $Fe(CO)_4(\eta^2\text{-}C_2H_4)$, the ethylene C–C axis lies in the equatorial plane. And that geometry is preferred by a substantial energy[2]. So why does this imidotungsten system deviate from the norm?

The coordination geometry of **1** actually may be described as a distorted trigonal bipyramid or a distorted square pyramid. The tungsten atom is coordinated in what we have called the equatorial plane by two imido ligands and the ethylene unit and along the trigonal bipyramid axis by two phosphine ligands. The N–W–N angle is approximately 140° (still another unusual feature), the W–N distances are 1.82 Å and 1.83 Å, respectively. The phosphine ligands are bent away from the ethylene unit, to give a P–W–P angle of approximately 164°. The C–C axis of the ethylene ligand is parallel to the W–P axis of **1**; the C–C distance is 1.42 Å.

The second reason for our interest in this compound is less specific (yet important), and turns away from the ethylene to the imido ligands. Organoimido [NR] and cyclopentadienyl $[\eta^5\text{-}C_5R_5]$ ligands show certain parallels[3,4]. If both are considered as anionic ligands, $[NR]^{2-}$ and $[\eta^5\text{-}C_5R_5]^-$, they can, in principle, make six electrons available for bonding to a metal cation[3,5]. These electrons in each case are available for metal-ligand bonding in one orbital of σ- and two of π-symmetry. If $[C_5R_5]^-$ binds to a d^n metal center (e.g. Ta^{5+}) and the dianion $[NR]^{2-}$ to an isoelectronic d^n M′ center from the following group in the periodic table (e.g. W^{6+}), two units with the same electron count and comparable valence orbitals result (e.g. $[(\eta^5\text{-}C_5R_5)Ta]^{4+}$ and $[W(NR)]^{4+}$). Schrock et al.[6] and Gibson et al.[7] have already pointed out theoretical and experimental parallels in the chemistry of complexes with the entities $[M(NR)_2]$

(M = Mo, W), $[(\eta^5\text{-}C_5R_5)M''(NR)]$ (M' = Nb, Ta) and $[(\eta^5\text{-}C_5R_5)_2M'']$ (M'' = Zr, Hf).

One incentive for explaining the chemistry of group 6 diimido complexes is due to this analogy, driven by the large impact of group 4 metallocenes in catalysis and synthetic organic chemistry. It is also worthwhile to explore the differences in the chemistry of these complex fragments in order to investigate reaction pathways in imido chemistry not known or not possible for group 4 metallocenes. Could imido complexes engage in chemistry not possible with a sterically demanding (and, in the size of its cone angles, limited) cyclopentadienyl ligand? One of us[1] as well as others[6,8] have synthesized and characterized trigonal bipyramidal compounds of the type $[M(NR)_2L_2L']$ (M = Mo, W; L = PR'_3, L' = PR'_3, $\eta^2\text{-}C_2H_4$, $\eta^2\text{-}C_2H_2$, $\eta^2\text{-}C_2Me_2$, etc.) which have no analogues in group 4 metallocene chemistry.

More generally, we are interested in the range and limitations of the imido-cyclopentadienyl analogy. One problem becomes apparent in the context of molecule **1**. If we count the NR ligand as 2^-, we are led to W as 4^+, d^2 in $W(NR)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$. And if each imido group is a 6-electron donor, the $W(NR)_2(PMe_3)_2$ fragment alone has 18 electrons, and does not need the olefin ligand. However, this problem is not new; it has been noted in the literature that the *cis*-$M(NR)_2$ group is not capable of forming two full M–N triple bonds[9]. The question remains: what is the nature of the bonding in this compound?

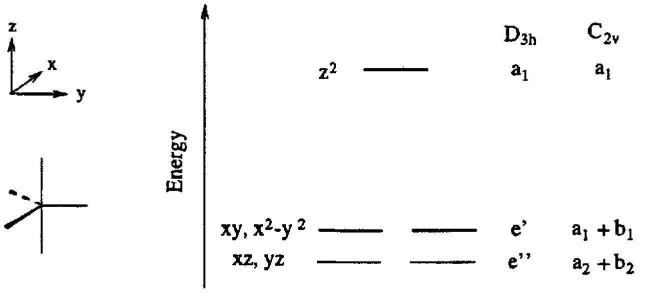
Stimulated by this variety of motives, we have undertaken approximate molecular orbital calculations of the extended Hückel type[10] in order to understand the bonding in olefin complex **1**. Details of the calculation are provided in the Experimental. The distances available from the X-ray structure determination of **1** were averaged and used in our calculations; they are listed in the Experimental. We symmetrized the molecule to a C_{2v} structure and replaced the mesityl groups attached to the imido nitrogen by methyl groups. At the outset we started with an idealized trigonal bipyramidal molecule with all equatorial L–M–L angles being 120° and axial L–M–L angles being 180°. This geometrical restriction was then relaxed. As a first step we investigated the $W(NMe)_2(PMe_3)_2$ fragment in some detail. Then we studied the ethylene complexes of this fragment and of the $Fe(CO)_4$ unit and compared both fragments in their binding to ethylene.

The Tungsten Fragment

Knowledge of the bonding capability of the $(NR)_2$ unit to the metal center is essential for an understanding of the electronic structure of **1**, as well as of some related complexes. To make our computations on this issue more transparent, we tentatively replace the two phosphine ligands by H^-. Furthermore, we saturate the free coordination site of the four-coordinate $[W(NMe)_2H_2]$ fragment by another H^- ligand, and remove two electrons, so as to have no W–N π antibonding orbitals filled. The model at this point is d^0-$[W(NMe)_2H_3]^-$. In time we will remove the H^- and study the interaction of the fragment with ethylene.

For a trigonal bipyramidal system with five equivalent σ-donors, L, D_{3h}-ML_5, the well-known crystal field splitting[11] is e'' (d_{xz}, d_{yz}) below e' ($d_{x^2-y^2}$, d_{xy}) below a_1 (d_{z^2}), Scheme 1. The group theoretical labels appropriate to the reduced symmetry of $W(NMe)_2H_3$ are also indicated.

Scheme 1



Now imagine that two of the equatorial ligands also bear π orbitals, formally filled ones for $[NR]^{2-}$. Then one would expect π bonding with the NR lone pairs of appropriate symmetry stabilized and the corresponding d orbitals pushed up in energy. We do not show the full interaction diagram for $[W(NMe)_2H_3]^-$ in Figure 1, just the resulting frontier orbitals. The π bonding orbitals (mainly N 2p in character) are shown in Scheme 2.

Scheme 2

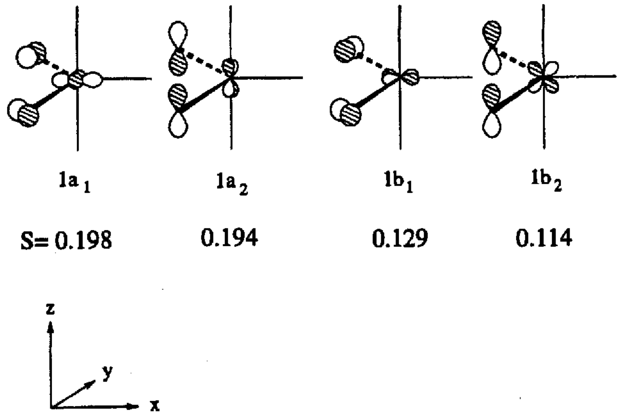
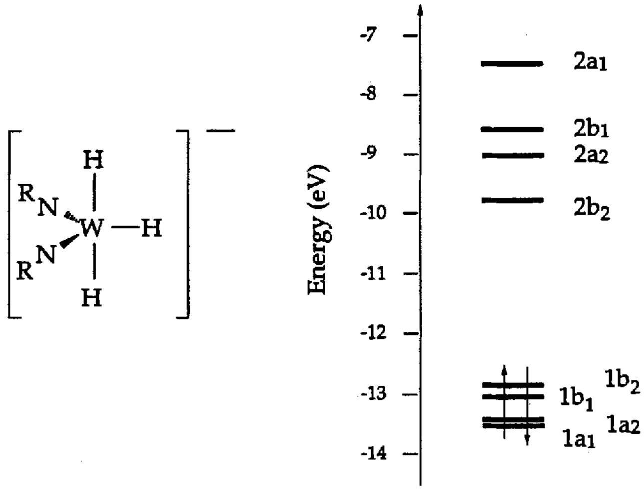


Figure 1. Π bonding and antibonding orbitals in $[W(NMe)_2H_3]^-$



The π bonds are not all equal. If we simply calculate fragment *overlaps* between various metal d orbitals and the corresponding N 2p combination, we get the overlap values shown below the orbital drawings in Scheme 2. The N lone pair–W $d_{x^2-y^2}$ and –W d_{yz} overlap are quite large, the other ones are smaller. It is clear that the π bonds that result from these overlaps will be quite unequal.

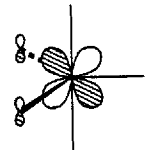
But how to define a π bond order in this system? One possibility – this is only a tentative suggestion – is to look at the *overlap population* contributions of each π interaction separately. Overlap populations shown are for one W–N bond of the two in the molecule:

$1a_1$	0.126
$1a_2$	0.118
$1b_1$	0.063
$1b_2$	0.035
total W–N	0.953

Notice that these *overlap populations* (the symptom) follow the *overlaps* (the cause) whose values were listed in Scheme 2. If we take the larger interactions ($1a_1$, $1a_2$) as roughly approximating a full π bond, we see that the $b_2(d_{xz})$-π-bond is particularly weak. As further support, the W–N overlap population due to π bonding of the hypothetical compounds with just *one* imido group ($[W(NMe)H_4]^{3-}$, trigonal bipyramidal, and $[W(NMe)H_5]^{2-}$, octahedral) is approximately 0.165.

The LUMO of the d^0 complex, $2b_2$, is a W–N π-antibonding orbital, the antibonding complement of the HOMO, and mainly W d_{xz} in character (see Scheme 3).

Scheme 3



$2b_2$

The calculated contribution to W–N overlap population for two electrons in this orbital is –0.084. For an electron count analogous to the tungsten fragment of **1**, we have to populate this MO with two electrons, leading to d^2-$[W(NMe)_2H_3]^{3-}$. This causes the W–N σ and π overlap population to decrease to 0.258 (π) and 0.869 (σ + π), respectively.

But to get back to our initial question: What kind of a bond do we have in **1**? It would be nice if the matter of defining the multiplicity of a bond were simple. But it isn't. Taking an overlap population of 0.126 as a rough standard for one W–N π-bonding orbital in the *cis*-$W(NR)_2$ system, the W–N π bond order might be thought of as being approximately 1 for each W–N bond in d^2-$[W(NMe)_2H_3]^{3-}$. Counting the imido ligand $[NR]^{2-}$ in the d^2-$[W(NMe)_2(PMe_3)_2]$ unit as a four electron donor (one σ and one – not two – π bonds to the central atom), we might then regard the resulting unit as a 16 VE fragment.

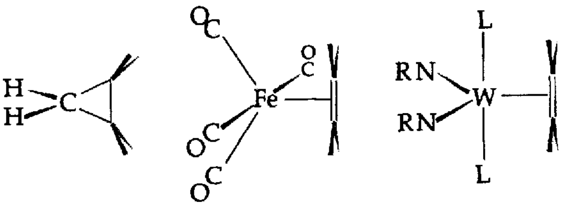
The $2b_2$ orbital, incidentally, is responsible for the opening of E–W–E angles observed in trigonal bipyramidal d^2-$M(E)_2L_3$ complexes (E = NR, O) containing a *cis*-ME_2 unit[7]. For the d^0 system we calculate a preference for an N–W–N angle of approximately 120°. The antibonding overlap in $2b_2$, occupied in d^2 compounds, decreases as the N–W–N angle opens, and indeed a Walsh diagram (varying the energy as a function of N–W–N angle) shows that the energy of $2b_2$ decreases with increasing N–W–N angle. The d^2 system optimizes at an N–W–N angle of approximately 163°. This is larger than the experimental value, but the distortion is certainly in the right direction. The structures of known similar complexes[12] of the type $M(E)_2L_3$ depend on the formal electron count for the central atom: d^0 complexes favor trigonal bipyramidal geometries, with E–M–E angles of 110°–120°, whereas d^2 compounds adopt geometries with E–M–E angles larger than 120°.

Ethylene Complexes Containing the $W(NR_2(PMe_3)_2$ and $Fe(CO)_4$ Unit – A Comparison of High-Valent and Low-Valent Complex Fragments

Turning to our model compound $W(NMe)_2(PMe_3)_2(\eta^2$-$C_2H_4)$, we wish to compare two trigonal bipyramidal fragments, one clearly, the other arguably a 16 VE unit. The first is the "low-valent" fragment $Fe(CO)_4$, and the other the "high valent" fragment of interest to us, $W(NMe)_2(PMe_3)_2$. One way to do this is to investigate idealized models for the complexation of both fragments with ethylene, in particular the influence of the complex fragment coordination on the ethylene ligand. Much theoretical work has already been done on ethylene complexes[2], so these form a useful stereoelectronic calibration.

It is instructive to preface our detailed analysis with some qualitative considerations emerging from the isolobal analogy. CH_2, $Fe(CO)_4$, $W(NR)_2(PMe_3)_2$ all form complexes with ethylene, shown in Scheme 4.

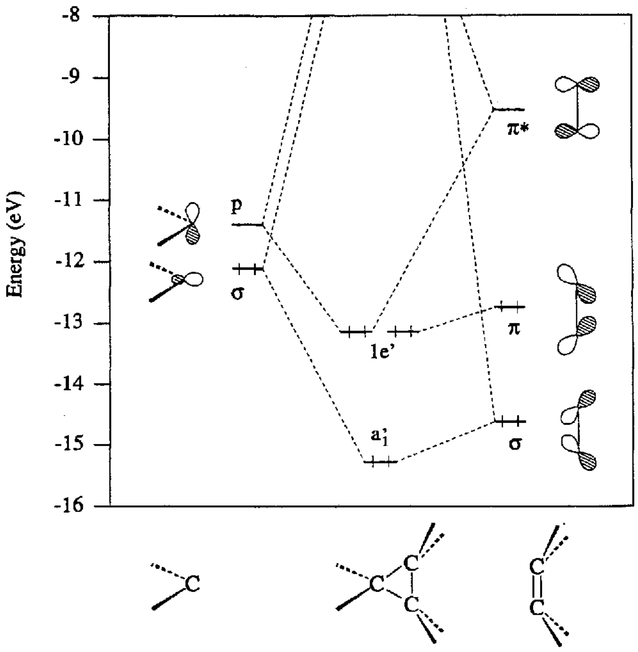
Scheme 4



The phrase "complex" is stretched a little when applied to cyclopropane, but the view of cyclopropane as an ethylene complex of methylene is a fruitful one, indeed is the beginning of a most productive view of orbital interaction. This is how A. D. Walsh viewed cyclopropane[13]; Figure 2 is the corresponding fragment molecular orbital diagram.

The isolobal analogy is a way of accounting for bonding similarities. So CH_2, $Fe(CO)_4$ and $W(NR)_2L_2$ use similar (not identical) orbitals in their interaction with ethylene. This similarity of each fragment – that each has a total of two electrons in a σ (a_1) and π (b_2) orbital capable of interaction with like orbitals in the ethylene – has been dis-

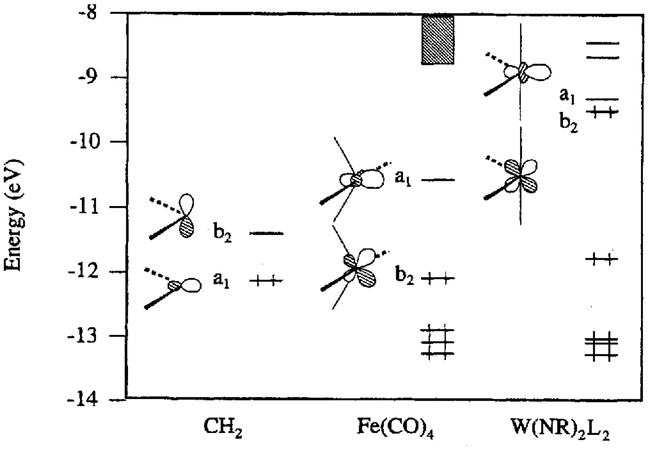
Figure 2. FMO diagram of cyclopropane



cussed previously for methylene and $Fe(CO)_4$[14]. But this viewpoint is less obvious for $W(NR)_2L_2$, so we will describe it in some detail here.

Note first of all that we chose in Scheme 4 a mode of representation that places the ethylene in the same "upright" geometry. The metal complex or organic fragment is then arranged in the position it assumes relative to a fixed ethylene in the preferred equilibrium structure. This leads to a rather unfamiliar geomerical perspective on $Fe(CO)_4$-(ethylene), but makes it easier to analyze the $W(NR)_2(PMe_3)_2$ complex. In this coordinate system, the frontier orbitals of each fragment are shown in Figure 3, with their computed energies.

Figure 3. Frontier orbitals of CH_2, $Fe(CO)_4$ and $W(NR)_2L_2$



In each fragment there are a_1 and b_2 frontier orbitals. The difference in the energetic ordering of these frontier orbitals (a_1 below or above b_2) has little consequence for the bonding capability of the fragments. The moment we interact them with another ligand fragment, the ordering of a_1 and b_2 becomes relatively unimportant, since both orbitals are strongly involved in bonding.

Note that in the $W(NR)_2L_2$ fragment there are also some other low-lying empty orbitals (of a_1 and b_1 symmetry). These also offer up some opportunities for bonding, and we will return to them below. But the heart of the isolobal analogy is in the a_1 and b_2 frontier orbital set.

Figure 4 shows the interaction of $Fe(CO)_4$ (right) and $W(NR)_2L$ (left) with an ethylene (in the center). To compare the bonding of the two complex fragments to the alkene ligand, we kept the ethylene unit planar, not allowing its hydrogen atoms to bend back. For free ethylene we chose the C–C distance used in the complex **1**.

The Dewar-Chatt-Duncanson bonding model[15] is a useful starting point for discussing any metal-olefin bonding. In the cases at hand, the high-lying occupied b_2 orbital of each complex fragment interacts with the ethylene π^*_{C-C} orbital, and the low lying vacant a_1 orbital mixes with π_{C-C}. The b_2 interaction, the back-donation, accounts for conformational preferences of most coordinated olefins. Within the coordinate system depicted in Figure 4, the metal component of the b_2 orbitals is in both cases d_{xz}, but note the different alignment of the two fragments mentioned above.

The $Fe(CO)_4$-ethylene interaction (Figure 4, right) is familiar. There is excellent mixing of the a_1 and b_2 orbitals of both fragments, resulting in substantial stabilization.

MO a_1 of the $W(NMe)_2(PMe_3)_2$ fragment, best described as W d_{x^2} in character, is pointing to the empty coordination site. This acceptor orbital indeed stabilizes the ethylene a_1 MO. We have included in the diagram the primarily N lone pair π bonding $1b_2$ orbital (discussed above for $[W(NMe)_2H_3]^{3-}$), because it also enters the bonding. The high lying π* ethylene orbital interacts effectively with both $2b_2$ and $1b_2$ in a three orbital interaction to form the $W-C_2H_4$ π bond, leaving $2b_2$ as the HOMO of the complex. $2b_2$ is mainly W d_{xz} in character, W–C bonding and W–N π antibonding. This MO, drawn another way in Scheme 5[16], is responsible for the alignment of the C_2H_4 unit perpendicular to the equatorial plane spanned by the central atom and the two imido nitrogen atoms. The same $2b_2$ orbital is also responsible for the opening of the N–W–N angle observed in the X-ray structure determination of $W(NMes)_2(PMe_3)_2(\eta^2-C_2H_4)$, for reasons discussed above.

Scheme 5

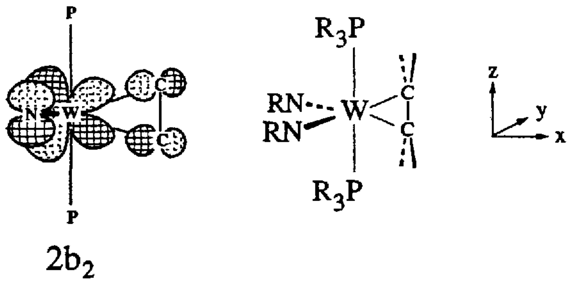
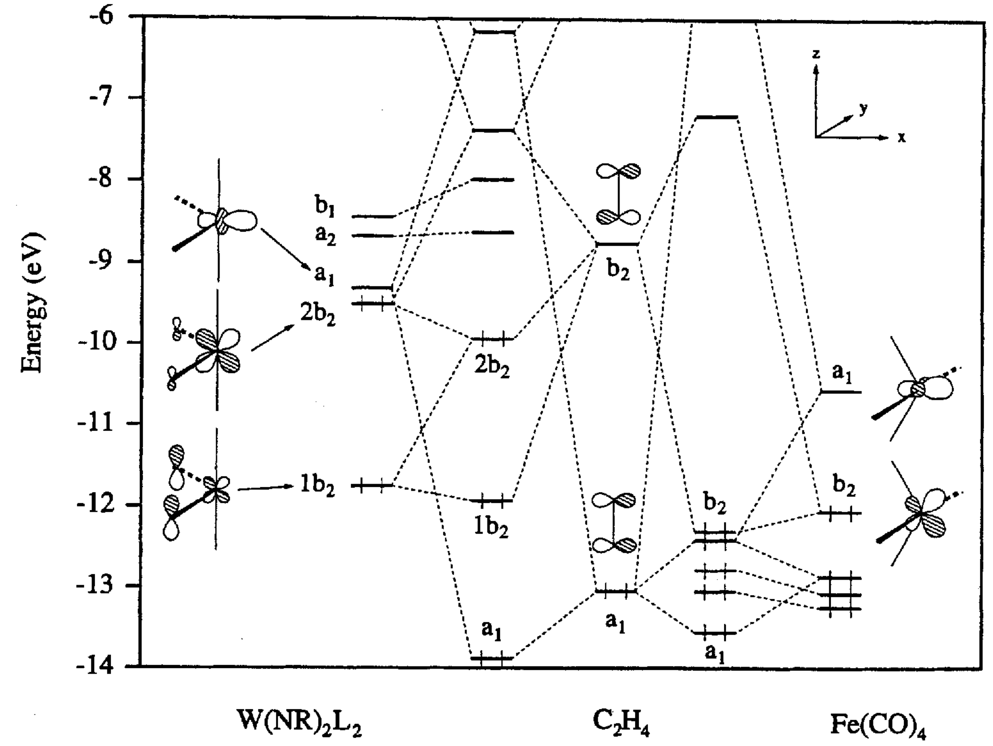


Figure 4. Interaction diagram of $Fe(CO)_4$ (right) and $W(NR)_2L_2$ (left) with an ethylene ligand



The direction of net charge transfer in metal-olefin bonding, as well as relative magnitude of the different contributions (σ or π) to the metal ethylene bond differs from case to case, and is difficult to assess quantitatively. Electron transfer from the olefin to the metal center is always accompanied by reverse charge transfer from the metal to the olefin. Calculated values of C−C overlap populations, fragment charges, atomic charges of the ethylene carbon atom, atomic populations of the C p_x orbitals and the occupations of the ethylene π and π* orbitals for free and complexed ethylene are given in Table 1.

Table 1. Differences in the bonding of $Fe(CO)_4$ ([Fe]) and $W(NMe)_2(PMe_3)_2$ ([W]) fragments to ethylene

	C_2H_4	$[Fe]\text{-}C_2H_4$	$[W]\text{-}C_2H_4$
C-C overlap population	1.218	1.034	0.996
C_2H_4 total charge	0.000	-0.039	-0.365
charge on $C_{ethylene}$	-0.090	-0.086	-0.292
atomic orbital pop. Cp_x	1.000	1.011	1.205
occupation of π	2.000	1.625	1.725
occupation of π*	0.000	0.397	0.686

The ethylene ligand coordinated to $Fe(CO)_4$ becomes slightly negatively charged, due to good back-donation into the π^*_{C-C} orbital; its population is 0.397 electrons. The donor capability of the ethylene ligand to the complex fragment may be measured by the depletion of the π orbital from 2.00 to 1.63 electrons. The $Fe(CO)_4$ unit is a somewhat better σ acceptor than $W(NMe)_2(PMe_3)_2$: the π_{C-C} electron density decreases less for $W(NMe)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$.

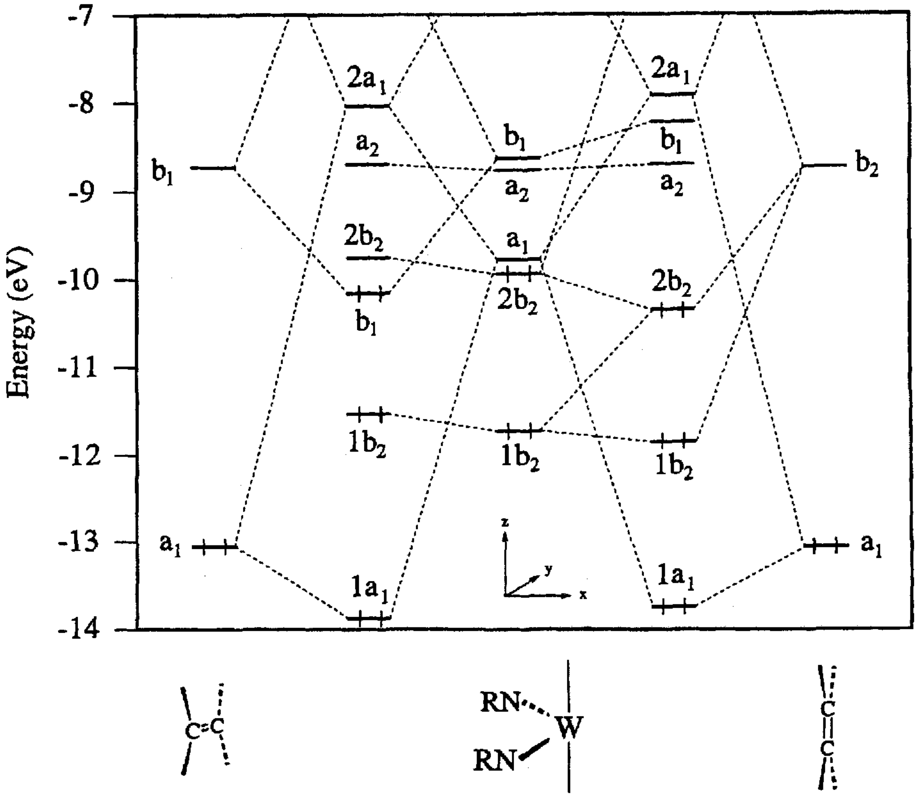
Despite its higher formal oxidation state, the $W(NMe)_2(PMe_3)_2$ unit is a much better net donor than $Fe(CO)_4$. This is due to the high-lying b_2 donor orbital; π^*_{C-C} is populated in the tungsten complex by 0.686 electrons, the net charge of the ethylene ligand being −0.365, compared to −0.039 in $Fe(CO)_4(\eta^2\text{-}C_2H_4)$. Deformations toward better geometries (for example if we allow the ethylene hydrogen atoms to "bend back") did not affect the general trends. Why is the $W(NMe)_2(PMe_3)_2$ fragment a much better π donor than the $Fe(CO)_4$? We think it is mainly that the occupied orbital $2b_2$ of the tungsten fragment lies so high in energy. In general, d orbitals of tungsten are higher in energy than Fe d orbitals. In addition, $2b_2$ is pushed up in energy due to its W−N π antibonding character (vide supra).

An Alternative Geometry for the Ethylene Complex of $W(NR)_2(PMe_3)_2$

The isolobal analogy is an expression of a similarity, not a one-to-one mapping. This is its strength, and its weakness too. So CH_2, $Fe(CO)_4$ and $W(NR)_2(PMe_3)_2$ are isolobal because they have two electrons in a pair of a_1 and b_2 frontier orbitals. However, for the $W(NR)_2L_2$ fragment b_2 is not the only relatively low lying d orbital. Figure 4 shows a_2 and b_1 orbitals near −8.5 eV: These are also apparent in the $W(NR)_2H_3$ model in Figure 1.

We want to explore here the possibility that the b_1 frontier orbital, not that much higher in energy than b_2 in $W(NR)_2L_2$, is used in bonding to the ethylene. We compare the two interaction diagrams in Figure 5, one utilizing $2b_2$, the other b_1 for back-bonding. To do so, we have a choice: either to keep the ethylene fixed and rotate the ML_n frag-

Figure 5. Interaction diagrams of two conformers of $W(NR)_2L_2(\eta^2\text{-}C_2H_4)$



ment, or the reverse. We choose the latter, freezing the $W(NR)_2L_2$ fragment.

The right side of Figure 5 shows the interaction diagram for the model $W(NMe)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$ resembling the geometry found for **1**, but now taking an idealized trigonal bipyramidal geometry at the tungsten atom. The C−C axis of the planar ethylene ligand is perpendicular to the "equatorial" N−W−N plane, parallel to the P−W−P axis. The interaction diagram for the alternative geometry – the ethylene ligand now perpendicular to the P−W−P axis of the molecule and in the N−W−N plane – is depicted on the left side of Figure 5. In this geometry the b_1 orbital of the $W(NR)_2L_2$ fragment is used for back-bonding to the alkene ligand, and becomes stabilized due to its good overlap with the alkene π^*_{CC} orbital.

A Walsh diagram for the rotation of the ethylene ligand around the $W-C_{2center}$ axis (left) and the relative energy required for this process (right) is shown in Figure 6. We used for this calculation the complex fragment geometry (α = 140°, β = 196°, see below) as found in **1**.

Note the barrier to ethylene rotation and one minimum. For our model of **1**, we calculate a barrier for the rotation of the ethylene – or the $W(NMe)_2(PMe_3)_2$ fragment! – of 0.64 eV or 14.8 kcal/mol. The barrier is the consequence of an avoided crossing of the orbitals of b symmetry in C_2, labeled in Figure 6 in C_{2v} symmetry as $2b_2$ (HOMO of the complex) and $1b_1$. Orbital $1b_2$ is only slightly affected.

Actually, this is an extremely rare and interesting case where in a trigonal bipyramidal ML_4(ethylene) complex there may be a double minimum potential to olefin rotation. The energetics of the system $W(NMe)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$ as a function of the angles N−W−N (α) and P−W−P (β) are summarized in Figure 7 and Table 2. Shown are the energies of two different possible geometries of our model, where the C_2 axis of the ethylene ligand is perpendicular (on the left) or parallel (on the right) to the N−W−N plane. The point resembling the experimentally observed structure (α = 140°; β = 196°) **II** is marked in Figure 7.

For model **I** (α = 140°, β = 180°) – the model we used in our calculations previously – the conformation in which the ethylene ligand is parallel to the N−W−N plane is actually favored in energy. This changes when we bend the phosphine ligands back towards the imido groups, for then the molecule favors the structure observed. However, if α is made smaller, we compute an energy minimum **IV** for a rotamer in which the C−C vector is lying in the N−W−N plane. Conceivably one could control α or β by multidendate ligand geometries, and so make the ethylene assume one geometry or another.

Concluding Discussion: The Isolobal Analogy and M−CO vs. M−NR Bonding

Both C_{2v} fragments, $d^2\text{-}W(NMe)_2(PMe_3)_2$ and $d^8\text{-}Fe(CO)_4$, have characteristic frontier orbitals: an occupied a_1, σ-type orbital and a vacant b_2, π-type orbital. Both are qualitatively similar to the frontier orbitals of CH_2, and thus these fragments may be regarded as isolobal to CH_2.

Figure 6. Walsh diagram for the rotation of the ethylene ligand in $W(NR)_2L_2(\eta^2\text{-}C_2H_4)$

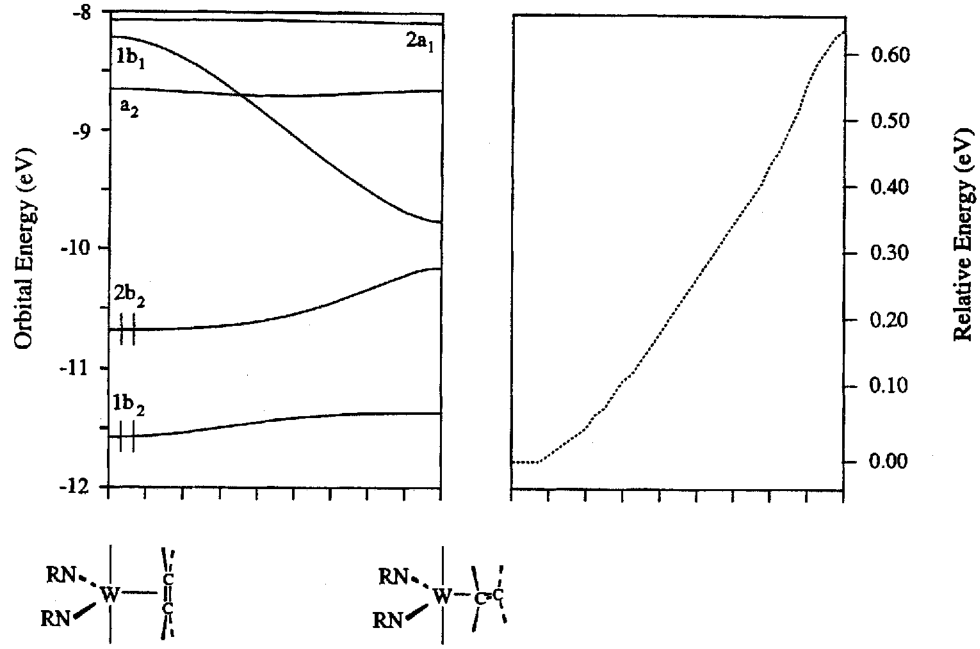
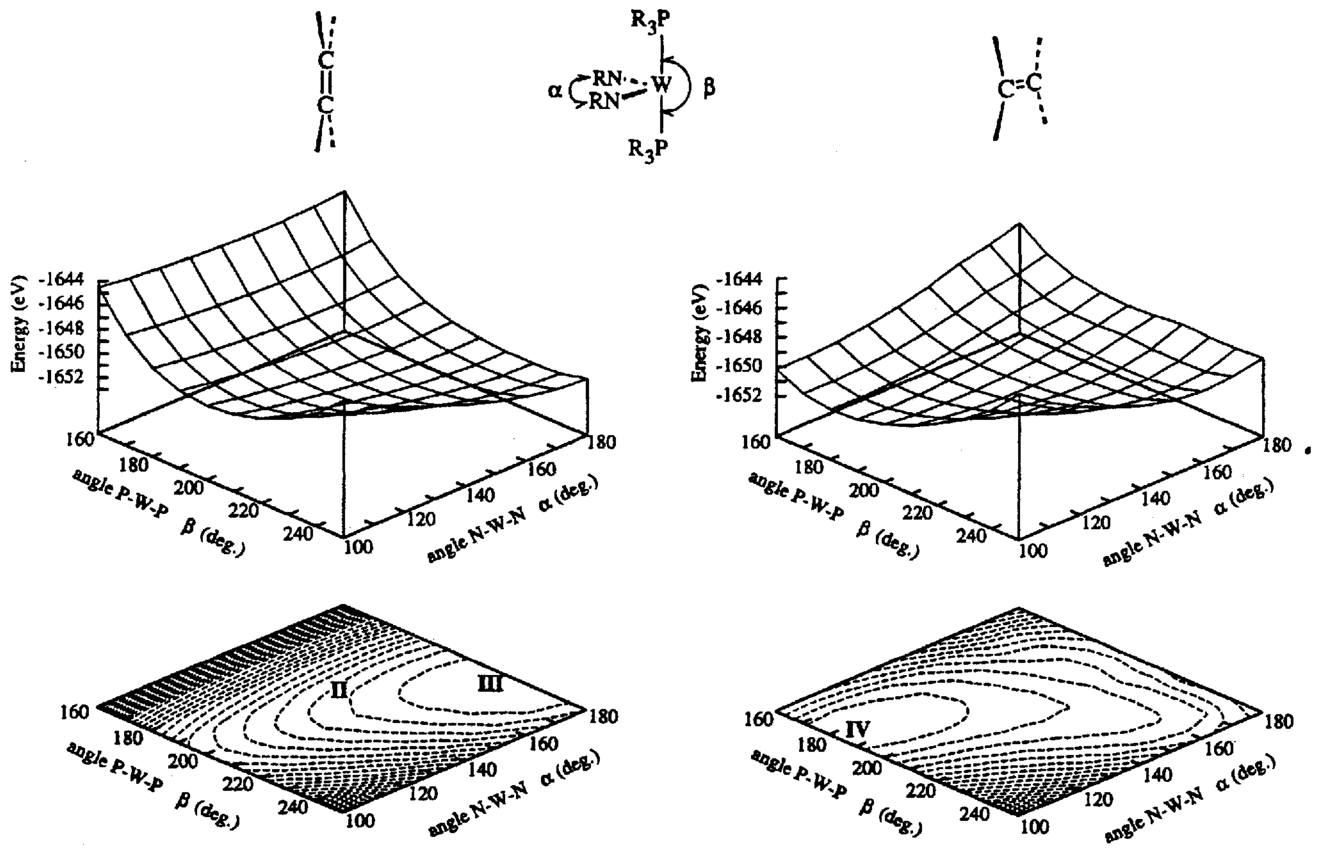


Figure 7. Energy surfaces and contour plots of two ethylene conformers of $W(NMe)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$ as a function of the angles N–W–N (α) and P–W–P (β); the C_2 axis of the ethylene ligand is perpendicular (on the left) or parallel (on the right) to the N–W–N plane; the difference between two contour lines is 0.32 eV



Two fragments are isolobal if the number, symmetry properties, shape, occupation and approximate energies of the frontier orbitals are similar[14a]. Thus we are able to compare low oxidation state metal complexes stabilized by

Table 2. Computed EH Energies (eV) of different possible geometries of $W(NMe)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)$. Shown are the energy values for our model **I**, for the experimental structure **II**, and the two minimum energy structures **III** (the C_2 axis of the ethylene ligand perpendicular to the N−W−N plane) and **IV** (the C_2 axis of the ethylene ligand parallel to the N−W−N plane); energies are relative to zero for the most stable model

	geometry	C_2 perpend. N_2W	C_2 parallel N_2W
I	$\alpha = 140°$; $\beta = 180°$	2.35	1.73
II	$\alpha = 140°$; $\beta = 196°$	0.94	1.58
III	$\alpha = 175°$; $\beta = 225°$	0.00	2.69
IV	$\alpha = 110°$; $\beta = 185°$	2.39	1.17

CO ligands with high oxidation state compounds stabilized by ligands such as O, NR, and OR. There are, however, some important differences between the high-valent and low-valent analogous that arise because of the different nature of the two classes of compounds.

The key difference between CO and the other ligands listed above is that the filled π orbitals of CO are low in energy, more localized on O than C, and by and large not available for π bonding to the metal. Instead, CO makes its empty π* anti-bonding orbitals available for π back-bonding. The filled p orbitals of $[NR]^{2-}$ ($[O]^{2-}$, $[OR]^-$, $[NR_2]^-$ etc.) are lone pairs which are available to form M−N dative π bonds. These ligands use orbitals of similar symmetry to those of CO, but ones which lie at opposite ends of the π acidity/basicity spectrum. The two classes of ligands (CO vs. O, NR, OR) may be regarded as complementary in stabilizing complexes in either "low" or "high" oxidation state. Figure 8 shows simplified interaction diagrams of a bare tungsten metal and the ligand NR (left) and of bare Fe and CO.

The π* acceptor orbitals of the CO ligand (on the right of Figure 8) lie above the metal d-orbitals in energy; the complex HOMO's have a high percentage of metal d character. The imido nitrogen π orbitals lie lower in energy than the metal d-orbitals, which results in π bonding orbitals with a large N contribution and a corresponding metal-N antibonding π* orbital dominated by metal contributions.

The filled frontier orbitals of the fragment $Fe(CO)_4$ are M−CO bonding, for d^2 $W(NMe)_2(PMe_3)_2$ they are W−N antibonding. They are of similar shape and have comparable contributions of metal-centered orbitals. But we can also see from Figure 8 significant differences in energy for the resulting M−NR antibonding (π*) and M′−CO bonding (π) orbitals. The actual energies of such orbitals will certainly differ depending on the metal and on the ligand environment, but generally, M−O, M−NR, or M−Cp π antibonding orbitals of early transition metals are higher in energy than π bonding orbitals in homoleptic $M'L_n$ fragments, where M′ is a late transition metal and L = CO. As a result of this, $W(NMe)_2(PMe_3)_2$ is a much better donor to ethylene than the $Fe(CO)_4$ fragment, despite being formally based on a metal with fewer d electrons. Also the early transition metal d levels lie at higher energy than those of the later transition metals.

The energy mismatch of the valence orbitals in low valent and high valent complex fragments influences the bonding in "early-late" heterobimetallic compounds[17]. Strongly polar M−M′ bonds can be obtained in complexes containing two metal centers close to one another in the periodic table[18]. A prerequisite for this is that one metal center be "electron deficient" because of its formally high oxidation state, the other metal "electron rich" because of a low valence. A detailed study on a heterodinuclear compound utilizing the fragments discussed here, $W(NR)_2L_2$ and $Fe(CO)_4$, is in progress and will be published later[19].

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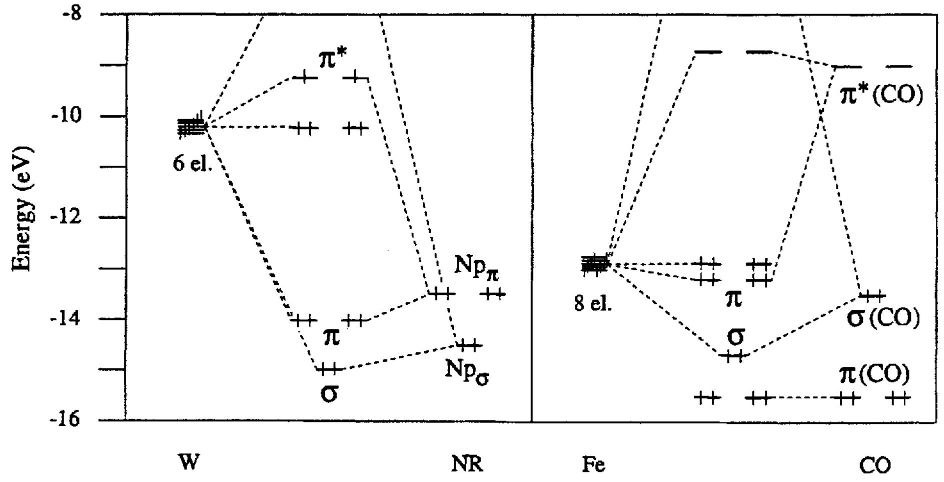
Figure 8. Simplified interaction diagrams of a bare tungsten metal and the ligand NR and of bare Fe and CO



Experimental

Details of the Calculation: Our calculations are of the Extended Hückel[10] type and were done using Greg Landrum's YAeHMOP program[20]. Extended Hückel parameters used in the calculations were taken from previous work[10a,21] and are listed in Table 3. Distances used in our calculations: Fe−W 2.62 Å, Fe−C 1.75 Å, W−H 1.75 Å, W−N 1.825 Å, W−P 2.54 Å, C−H 1.10 Å, C−N 1.40 Å, C−P 1.82 Å, C−O 1.16 Å.

Table 3. Extended Hückel method parameters used in the calculation

		Hii	ζ1	c1	ζ2	c2
Fe	4s	-9.10	1.900			
	4p	-5.32	1.900			
	3d	-12.60	5.350	0.5505	2.00	0.6260
W	6s	-8.26	2.341			
	6p	-5.17	2.309			
	5d	-10.37	4.982	0.6940	2.068	0.5631
N	2s	-26.0	1.950			
	2p	-13.4	1.950			
C	2s	-21.40	1.625			
	2p	-11.40	1.625			
P	3s	-18.6	1.750			
	3p	-14.0	1.300			
H	1s	-13.60	1.300			

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