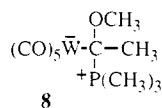


not consistent with the magnitudes of the ^{15}N chemical shifts, $^1J_{\text{CN}}$ and $^1J_{\text{NN}}$.¹⁶

Our results are consistent with the mechanism shown in Scheme I, in which nucleophilic attack of **2c** on the carbene gives the zwitterionic species **3**. Rearrangement of **3** through the transient metallacycle **4**¹⁷ would then yield the observed zwitterion **5**. Cleavage of the N-N bond in **5** would then lead to the organic product **6**. The organometallic product of cleavage would be an unobserved low-valent tungsten nitrene species $(\text{CO})_5\text{W}=\text{NPh}$ (**7**) which decomposes.

Fischer carbenes are well known to undergo nucleophilic attack at the carbene carbon.¹⁸ Precedent for the formation of zwitterionic species **3** occurs in the reaction of **1** with $\text{P}(\text{CH}_3)_3$ to give ylide **8**.¹⁹ In addition, zwitterionic or dipolar species have been



proposed in the cyclopropanation and olefin metathesis pathways of several electrophilic carbene complexes.²⁰ Conversion of dipolar intermediates to metallacycles has been observed^{20b} and invoked^{20a,c,e} in various systems. Formation of **5** is, in effect, insertion of azobenzene into the metal-carbene bond. Such insertions have previously been reported for nitriles,^{21a,b} isocyanides,^{21c} cyanates,^{21d} cyanamides,^{21e} and electron-rich acetylenes.^{20e,21f}

Metallacyclobutane intermediates in metathesis and cyclopropanation are often formed from carbene-olefin complexes $(\text{CO})_4(\text{olefin})\text{W}=\text{C}(\text{OR})\text{R}$.²² Since reaction of **1** with **2c** occurs upon mixing while CO exchange in $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$ is slow²³ and 1 atm of CO does not depress the reaction rate, CO loss and precoordination of **2c** cannot be involved. Conversion of **3** to **5** most likely occurs through an 18-electron seven-coordinate metallacycle^{22a} (**4**) in which five CO ligands are retained.

Cleavage of **5** to give **6** should also produce the metal nitrene complex $(\text{CO})_5\text{W}=\text{NPh}$ (**7**). Such low-valent nitrene complexes are unknown, and reactions that might be expected to generate them have produced phenyl isocyanide²⁴ and phenyl isocyanate²⁵ complexes instead. Neither these complexes nor the free ligands can be observed in IR spectra of the reaction mixtures. Alternatively, if **7** is a source of free phenylnitrene, the expected products in benzene solution would be low yields of aniline and

azobenzene.²⁶ GC/MS of the reaction mixtures does indeed show the presence of aniline.^{27,28} Further studies on the reactivity of the phenylnitrene fragment are in progress.

We have shown that photochemical azo metathesis by the tungsten carbene **1** is initiated by nucleophilic attack of *cis*-azobenzene on the carbene. A zwitterionic intermediate (**5**) has been isolated and spectroscopically characterized. It is believed to arise via an unprecedented zwitterion-metallacycle-zwitterion rearrangement. Although our current study only involves tungsten complexes, it is reasonable that the azo metathesis product found in the chromium carbene reaction¹ arises through a similar pathway.

Acknowledgment. Funding was provided by the Petroleum Research Fund and the Research Corporation. We thank Professor L. S. Hegeudus for disclosure of unpublished data. We are also grateful to Professors J. L. Templeton and M. Brookhart for helpful discussion.

Note Added in Proof. Geoffroy has just reported evidence for the transient formation of **7** in the metathesis of $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$ with nitrosobenzene.³⁰

(26) For recent reviews of the chemistry of aryl nitrenes, see: Smith, P. A. S. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: Orlando, FL, 1984; pp 95-204. Scriven, E. F. V. In *Reactive Intermediates, Vol. 2*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; pp 1-54.

(27) Hegeudus had also reported the presence of aniline following acid hydrolysis of the organometallic residue from the chromium reaction.¹

(28) GC/MS also shows traces of phenyl isocyanate ($\text{PhNH}_2:\text{PhNCO} \approx 50:1$). Since neither ^1H NMR nor IR of the reaction mixtures shows free phenyl isocyanate and it has been claimed that PhNCO does not bind to the $(\text{CO})_5\text{W}$ fragment,²⁹ the origin of the isocyanate is not clear.

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First-Principle Calculations of the Ionization Potentials and Electron Affinities of the Spheroidal Molecules C_{60} and LaC_{60}

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Shortly after the discovery of the remarkable stable C_{60} molecule,¹ experimental evidence has been presented for a new class of organometallic clusters of the type M_mC_n , where $\text{M} = \text{La}, \text{K}, \text{Cs} \dots$ ²⁻⁶ In the first experiment with La_2 ² only LaC_n complexes were studied with a dominating abundance of LaC_{60} and with a similar stability as for the earlier studied C_{60} cluster. Further, the LaC_{60} complex was inert to react with different molecules⁶ similar to the C_{60} molecule.⁷ To explain the inertness and the stability of LaC_{60} , the metal atom was suggested to be located within the spheroidal carbon cage.² The idea has also gotten further support by observation of C_2 fragments from laser photodissociation studies of MC_n^+ similar to C_{60} for $n > 30$,⁶ while

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(17) A referee has suggested that the conversion of **3** to **5** could also occur via dissociation to $\text{W}(\text{CO})_5$ and the zwitterion $\text{CH}_3(\text{CH}_3\text{O})\text{CNPhNPh}$ followed by recombination of the fragments. We believe the observation of heterocyclic products in the analogous chromium reaction¹ suggests the intermediacy of a metallacycle but our data do not exclude the dissociative mechanism.

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photofragment studies of 2–30 atom carbon clusters gave fragments of C_3 , supporting the assumption of an open structure for smaller clusters.⁸

A chemically bound metal atom surrounded by a carbon cage would consist of a positively or negatively charged core with a surrounding shell of opposite charge. The idea of this structure which has similarities to the "super atom" concept, was proposed for semiconductor heterostructures with a spherical core doped with donors and a surrounding impurity-free matrix of greater electron affinity.^{9–11} The donors are ionized under certain conditions, resulting in a shell of negative charge outside the core. Depending on the charge transfer, LaC_{60} could thus be considered as a "super atom" or an "antisuper atom".

The question concerning the LaC_{60} structure is still open, with different suggestions as to the "deflated soccer ball" of Cox.³ However, further support for a metal-containing cage is obtained from the intercalation reaction of graphite where obviously metal atoms reside within the graphite structure. It is well-known that potassium adsorbed on graphite reacts with the surface forming layers of potassium inside the graphite structure.¹² Assuming the hard sphere model with the ion radius of La and K atoms shows that up to three metal atoms could be located inside C_{60} neglecting the Coulomb repulsion. The recent result of Cox et al. shows that up to three potassium can be attached to the C_{60} clusters.⁵

Recently, we applied the CNDO/S method¹³ to calculate the ionization energy, electron affinity, and the optical transition energies of C_{60} .¹⁴ Calculations were performed for both the alternating bond length case (1.474 and 1.400 Å) as proposed by Newton and Stanton¹⁵ and for equal bond lengths. Our calculated ionization energy of 7.55 eV and optical transitions for the alternating bond length case was found to be in good agreement with the experimentally determined threshold between 6.42 and 7.87 eV³ and UV absorption spectra.¹⁷ Recently the calculated electron affinity of 2.4 eV was also found to be in good agreement with an experimental value in the range of 2.6–2.8 eV.¹⁶

In this work we present results calculated within the local density approximation (LDA)¹⁸ for the spheroidal LaC_{60} molecule, as a complement to recent LDA calculations for C_{60}^+ , C_{60} , and C_{60}^- .¹⁹ The one-electron equation was solved with the exchange-correlation potential of von Barth and Hedin (BH),²⁰ by using the discrete variational method (DVM) and the self-consistent charge (SCC) approximation.²¹ The basis functions were generated with an atomic LDA code for the configurations $C \dots 2s^2 2p^2$, $C^{2+} \dots 2s^2 2p^0$, $La \dots 5d^1 4f^0 6s^2 6p^0$, and $La^{1+} \dots 5d^0 6s^2 6p^0$. The carbon 1s and La cores were treated within the "frozen core approximation". The symmetry used was C_s , giving groups of levels of gerade and ungerade symmetry corresponding to levels in the I_h group.

Results for the ground-state calculations of C_{60} and LaC_{60} are presented in Figure 1 and eigenvalues of the La atom. The molecular and atomic origin of the levels in LaC_{60} , identified through a density of state analysis, are denoted by dashed lines.

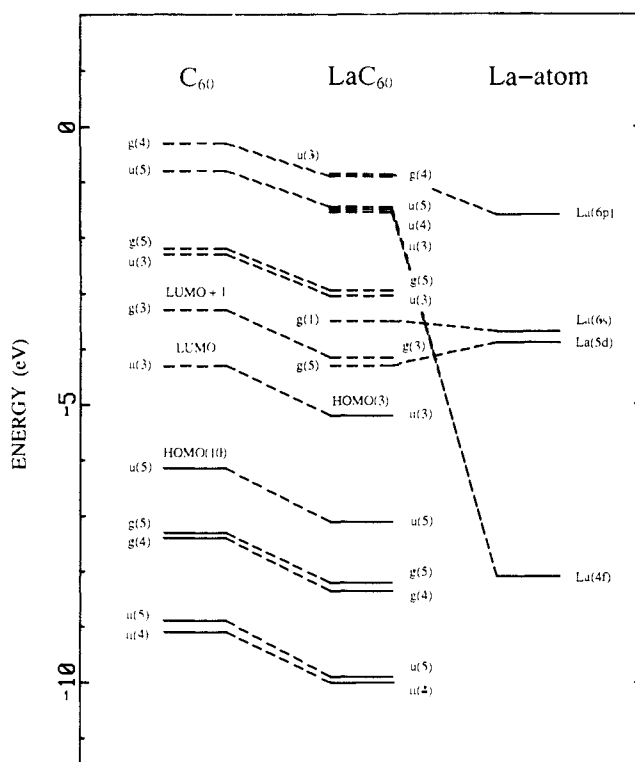


Figure 1. Comparison of the one-electron eigenvalues for C_{60} , LaC_{60} , and the La atom. The symmetry of the levels and the degeneracy divided by two are given as $g(n)$ and $u(n)$. The occupied levels are denoted by solid lines, while dashed lines denote unoccupied levels. Occupation numbers are given for the HOMO levels.

Table I. Comparison of Experimental and Theoretical Values, Calculated with the von Barth and Hedin (BH) Exchange-Correlation Potential, of Ionization Potentials (IP) and Electron Affinities (EA) in eV for C_{60} and LaC_{60}

	C_{60}		LaC_{60}	
	theor	exp	theor	exp
ϵ (LUMO + 1)	-3.3		-4.2	
ϵ (LUMO)	-4.3		-4.3	
ϵ (HOMO)	-6.1		-5.2	
IP	7.8	6.4–7.9	6.9	<6.4
EA	2.7	2.6–2.8	3.8	

The HOMO level in LaC_{60} is of carbon character which may explain the similarities in reactivity for these molecules. The LUMO level is of gerade symmetry and originates from the La 5d state. A Mulliken analysis of the molecular levels gave a gross negative charge of 2.85 for the surrounding carbon atoms. The "super atom" hypothesis with a La atom in the center is therefore quite plausible.

Eigenvalues for the HOMO, LUMO, and LUMO + 1 levels, ionization potentials, and electron affinities are presented in Table I. The ionization potentials and electron affinities were calculated by using the transition-state procedure.^{22,23} The C_{60} ionization potential is in good agreement with our earlier calculations¹⁴ as well as the value of 7.92 eV obtained in the large scale Hartree-Fock calculations by Lüthi and Almlöf.²⁴ Their electron affinity of 0.80 eV differs, however, significantly from our value of 2.7 eV, which agrees well with the experimental prediction of 2.6–2.8 eV.¹⁶ Cox et al. measured the ionization threshold of LaC_{60} and found a value below 6.42 eV (the ArF laser photon energy).³ Our calculated ionization potential of 6.9 eV is somewhat too high, but the trend of change between C_{60} and LaC_{60} is, however, correct. Determination of more precise values of the

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LaC₆₀ ionization threshold and electron affinity should, however, be of great help for checking this calculation and maybe resolve the question concerning the LaC₆₀ structure.

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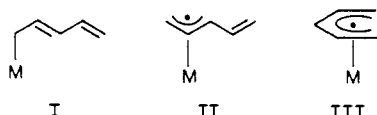
Pentadienyl Chemistry of Niobium and Tantalum: Surprising Differences and New Diene and Dienyl Coordination Patterns

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Recently there has been a significant increase in the attention being given to metal-pentadienyl chemistry.² Much of this has arisen from the realization that pentadienyl ligands may adopt a variety of bonding modes, e.g., η^1 , η^3 , or η^5 (I-III),³ and that



they readily partake in catalytic, "naked metal", and coupling reactions,⁴ even though the pentadienyl ligand may bond more strongly than cyclopentadienyl.^{4e,5}

A part of our efforts in this area has focused on complexes that simultaneously contain both pentadienyl and cyclopentadienyl ligands, so that the bonding and reactivity patterns of the two may be directly compared. Some of our results for various "half-open metallocenes" have already been described.^{4e,6} Herein we report our initial results on related chemistry of niobium and tantalum, including the observation of dramatic differences between the behaviors of these two similar metals,⁷ the first definitive demonstration of simultaneous *cis*- and *trans*- η^4 -diene coordination to a metal center⁸ (η^4 -*trans* coordination being rare in any event⁹),

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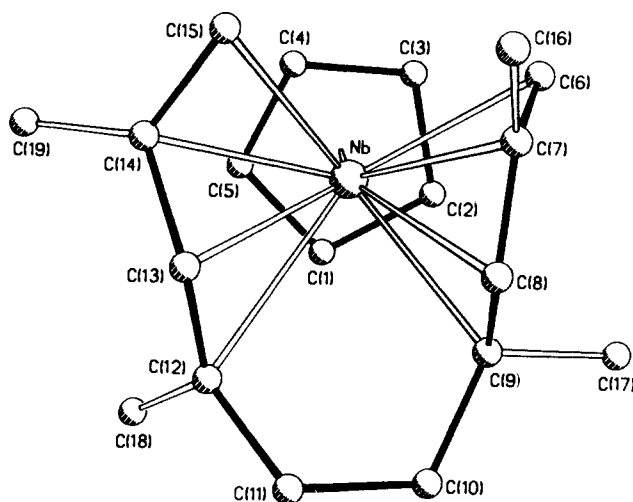


Figure 1. Perspective view and numbering scheme for Nb(C₅H₅)(η^8 -C₁₄H₂₂). Pertinent bonding distances (Å): Nb-C (Cp, av) = 2.38 (1), C(9)-C(10) = 1.48 (2), C(10)-C(11) = 1.54 (2), C(11)-C(12) = 1.48 (2).

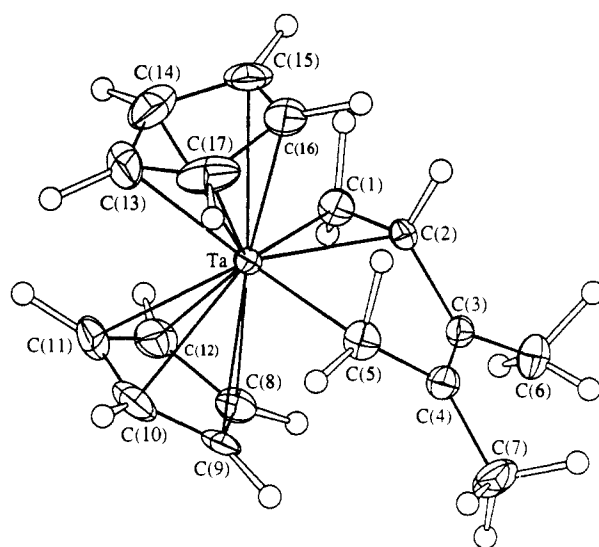


Figure 2. Perspective view and numbering scheme for Ta(C₅H₅)₂(η^3 -2,3-C₇H₁₁). Pertinent bonding distances (Å): Ta-C (Cp, av) = 2.416, Ta-C(1) = 2.302 (4), Ta-C(2) = 2.245 (4), Ta-C(5) = 2.296 (5), C(1)-C(2) = 1.434 (6), C(2)-C(3) = 1.499 (5), C(3)-C(4) = 1.333 (6), C(4)-C(5) = 1.517 (6), C(3)-C(6) = 1.497 (6), C(4)-C(7) = 1.512 (6).

and the first observation of a new η^3 -pentadienyl mode of coordination.

The reaction of Nb(C₅H₅)Cl₄¹⁰ with 4 equiv of K(2,4-C₇H₁₁)¹¹ (C₇H₁₁ = dimethylpentadienyl) initially yields a metastable product, apparently Nb(C₅H₅)(2,4-C₇H₁₁)₂ from spectroscopic data,¹² which subsequently undergoes an intramolecular coupling reaction, yielding an unusual Nb(C₅H₅)(η^8 -C₁₄H₂₂) (C₁₄H₂₂ = 2,4,7,9-tetramethyl-1,3,7,9-decetetraene) complex.¹³ While other Nb(C₅H₅)(η^4 -diene)₂ species have been reported,^{9b} structural

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(12) The orange Nb(III) complex may be isolated at low temperatures. It possesses a ν (C=C) of 1606 cm⁻¹ and four CH₂ resonances in the ¹³C NMR spectrum, three in the usual region (41.8, 45.8, and 46.6 ppm) and the fourth at 114.1 ppm (all C-H couplings in the range of 148-155 Hz).

(13) Synthetic, spectroscopic, and analytical details for new compounds are included in the Supplementary Material. Yields for the niobium reactions ranged from 55-62%, compared to 20-30% for tantalum.