Organometallics **1999,** *18,* 1087−1090

Bonding in Bis(pentalene)dimolybdenum: Density Functional Calculations on $Mo_2(C_8H_6)_2$ and Photoelectron Spectroscopy of $Mo_2(C_8H_4(1,4\text{-}SiPr^i{}_3)_2)_2$

F. Geoffrey N. Cloke,† Jennifer C. Green,*,‡ Christian N. Jardine,‡ and Matthew C. Kuchta†

The Chemistry Laboratory, University of Sussex, Brighton BN1 9QJ, U.K., and Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

Received September 21, 1998

He I and He II photoelectron spectra are reported for $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$. Density functional calculations on the model compound $Mo_2(C_8H_6)_2$ give a structure with bond lengths and ionization energies in good agreement with those found for $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$. Fragment analysis of the bonding in $Mo_2(C_8H_6)_2$ indicates a double bond between the two Mo atoms. The bonding to the pentalene ligands is very covalent and resembles that found for simple metallocenes.

Introduction

In recent times the chemistry of the pentalene ligand[1,2] has been considerably extended.[3−7] Although simple bimetallic bispentalene complexes $M_2(C_8H_6)_2$, where M = Ni[8] and Co,[9] were first synthesized over 25 years ago, the proposed structures of these complexes were never confirmed by crystallography. The electronic structure of these compounds was examined by extended Hückel methods and discussed by Burdett and Canadell.[10] They calculated the Co−Co distance to be 2.6 Å when the pentalene was constrained to be planar and 2.5 Å when the pentalene was allowed to fold by 5°. The metal−metal overlap populations for both the Co and Ni compounds were found to be effectively zero, indicating no net metal−metal bonding.

Very recently, Cloke et al. reported the tris(isopropylsilyl)-substituted bis(pentalene)dimolybdenum complex $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$, **1**,[7] which was demonstrated by X-ray diffraction to have a "sandwich"-type structure and a metal−metal distance of 2.34 Å. The molybdenum dimer raises interesting questions as to the mode of coordination to the pentalene ligands and the extent of metal−metal bonding. The observed distance is shorter than that observed for assigned Mo−Mo double bonds, ca. 2.49−2.89 Å,[11−24] yet longer than that for most complexes with Mo−Mo quadruple bonds, ca. 2.01−2.24 Å.[25]

As **1** is both an organometallic sandwich compound and possesses a metal−metal bond, it poses classification questions both with respect to the 18-electron rule and with respect to the bond order between the metal atoms. In this article we use the term bond order in its ordinal sense.[25] Extension of the 18-electron rule to bimetallic species predicts an electron count of $(36 - 2n)$, where n is the bond order. Thus, for example, $Mo_2(\eta\text{-}C_5H_5)_2(CO)_6$, with a single bond between metal atoms, has an electron count of 34 and $Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$, with a triple bond, has an electron count of 30. Examples of formal quadruple bonds for group 6 metal dimers are the carboxylates, $M_2(O_2CR)_4L_2$, with a count of 28. However, the bismolybdenum tetracarboxylates do not readily coordinate axial ligands, most commonly form with the stoichiometry $Mo_2(CO_2R)_4$, and consequently have an electron count of 24 and a short quadruple bond. Axial coordination by, for example, pyridine lengthens the Mo−Mo bond.[25]

---

† University of Sussex.
‡ University of Oxford.

(1) Knox, S. A. R.; Stone, F. G. A. *Acc. Chem. Res.* **1974**, *7*, 321.

(2) Butenschön, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1695.

(3) Abbasali, O. A.; Cloke, F. G. N.; Hitchcock, P. B.; Joseph, S. C. P. *J. Chem. Soc., Chem. Commun.* **1997**, 1541.

(4) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 7899.

(5) Jonas, K.; Kolb, P.; Kollbach, G.; Gabor, B.; Mynott, R.; Angermund, K.; Heinemann, O.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1714.

(6) Jonas, K.; Gabor, G.; Mynott, R.; Angermund, K.; Heinemann, O.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1712.

(7) Kuchta, M. C.; Cloke, F. G. N.; Hitchcock, P. B. *Organometallics* **1998**, *17*, 1934, and references therein.

(8) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281.

(9) Katz, T. J.; Acton, N.; McGinnis, J. *J. Am. Chem. Soc.* **1972**, *94*, 6205.

(10) Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805.

(11) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(12) D'Errico, J. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 4479.

(13) Green, M.; Norman, N. C.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2455.

(14) Boileau, A. M.; Orpen, A. G.; Stansfield, R. F.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 187.

(15) Potenza, J. A.; Johnson, R. J.; Chirico, R.; Efraty, A. *Inorg. Chem.* **1977**, *16*, 2354.

(16) Bott, S.; Connelly, N. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Paxton, J. F.; Shaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1983**, 378.

(17) Brun, P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 926.

(18) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221.

(19) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1269.

(20) Connelly, N. G.; Metz, B.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2109.

(21) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

(22) Connelly, N. G.; Metz, B.; Orpen, A. G.; Reiger, P. H. *Organometallics* **1996**, *15*, 729.

(23) Herrmann, W. A.; Bell, L. K.; Zeigler, M. L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* **1983**, *247*, 39.

(24) Bott, S. G.; Brammer, L.; Connelly, N. G.; Green, M.; Orpen, A. G.; Paxton, J. F.; Schaverien, C. J.; Bristow, S.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1957.

(25) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Oxford University Press: Oxford, 1993.

10.1021/om980792u CCC: $18.00

Bispentalene complexes of group 6 metal dimers have an electron count of 28, which might be taken as indicative of a quadruple bond, but the metal−metal distance in **1** lies between the range of values for a quadruple and a double bond.[7,11−25] Also the lack of axial symmetry about the Mo−Mo vector and the absence of axial ligands in the crystallized compound suggest that simple electron counting may not, in this case, successfully predict the Mo−Mo bond order. In such circumstances a detailed molecular orbital picture of the bonding is required.

To elucidate such points, and the mode of binding of the pentalene ligand, we have undertaken an investigation of the electronic structure of **1**. We report here the He I and He II photoelectron (PE) spectra of **1** and density functional calculations on the model compound $Mo_2(C_8H_6)_2$, **2**.

Experimental Section

Compound **1** was synthesized by the literature procedure.[7]

Photoelectron spectra were measured using a PES laboratories 0078 spectrometer interfaced with an Atari microprocessor. Spectra were calibrated with He, Xe, and N_2. To obtain a suitable vapor pressure, the sample was held at a temperature of 240 °C.

All calculations were performed using density functional methods of the Amsterdam Density Functional package (Version 2.3).[26] The basis set used triple-ζ accuracy sets of Slater-type orbitals, with relativistic corrections, with a single polarization functional added: 2p on hydrogen and 3d on carbon atoms. The cores of the atoms were frozen: carbon up to the 1s orbital, and molybdenum to the 3d orbitals. The GGA (nonlocal) method was used, using Vosko, Wilk, and Nusair's local exchange correlation[27] with nonlocal exchange corrections by Becke[28] and nonlocal correlation corrections by Perdew.[29] The nonlocal correction terms were not utilized in calculating gradients during geometry optimizations. Vertical ionization energies were estimated, using the optimized structure, from the difference between the total energy for the molecule and that for the molecular ion in the appropriate state.

Results and Discussion

Geometry optimization of **2** was carried out with a constraint of D_{2h} symmetry. A frequency calculation on the optimized structure showed only positive frequencies, demonstrating that the structure found was a local minimum. The resulting structure is illustrated in Figure 1. Bond lengths and angles were close to those found experimentally for **1** (Table 1); in particular the Mo−Mo distance was in excellent agreement.

The experimental structure shows the pentalene rings to be twisted 10° relative to one another around the *z*-axis. We tested the possibility of such a local minimum for **2** by carrying out a further geometry optimization under D_2 symmetry constraints, starting from a structure with a twist of 20°. The final geometry was of D_{2h} symmetry. A D_2 structure optimized with the twist constrained to 10° had an energy 12.5 kJ mol^{-1} above that of the D_{2h} structure. This suggests that the twist angle in the crystal structure of **1** may be a result of the bulky substituents.

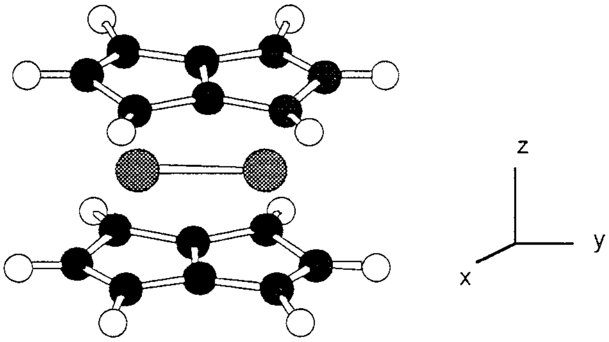

Figure 1. Calculated structure of **2** and coordinate system chosen.

Table 1. Comparison of Selected Experimental Distances (Å) and Angles (deg) for 1 with Those Calculated for 2

parameter	experimental **1**	calculated **2**
Mo−Mo	2.340	2.340
Mo−C(bridge)	2.360−2.432	2.364
Mo−C(α)	2.263−2.298	2.240
Mo−C(β)	2.258−2.260	2.239
C(bridge)−C(bridge)	1.447−1.458	1.451
C(bridge)−C(α)	1.445−1.476	1.450
C(α)−C(β)	1.410−1.453	1.434
ligand fold angle	mean 1.73−3.03	to C(α) 2.6 to C(β) 4.2

The advantage of high symmetry for both MO descriptions and for calculation of ionization energies led us to adopt the D_{2h} idealized structure for subsequent analysis.

The bonding in **2** was analyzed by a fragment approach that considered the interaction of an uncharged Mo−Mo dimer with neutral pentalene ligands. In such a fragment analysis the distances used in the fragments are identical with those of the optimized structure. A molecular orbital (MO) scheme showing the principal interactions between the fragment orbitals is given in Figure 2. The one-electron energies calculated for the fragments are given in the left- and right-hand columns, and those for the molecule are given in the central column. The labels for the Mo_2 dimer are given in $D_{\infty h}$ symmetry. Eight levels (four of them with 2-fold degeneracy) are shown in the valence region arising from the 5s and 4d orbitals of the Mo atoms. Isosurfaces for representative MOs are shown in Figure 3. The percentage metal and pentalene contributions to the orbitals are listed in Table 2.

We can make a gross division of the occupied MOs into those of principal metal and those of principal ligand character. Examination of the occupied orbitals shows that there are four of predominant metal character: $8b_{2u}$, $11a_g$, $6b_{3u}$, and $9a_g$. The highest lying pair, $8b_{2u}$ and $11a_g$, are weakly antibonding and bonding, respectively, between the metal atoms and together do not contribute to Mo−Mo bonding. The $8b_{2u}$ HOMO involves some back-bonding to the ligand π_6 orbitals. These two orbitals may be regarded as effectively representing two electron pairs lying across the face of the pentalene rings occupying Mo $4d_{x^2}$-type orbitals. The $6b_{3u}$ orbital is strongly Mo−Mo π bonding in the *xy* plane, and the $9a_g$ strongly Mo−Mo σ bonding. For electron-counting purposes, these four orbitals hold the eight metal electrons of the Mo_2^{4+} dimer and suggest a double bond between the two Mo atoms.

---

(26) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.
(27) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1990**, *58*, 1200.
(28) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 2398.
(29) Perdew, J. P. *Phys. Rev.* **1985**, *B33*, 8822.

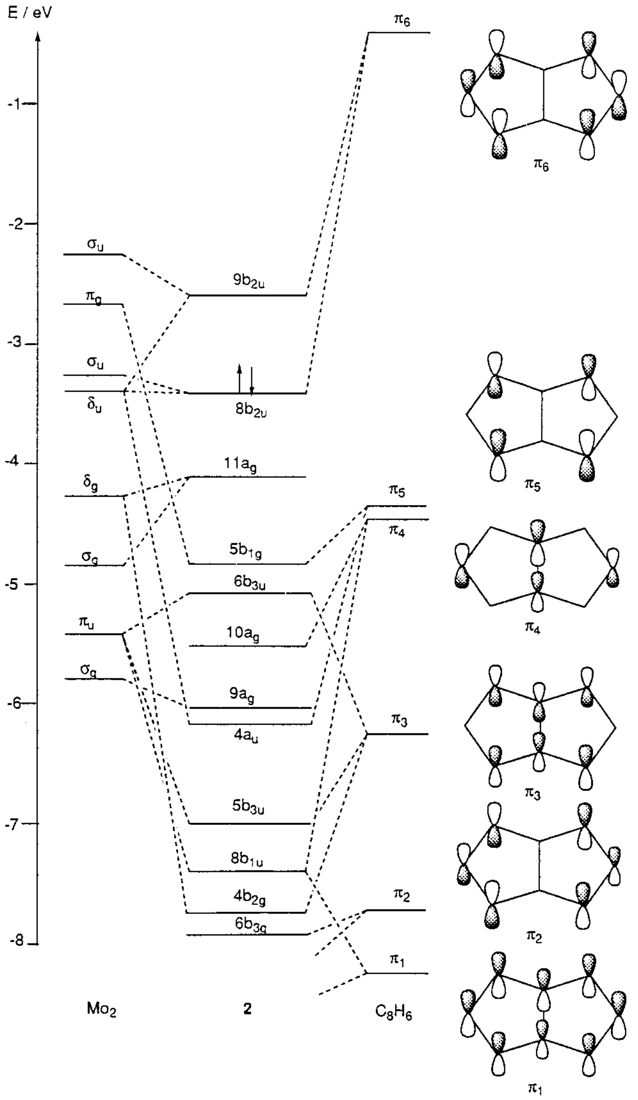

Figure 2. MO scheme for **2** showing the interaction of a Mo_2 dimer with two pentalene ligands in D_{2h} symmetry. The one-electron energies calculated for the fragments are given in the left- and right-hand columns, and those for the molecule are given in the central column. The labels for the Mo_2 dimer are given in $D_{\infty h}$ symmetry. The levels for the Mo_2 fragment are composed of contributions from both the Mo 4d and 5s orbitals.

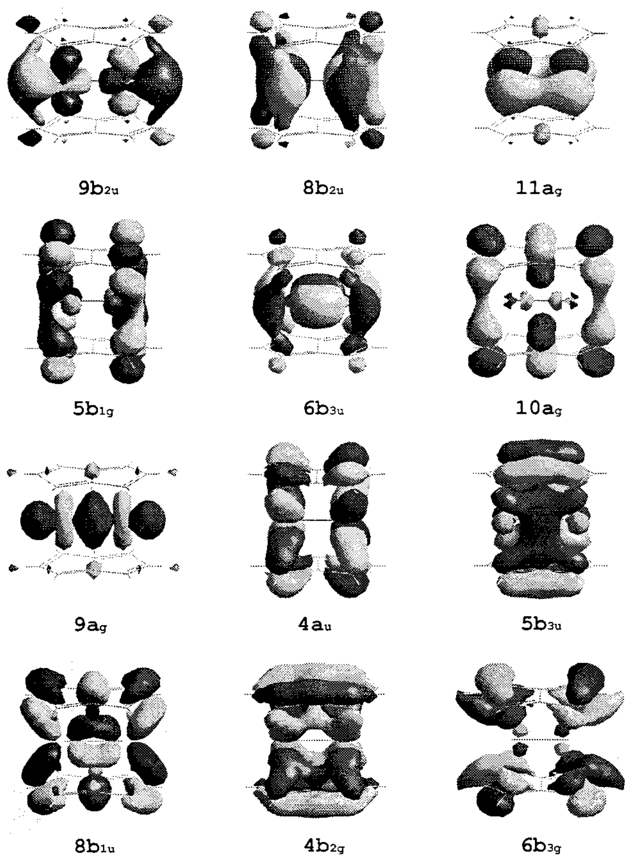

Figure 3. Isosurfaces for selected one-electron wave functions of **2**.

Table 2. Orbital Energies, Orbital Type, and Calculated IE for $Mo_2(\eta^5,\eta^5\text{-}C_8H_6)_2$ and Experimental IE for $Mo_2(\eta^5,\eta^5\text{-}C_8H_4(SiPr_3)_2)_2$

symmetry	orbital energy	% Mo	% C (π_n)	IE calc	IE expt	band
$9b_{2u}$ (LUMO)	−2.596	45.1 σ_u 30.7 δ_u	10.3 π_6			
$8b_{2u}$ (HOMO)	−3.403	19.7 σ_u 46.6 δ_u	31.0 π_6	5.69	5.34	A
$11a_g$	−4.099	9.2 σ_g 69.7 δ_g		6.38	6.02	B
$5b_{1g}$	−4.833	11.5 π_g	87.4 π_5	6.96	6.78	C_1
$6b_{3u}$	−5.077	71.8 π_u	14.5 π_3	7.33	7.11	C_2
$10a_g$	−5.556	5.1 σ_g	91.7 π_4	7.68	7.42	C_3
$9a_g$	−6.050	86.3 σ_g		8.54	9.1	D
$4a_u$	−6.121	32.6 δ_u	57.9 π_5	8.29	7.94	C_4
$5b_{3u}$	−7.031	14.5 π_u	80.8 π_3	9.26	9.1	D
$8b_{1u}$	−7.381	27.7 π_u	41.6 π_4 17.6 π_1	9.62	9.1	D
$4b_{2g}$	−7.864	21.1 δ_g	60.4 π_3	10.078		
$6b_{3g}$	−7.866	9.2 π_g	77.4 π_2	10.09		

This is confirmed by a more detailed analysis of the fragment occupations. Taking σ_g, π_u, and δ_g as metal–metal bonding and σ_u, π_g, and δ_u as antibonding and summing the fragment occupations, a fractional bond order can be calculated of 1.86.

In the other orbitals the ligand character dominates. The two that contribute most to metal ligand bonding are the $4a_u$ and the $8b_{1u}$ orbitals. These involve the Mo d_{xz} and d_{yz} orbitals, respectively, and resemble the interactions between upper occupied cyclopentadienyl π orbitals and the metal of a sandwich compound. The $8b_{1u}$ orbital is well set up to be both metal–ligand and metal–metal bonding, while the $4a_u$ orbital has metal–metal δ antibonding character. Small, but not insignificant, amounts of metal character contribute to other orbitals. Mulliken population analysis gives the charge on Mo as +0.85.

The lowest unoccupied MO (LUMO), $9b_{2u}$, lies 0.8 eV above the highest occupied MO (HOMO) and is σ antibonding. Its spatial location, outward pointing along the *y*-axis, suggests the possibility of further coordination of donor ligands, but, as yet, no experimental evidence for Lewis acid behavior has been obtained. Compound **1** does not react with CO or PMe_3.

The overall bonding picture is of substantial mixing between the metal and ligand fragment orbitals on forming the bispentalene complex. In the final level ordering the metal–metal bonding orbitals are interleaved with the ligand π orbitals, and, in addition, the ordering of the predominantly ligand levels is not exclusively that of the free ligand, but is determined in part by the metal–ligand bonding interactions.

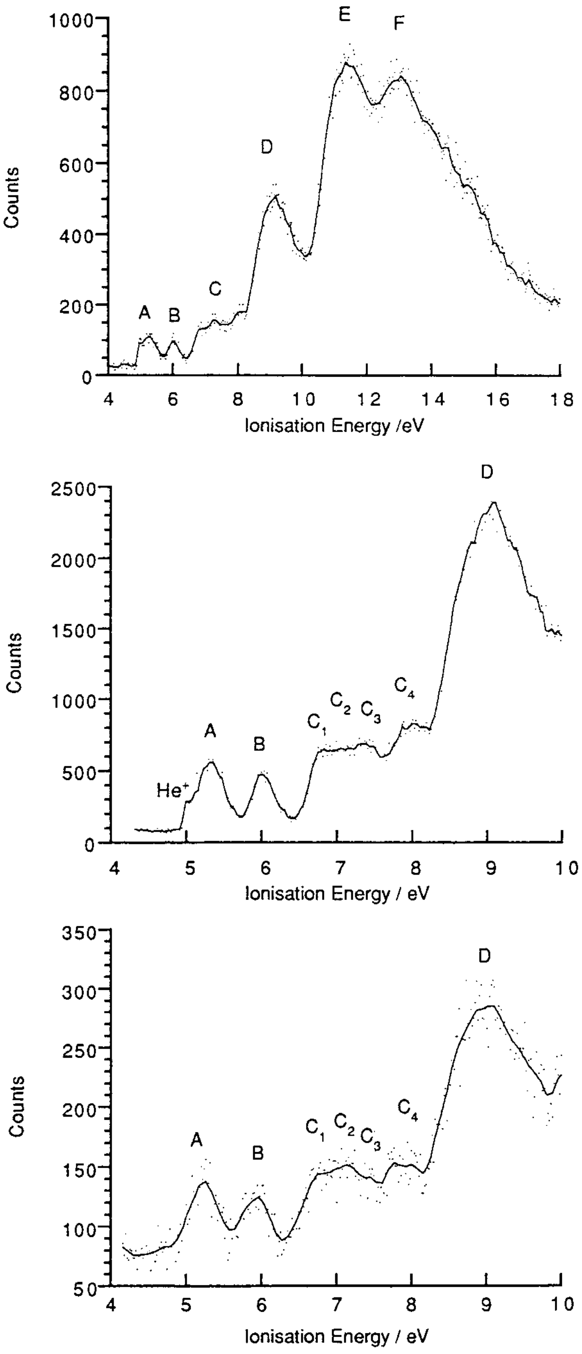

Figure 4. PE spectra of **1**: (a) He I full range, (b) He I low IE range, (c) He II low IE range.

He I and He II PE spectra are shown in Figure 4. Experimental ionization energies (IE) are given in Table 2. The first band, A, overlaps with the He self-ionization band (He ionized by He IIα) in the He I spectrum of compound **1**. The most intense bands in the spectra, D, E, and F, result from ionizations localized on the ligands; in particular band D is in a IE region characteristic of ionizations from C−Si bonds. Similar PE bands were observed in the PE spectra of Th(η^8-C_8H_4(1,4-$SiPr^i_3$)$_2$)$_2$ and U(η^8-C_8H_4(1,4-$SiPr^i_3$)$_2$)$_2$.[30] The low-energy bands A−C, which are associated with the highest occupied orbitals of the molecule, are considerably less intense, making acquisition of a He II spectrum in this region difficult. Nevertheless, sufficiently good statistics were achieved to show that there are no very significant relative intensity changes among bands A−C as the photon energy is changed. Also bands A−C increase in intensity relative to band D in the He II spectrum, which is expected for metal d or carbon 2p ionizations relative to Si 3p ionizations. The absence of any marked change among bands A, B, and C suggests that metal character is distributed throughout this ionization region. Some further assignment is possible empirically. In the PE spectra of Th(η^8-C_8H_4(1,4-$SiPr^i_3$)$_2$)$_2$ and U(η^8-C_8H_4(1,4-$SiPr^i_3$)$_2$)$_2$, the first band associated with ligand π ionization has a vertical IE of 6.4 and 6.5 eV, respectively. Thus it seems likely that band C_1 is also a predominantly ligand ionization and that bands A and B are associated with the two Mo lone pair ionizations from the $8b_{2u}$ and $11a_g$ orbitals. We associate C_2 with ionization of the Mo−Mo π bond, the $6b_{3u}$ orbital. Otherwise we must rely on calculation of the ion state energies for further assignment. The resultant calculated IEs for **2** are given in Table 2. Agreement of the pattern of calculated IE for **2** with the experimental PE band structure for **1** is very good; the calculated IEs all lie ca. 0.2−0.4 eV higher than the experimental ones. Part of this shift may be attributed to the presence of Si substituents in **1**. The calculations suggest that the Mo−Mo σ bonding ionization, $9a_g$, lies under band D, which has a maximum at 9.1 eV but spreads from 8.2 to at least 10 eV. The lack of marked relative intensity changes is also explicable on inspection of the population analysis given in Table 2. Although individual ionizations encompassed by band C might be expected to show relative intensity changes, they lie sufficiently close in energy that they overlap, and individual band profiles cannot be reasonably assigned.

Conclusions

The interaction between the pentalene ligands and the Mo_2 dimer in **1** is highly covalent. The π_4 and π_5 orbitals of pentalene, which have two nodal planes intersecting the ring, are well matched by one of the π_u and one of the δ_u orbitals of the Mo_2 unit, respectively.

The bond between the two molybdenum atoms is best described as a double bond consisting of a σ bond and a π bond in the plane parallel to the pentalene rings. The electron count of 28 for **1** is less than the 32 expected for a doubly bonded metal dimer that satisfies the 18-electron or effective atomic number rule. Although further coordination of ligands along the metal−metal axis may be possible by utilizing the LUMO, it has not yet been achieved experimentally. The very low first IE of **1**, 5.34 eV, may indicate that the LUMO is not sufficiently stable. The lack of axial coordination is reminiscent of that commonly found in quadruply bonded Mo_2 complexes.

Acknowledgment. We thank EPSRC for a studentship (C.N.J.) and the NSF-NATO Postdoctoral Fellowship Program for funding (M.C.K.) (Grant No. DGE-9710868). This material is based on work supported by the North Atlantic Treaty Organization under a grant awarded in 1997.

OM980792U

---

(30) Cloke, F. G. N.; Green, J. C.; Jardine, C. N. *Organometallics* **1999**, *18*, 1080.