in the second one the two bonds are broken successively and the metallacycle intermediate is known to be a stable molecule. The most likely explanation is that there is a thermodynamic drive for the reaction: the Ta(V) complex, $Cp_2TaO(CH_3)$, is much more stable than the metallacycle. The energy of the transition state should also become lower. Again, if the hypothetical ethylene oxide adduct of $Cp_2Ta(CH_3)$ is compared to the tantalaoxetane, it is seen that, on geometrical grounds, forming ethylene from the first requires much less atomic motion than converting it to the second. On the same line of reasoning, as two molecules result from the reaction, the entropic contribution is also clearly in favor of the concerted reaction.

Conclusions

The thermodynamic O-*anti*-tantalaoxetane isomer is rationalized to be more stable than the O-syn isomer because it has stronger tantalum–carbon bonds. In this study it has been explained that aldehydes prefer to add to the syn side of a $Cp_2Ta(CH_2)(CH_3)$ complex due to electronic as well as steric grounds, the latter being more important. The O-*syn*-tantalaoxetane is thus the kinetic product of the reaction. The following isomerisation to the thermodynamically favored form may proceed via ligand (L) migration to a cyclopentadienyl ring followed by a rotation of the hereby formed η^4-C_4H_5L ligand. This path shows base catalysis as the intermediate is stabilized by ~10 kcal/mol by coordination of PH_3. Pseudorotations were excluded from energetic reasoning. The possibility of an acid-catalyzed breaking of the tantalum–oxygen bond cannot be excluded from these calculations as the overlap population of this bond was only slightly affected by binding of hydrogen to the oxygen atom. The reduction of epoxides by a $Cp_2Ta(CH_3)$ complex is proposed to follow a nonactivated direct abstraction pathway of the oxygen atom of the three-membered ring by the tantalum center without formation of tantalaoxetanes.

Acknowledgment. We are thankful to John E. Bercaw and Roald Hoffmann for introducing us to this chemistry prior to publication and for helpful comments. For the careful preparation of the drawings we thank Arne Lindahl and Henrique Nuno. M.J.C. and A.M.G. thank Junta Nacional de Investigação Científica e Tecnológica (PMCT/C/CEN/367/90).

Appendix

The extended Hückel molecular[7] approach is used throughout the study. The bond distances and angles of the various tantalum complexes and of the involved small organic molecules are in accordance with literature data.[12,13,27] Atomic parameters are listed in Table I.

OM920200M

---

[27] (a) Turner, T. E.; Howe, J. A. *J. Chem. Phys.* **1956**, *24*, 924. Cunningham, Jr., G. L.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D.; Le Van, W. I. *J. Chem. Phys.* **1951**, *19*, 676. (b) Allen, H. C.; Plyler, E. K. *J. Am. Chem. Soc.* **1958**, *80*, 2673. Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906. (c) Glockler, G. *J. Phys. Chem.* **1958**, *62*, 1049. Takagi, K.; Oka, T. *J. Phys. Soc. Jpn.* **1963**, *18*, 1174.

Study of Metal–Ligand Multiple Bonding in Osmium and Iridium Imido Complexes: Evidence for the Cyclopentadienyl–Imido Analogy

David S. Glueck,[†] Jennifer C. Green,[*,‡] Richard I. Michelman,[†] and Ian N. Wright[‡]

Department of Chemistry, University of California, Berkeley, California 94720, and Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

Received July 2, 1992

He I and He II photoelectron spectra are reported for Os(η-C_6Me_6)NBu^t, Os(η-1,4-$(CHMe_2)MeC_6H_4$)NBu^t, and Ir(η-C_5Me_5)NBu^t. Photoelectron bands are assigned using simple molecular orbital models for the complexes. The bonding of the osmium and iridium compounds shows similarities to that of the metallocenes but the metal a_1 orbital is more destabilized in the case of the imido complexes.

Introduction

Terminal transition metal imido complexes are known for most transition metal groups.[1] They show varied and interesting reactivity; for example, osmium imido complexes have been used as either stoichiometric or catalytic reagents for oxyamination of a variety of alkenes[2-5] and group IV imido complexes have been implicated in C–H bond activation.[6] They also are increasingly used as ancillary ligands in organometallic chemistry, in which they are widely regarded as analogous to cyclopentadienyl ligands both in their frontier orbitals and in the way that their steric and electronic requirements can be varied by

---

[†] University of California, Berkeley.

[‡] Oxford University.

[1] Nugent, W.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

[2] Herranz, E.; Biller, S. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1978**, *100*, 3596.

[3] Sharpless, K. B.; Patrick, D. W.; Truesdale, L. K.; Biller, S. A. *J. Am. Chem. Soc.* **1975**, *97*, 2305.

[4] Hentges, S. G.; Sharpless, K. B. *J. Org. Chem.* **1980**, *45*, 2257.

[5] Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.

[6] Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2983.

0276-7333/92/2311-4221$03.00/0

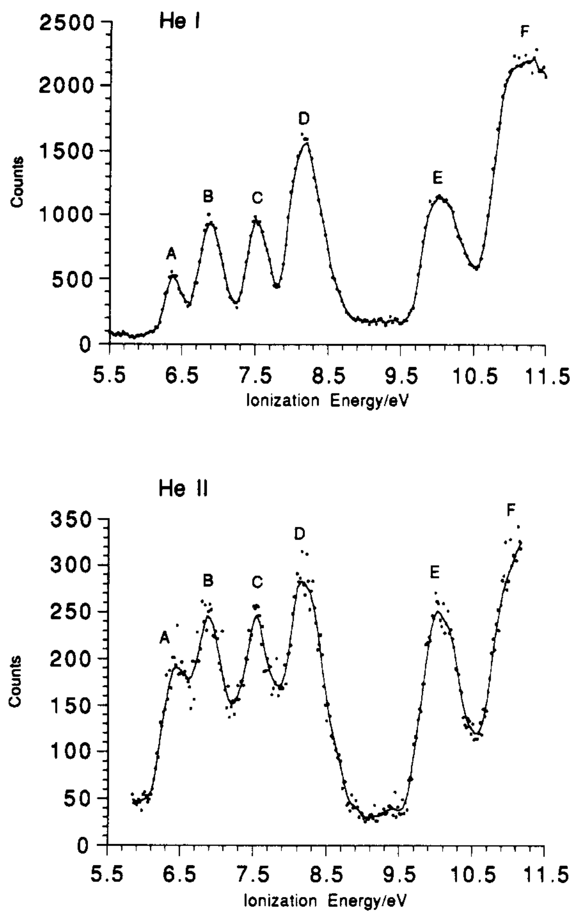

Figure 1. He I and He II spectra of Os(η-C_6Me_6)NBu^t.

changing the organic group.[7-9]

The metal–ligand bond order in imido compounds is generally considered to vary between 2 and 3. A triple bond between the metal and nitrogen is associated with a linear structure, whereas a double bond may result in a bent structure with the N lone pair in an sp^2 type orbital, or if a linear geometry is maintained, the nitrogen "lone pair" may be localized in a pπ orbital on the N or delocalized onto the organic group as is presumed to be the case with silylimido complexes. Geometry is therefore not necessarily a guide to bond order.

Vibrational spectroscopy, X-ray diffraction, and nuclear magnetic resonance have all been used extensively to ascertain M–N bond orders.[1] In the work described here we seek to characterize the ionization energies associated with such metal–ligand multiple bonds by means of photoelectron (PE) spectroscopy. Some previous PE studies on uranium imido complexes have been reported[10] though the assignment of the N pπ bands has been challenged on the basis of discrete variational local density functional (Xα) calculations.[11]

The studies reported below are on Os(η-C_6Me_6)NBu^t, Os(η-1,4-($CHMe_2$)MeC_6H_4)NBu^t,[12] and Ir(η-C_5Me_5)NBu^t,[13] examples of later transition metal imido compounds. They show enhanced reactivity toward a variety of X–H bonds (X = N, O, S) leading to such reactions as amine/imido exchange.

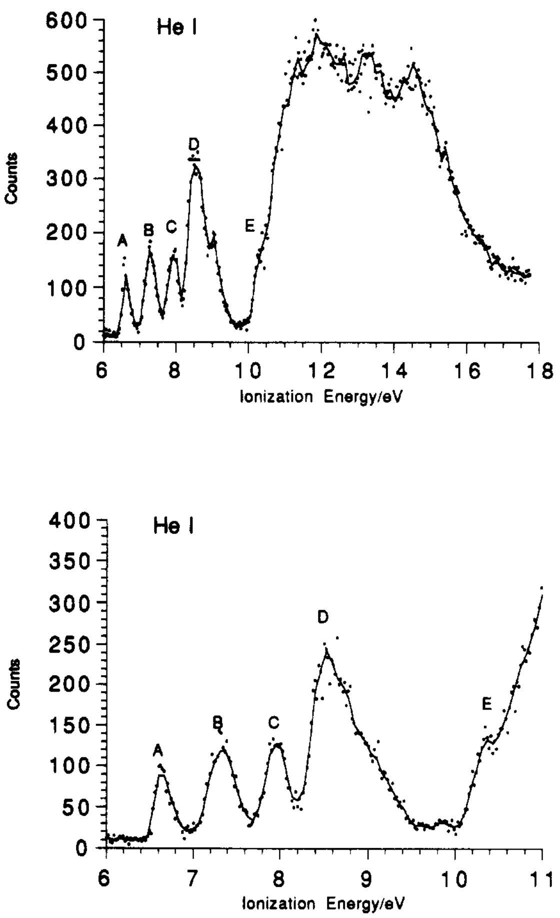

Figure 2. He I spectra of Os(η-1,4-($CHMe_2$)MeC_6H_4)NBu^t.

Table I. Vertical Ionization Energies (eV) of Os(η-C_6Me_6)NBu^t (I), Os(η-1,4-($CHMe_2$)MeC_6H_4)NBu^t (II), and Ir(η-C_5Me_5)NBu^t (III) and Band Assignments

band	I	II	III	assgnt
A	6.35	6.65	7.50	$^2A_1$
B	6.90	7.35	7.80	$^2E_{5/2}$
C	7.55	8.00	8.40	$^2E_{3/2}$
D	8.30	8.70	7.90	$^2E_1$
E	10.10	10.50	10.00	$^2E_1$
F	11.15		11.15	

Experimental Section

The compounds Os(η-C_6Me_6)NBu^t, Os(η-1,4-($CHMe_2$)MeC_6H_4)NBu^t, and Ir(η-C_5Me_5)NBu^t were prepared by the literature methods.[12,13]

Photoelectron spectra were recorded using a PES Laboratories 0078 spectrometer, interfaced with a RML 380Z microcomputer. Data were collected by repeated scans of about 54 s in order to minimize intensity variations due to pressure fluctuations. There was no apparent drift during data collection. The compounds were heated to ca. 60 °C to provide sufficient counts for data collection. The principal ionization features were calibrated using He, Xe, and N_2. Vertical ionization energies were taken as the band maxima and are accurate to ±0.05 eV. Where the band was broad, the center of the maximum was taken.

Results

The PE spectra are given in Figures 1–3, and the vertical ionization energy data, in Table I. There are clear re-

---

[7] Schrock, R. R. Presented at the 201st Meeting of the American Chemical Society, Atlanta, GA, 1991; INOR 363.

[8] Williams, D. S.; Anhaus, J. T.; Schofield, M. H.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 5480.

[9] Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739.

[10] Brennan, J. G.; Green, J. C.; Redfern, C. M. *Inorg. Chim. Acta* **1987**, *139*, 331.

[11] Bowmaker, G. A.; Görling, A.; Häberlen, O.; Rösch, N.; Goodman, G. L.; Ellis, D. E. *Inorg. Chem.* **1992**, *31*, 577.

[12] Michelman, R. I.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 5100.

[13] Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

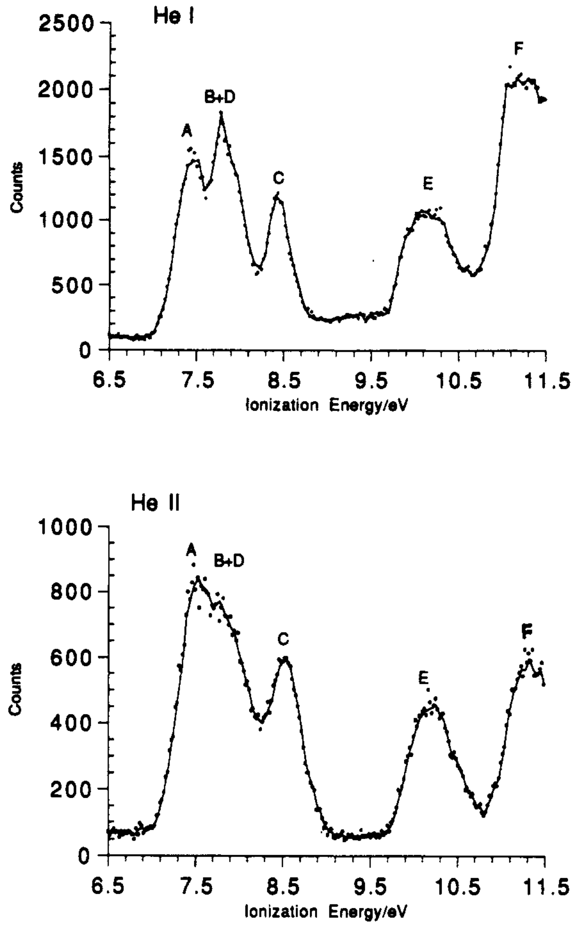

Figure 3. He I and He II spectra of Ir(η-C_5Me_5)NBu^t.

semblances between the spectra of the two osmium compounds, though the iridium spectra look at first sight rather different. The first three bands, A–C, in the spectra of Os(η-C_6Me_6)NBu^t and Os(η-1,4-($CHMe_2$)MeC_6H_4)NBu^t show a relative increase in intensity in the He II spectra and appear to be associated with primarily metal 5d ionizations. Bands D and E are largely ligand in origin. In the spectrum of the hexamethylbenzene compound, band E is fairly well resolved from the main band, F, and it increases in intensity relative to band D on increasing the photon energy. In the case of the *p*-cymene derivative, band E appears as a shoulder. Band E has a clear analogue in the spectrum of Ir(η-C_5Me_5)NBu^t, where it is also distinct from the main band. In considering the low-IE region, we argue below that bands A–C lie at higher IE than for the Os compounds and band D at lower IE such that bands B and D overlap.

Discussion

In investigating the bonding in imido compounds, we are interested in examining the similarities and differences between the bonding requirements of an imido ligand and that of a ring system such as a cyclopentadienyl or arene ligand. In an oxidation state formalism they carry charges of 2-, 1-, and 0, respectively.

The imido ligand has one σ and two π orbitals available for bonding to a metal. A carbocyclic ring has three low-lying π orbitals of a_1 and e_1 symmetry; the a_1 orbital is σ and the e_1 π with respect to the metal–ring axis. The carbocyclic ring systems also provide an e_2 pair of δ symmetry unoccupied acceptor orbitals, which have been shown to be important in metal–arene bonding. The compounds examined here are therefore analogues of the group 8 metallocenes, and the resemblance of the spectra of the (arene)osmium imido compounds to those of the bis(cyclopentadienyl) compounds of osmium is particularly striking.[14-17]

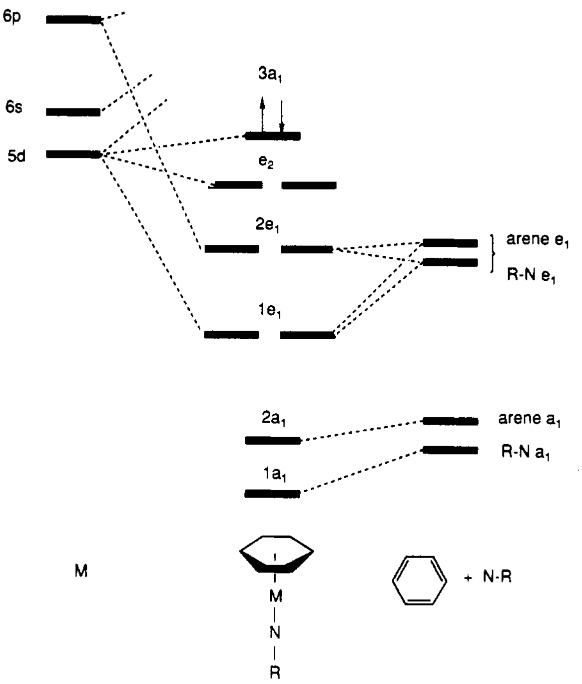

Figure 4. Schematic MO diagram for Os(η-C_6H_6)NR.

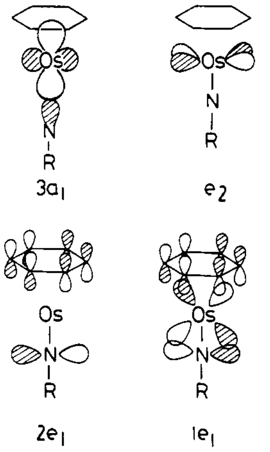

Figure 5. Selected MOs for the imido complexes.

Table II. Transformation Properties of the Basis Orbitals of Os(η-C_6H_6)NR and Ir(η-C_5H_5)NR in the Symmetry Groups C_{6v} and C_{5v}, Respectively

orbital	irreducible representation	orbital	irreducible representation
metal d		ring π	
z^2	a_1	a_1	a_1
xz, yz	e_1	e_1	e_1
$x^2 - y^2, xy$	e_2	e_2	e_2
metal s	a_1	imido N	
metal p		$p\sigma$	a_1
z	a_1	p_x, p_y	e_1
x, y	e_1		

In order to proceed further with spectral assignment, we have drawn up a schematic molecular orbital (MO) diagram for Os(η-C_6H_6)NR (Figure 4) on the basis of

---

[14] Evans, S.; Green, M. L. H.; Jewitt, B.; Orchard, A. F.; Pygall, C. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *1972*, 1874.

[15] Cooper, G.; Green, J. C.; Payne, M. P. *Mol. Phys.* **1988**, *63*, 1031.

[16] O'Hare, D.; Green, J. C.; Chadwick, T. P.; Miller, J. S. *Organometallics* **1988**, *7*, 1335.

[17] Lichtenberger, D. L.; Copenhaver, A. S. *J. Chem. Phys.* **1989**, *91*, 663.

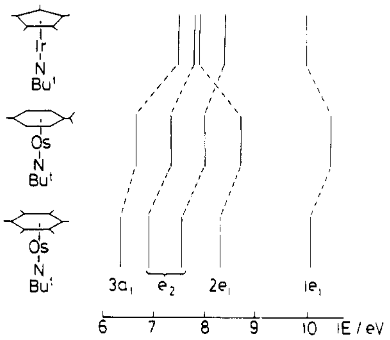

Figure 6. Correlation among the vertical IEs of $Ir(\eta\text{-}C_5Me_5)NBu^t$, $Os(\eta\text{-}1,4\text{-}(CHMe_2)MeC_6H_4)NBu^t$, and $Os(\eta\text{-}C_6Me_6)NBu^t$.

symmetry requirements and normal electronegativity considerations. That for $Ir(\eta\text{-}C_5Me_5)NBu^t$ would be expected to be similar. The transformation properties of the basis orbitals in the symmetry groups C_{6v} and C_{5v} are given in Table II, and representations of selected resulting MOs, for the compounds in Figure 5. Both ligands provide an e_1 set for bonding with the metal d_{xz} and d_{yz} orbitals, and the mixing of these three sets giving three resulting MOs will depend critically on their relative energies and overlap. The e_1 set represented by the metal 6p orbitals is expected to lie rather high in energy, to be very diffuse, and consequently to make less contribution to the bonding.

The spectra of $Os(\eta\text{-}C_6Me_6)NBu^t$ and $Os(\eta\text{-}1,4\text{-}(CHMe_2)MeC_6H_4)NBu^t$ may be assigned in parallel. Bands A–C are assigned to the ion states $^2A_{1/2}$, $^2E_{3/2}$, and $^2E_{1/2}$, respectively. Band A shows the larger relative increase in the He II spectra characteristic of a_1 ionizations.[18] Ionization from the $e_2{}^4$ configuration gives rise to two bands due to significant spin–orbit splitting of the $^2E_2$ ion state. The separation between bands B and C is 650 meV comparable to that found for the $^2E_{5/2}$ and $^2E_{3/2}$ ion states of osmocene and its derivatives of 640 meV, indicating a similar degree of localization on the Os. In contrast to $[Os(\eta\text{-}C_5H_5)_2]^+$ and its derivatives,[14-17] $^2A_{1/2}$ is the ground state for $[Os(\eta\text{-}C_6Me_6)NBu^t]^+$ and $[Os(\eta\text{-}1,4\text{-}(CHMe_2)MeC_6H_4)NBu^t]^+$; in the former cases the $^2A_{1/2}$ state lies intermediate in energy between the two ^2E states.

The IEs of A–C are lower for $Os(\eta\text{-}C_6Me_6)NBu^t$ than for $Os(\eta\text{-}1,4\text{-}(CHMe_2)MeC_6H_4)NBu^t$, in line with the relative donor effects of hexamethylbenzene and *p*-cymene. Band A differs in its IE by 0.3 eV between the two compounds whereas bands B and C differ by 0.45 eV.

Bands D and E are assigned to the two e_1 ionizations. Both shift by 0.4 eV to lower IE on replacement of *p*-cymene by hexamethylbenzene. (The shift of band E is less well defined than that of band D as band E is a shoulder in the spectrum of $Os(\eta\text{-}1,4\text{-}(CHMe_2)MeC_6H_4)NBu^t$, but the maximum is at least 0.3 eV and probably 0.4 eV higher.) This strongly suggests that the arene e_1 orbitals are significant contributors to both $1e_1$ and $2e_1$. The intensity increase of band E in the He II spectrum of $Os(\eta\text{-}C_6Me_6)NBu^t$ relative to band D could imply a higher 5d content in the associated orbital $1e_1$, thus suggesting that it is the analogue of a metallocene e_{1g} orbital. However, one should treat this conclusion cautiously as N 2p orbitals are also expected to increase in their cross section relative to C 2p orbitals when the ionization ratio is changed from He I to He II. Thus, the intensity increase noted might also be occasioned by the imido contribution to the $1e_1$ orbital being greater than the arene contribution.

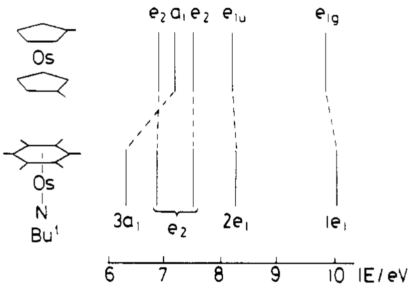

Figure 7. Comparison of the vertical IEs of $Os(\eta\text{-}C_6Me_6)NBu^t$ and $Os(\eta\text{-}C_5H_4Me)_2$.[14]

Figure 6 plots the vertical IE of the three compounds investigated and suggests a correlation between the bands. We are led to propose this correlation by the following considerations. First, as one changes from Os to Ir the nuclear charge increases so the d electrons should be more tightly bound, and bands A–C should occur at higher IE in the PE spectrum of $Ir(\eta\text{-}C_5Me_5)NBu^t$. Second, the spin–orbit splitting of the $^2E_2$ state should be greater for Ir than Os. Third, ionizations associated with the e_1 level of the carbocyclic ring should be of lower energy for C_5Me_5 than for C_6Me_6 or $1,4\text{-}(CHMe_2)MeC_6H_4$. The correlation proposed in Figure 6 is really the only one that fits these constraints. When the He I/He II intensity changes in the spectra of $Ir(\eta\text{-}C_5Me_5)NBu^t$ are examined, it is clear that bands A and C increase in intensity relative to the composite band B/D, confirming that the former two are metal-based ionizations. Assignments of the spectrum of $Ir(\eta\text{-}C_5Me_5)NBu^t$, listed in Table I, are therefore made on the basis of the established correlation with the spectra of the Os compounds.

If band E arose from an orbital localized on the metal–imido π-bond, we would expect its ionization energy to increase on passing from the osmium to the iridium compounds; as it is, it shows a significant decrease, suggesting again substantial ring π character. Band D shows a slightly greater decrease implying that the ring contribution to the $2e_1$ orbital is greater than that to the $1e_1$ orbital. The shifts found in bands D and E are thus consistent with the model of extensive interligand mixing in the e_1 MO and mimic that found in a sandwich compound where the more stable of the two e_1 MO has a substantial metal d contribution.

The metallocene analogy may be emphasized by comparing the vertical IEs of $Os(\eta\text{-}C_5H_4Me)_2$ with those of $Os(\eta\text{-}C_6Me_6)NBu^t$ (Figure 7). Careful choice of substituents gives a close correspondence of the two sets of IEs except for that of the $3a_1$ ionization. This orbital seems to be destabilized in the imido complex relative to the metallocene. The nonbonding nature of the a_1 orbital in sandwich compounds is well established.[19] The nodal cone of the d_{z^2} orbital intersects the lobes of the ring $p\pi$ orbitals resulting in minimal overlap. In the case of imido complexes the d_{z^2} orbital is expected to interact with the σ-donor orbital of the NR group. The interaction appears to result in a destabilization of the upper filled a_1 orbital.

One notable feature of the reaction chemistry of these Os and Ir imido compounds is the ready exchange that the imido ligand undergoes; this is in contrast to the relative inertness of many other imido compounds. We can identify two features of the bonding that may help to explain such reactivity. The first discussed above is the a_1 interaction leading to a destabilization of the σ bond between the metal and the imido group; this should lead to a relative weakening of the metal–nitrogen bond. The second

---

(18) Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; van Tilborg, J.; Robbins, J.; Smart, J. *J. Electr. Spectrosc. Relat. Phenom.* **1980**, *19*, 327.

(19) Cloke, F. G. N.; Dix, A. N.; Green, J. C.; Perutz, R. N.; Seddon, E. A. *Organometallics* **1983**, *2*, 1150.

is the nature of the $2e_1$ orbital as an in-phase (pseudo ungerade) combination of ring e_1 and nitrogen $p\pi$ orbitals with probably only a small combination of metal 6p to stabilize it. Thus, the $2e_1$ orbital may be regarded as approaching nonbonding character. This should also lead to a relative weakening of the bond and a further thermodynamic factor leading to its reactivity. The PES study has demonstrated that the $2e_1$ orbital is to a considerable extent localized on the nitrogen. It has also established an IE for this orbital which is compatible with significant proton affinity. Thus, a reaction pathway of electrophilic attack on the nitrogen suggests itself for an imido exchange reaction.

Acknowledgment. We thank the SERC for financial support, Dr. R. A. Andersen and Dr. R. G. Bergman for helpful discussions, and Dr. M. Bown for the sample of $Os(\eta\text{-}C_6Me_6)NBu^t$.

OM920396Q

Cleavage of Carbon–Silicon Bonds in the Presence of Silicon–Silicon Bonds by Electron-Transfer Reagents

A. Louis Allred,* Reginald T. Smart, and Donald A. Van Beek, Jr.

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received June 22, 1992

The unexpected undecamethylcyclohexasilyl anion, $Si_6Me_{11}^-$, was obtained in solution from the reactions of electron-transfer reagents including methyllithium, alkali metals, or trimethylsilyl anion with dodecamethylcyclohexasilane, Si_6Me_{12}, in the presence of either hexamethylphosphoramide or of 18-crown-6 in ether solvents. $Si_6Me_{11}^-$ was also prepared from Si_6Me_{12} in hexamethylphosphoramide by electrolytic reduction. $Si_6Me_{11}^-$ is a stable and useful intermediate that can be derivatized with a variety of electrophiles.

Introduction

Examples of the well-known cleavage of silicon–silicon bonds with alkali metals to give organosilanyl derivatives include the preparation of 1,4-dilithiooctaphenyltetrasilane from octaphenylcyclotetrasilane and lithium metal[1] and the cleavage of decamethyltetrasilane by sodium–potassium alloy to give a mixture of products of varying chain lengths.[2] Dodecamethylcyclohexasilane (Si_6Me_{12}, 1) has been cleaved by both sodium–potassium alloy[3] and lithium metal,[4] and in both cases the products were reported to be the linear chain compounds $M(SiMe_2)_nM$ (n = 2–6; M = Li, Na, K).

Alkylsilanyl anions may be prepared by several other routes. Bis(trialkylsilyl)mercury compounds have been cleaved by alkali metal to give $MSiR_3$ (M = Li, Na, K; R = Me, Et).[5] $LiSiMe_3$ is more easily prepared by the reaction of hexamethyldisilane with methyllithium in the presence of hexamethylphosphoramide (HMPA).[6] In a similar manner $KSiMe_3$ is prepared from hexamethyldisilane and potassium methoxide in a hexane solution of 18-crown-6.[7] In these reactions both HMPA and crown ether appear to enhance the reactivity by strongly solvating the alkali metals. Peralkylpolysilanyl anions such as $LiSi(SiMe_3)_3$ have been prepared by the cleavage of $Si(SiMe_3)_4$, or related compounds, by methyllithium.[8] The observed high stability of $LiSi(SiMe_3)_3$ was attributed to charge delocalization over contiguous silicon atoms.

Permethylcyclopolysilanes can also be reduced chemically and electrochemically at low temperatures to form anion radicals.[9] ESR spectra of $(SiMe_2)_n^{\bullet -}$ (n = 5–7) indicate that the unpaired electron density is delocalized over the ring, with hyperfine splitting showing equivalent interaction with all of the ring methyl groups. Several substituted methylcyclopolysilanes have also been reduced,[10] but in no case was carbon–silicon bond cleavage reported.

Apparently, facile cleavage by metallic or organometallic reagents of Si–alkyl bonds in compounds containing Si–Si bonds has not been reported. The Si–aryl bond in $SiPh_4$ is readily cleaved with potassium metal.[11] The resultant triphenylsilanyl anion bonds to a methyl group from the dimethoxyethane solvent to give $SiPh_3Me$, and subsequent reactions proceed to generate $SiPhMe_3$ and thus reflect the relative stability of the Si–alkyl bond.

To prepare synthetically useful organopolysilane intermediates, including α,ω-dilithiopermethylpolysilanes and related alkali metal derivatives of methylsilanes, we started an investigation of ring cleavage of dodecamethylcyclohexasilane (1) using organometallic and alkali metal reagents known to break silicon–silicon bonds. Observation of an unexpected reaction led to the synthesis and utilization of a cyclic methylpolysilane reagent, $Si_6Me_{11}^-$, as described herein.

Results

Preparation and Derivatization of $Si_6Me_{11}^-$ (2). The reaction of Si_6Me_{12} (1) with lithium metal in HMPA/Et_2O solution did not proceed with silicon–silicon bond cleavage as expected to give $Li(SiMe_2)_6Li$ but instead gave a red intermediate, $Si_6Me_{11}^-$ (2), the product of Si–C bond cleavage. Evidence that the formation of this product

---

[1] Jarvie, A. W. P.; Winkler, H. J. S.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1961**, *83*, 1921.

[2] Stolberg, U. G. *Z. Naturforsch.* **1963**, *18B*, 765.

[3] Stolberg, U. G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 150.

[4] Gilman, H.; Fearon, F. W. G.; Harrell, R. L. *J. Organomet. Chem.* **1966**, *5*, 592.

[5] Gladyshev, E. N.; Fedorona, F.; Yuntila, L. O.; Razuvaev, G. A.; Vyazankin, N. S. *J. Organomet. Chem.* **1975**, *96*, 169.

[6] Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.

[7] Sakurai, H.; Kira, M.; Umino, H. *Chem. Lett.* **1977**, 1265.

[8] Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1968**, *14*, 91.

[9] Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.

[10] (a) West, R.; Kean, E. S. *J. Organomet. Chem.* **1975**, *96*, 323. (b) Buchanan, A. C., III; West, R. *J. Organomet. Chem.* **1979**, *172*, 273.

[11] Benkeser, R. A.; Severson, R. G. *J. Am. Chem. Soc.* **1951**, *73*, 1424. Wan, Y.-P.; O'Brien, D. H.; Smentowski, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7680.

0276-7333/92/2311-4225$03.00/0