Inorg. Chem. **1985**, *24*, 567-570

Contribution from the Department of Chemistry, University of California,
and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Photoelectron Spectroscopic Study of the Bonding in Borane Adducts

DAVID B. BEACH and WILLIAM L. JOLLY*

Received April 11, 1984

The bonding in the adducts $BH_3\cdot NH_3$, $BH_3\cdot N(CH_3)_3$, $BH_3\cdot CO$, $BH_3\cdot CNCH_3$, $BH_3\cdot PF_3$, and $BH_3\cdot P(CH_3)_3$ are studied by using a combination of valence ionization potentials and core binding energies. The data indicate that π back-bonding is significant only in $BH_3\cdot CO$ and $BH_3\cdot PF_3$. The stabilization of the Lewis base lone pair upon coordination to BH_3 is correlated with the proton affinity of the Lewis base. It is proposed that the strengthening of the C–O bond in CO and the C–N bond in CH_3NC upon coordination to BH_3 is a consequence of rehybridization of the carbon σ orbitals.

In a transition-metal carbonyl compound, the bonding between the metal atom and carbonyl group is due principally to the overlap of the filled dπ orbitals of the metal with the empty π^* orbital of the carbon monoxide. The marked decrease in the C–O stretching force constant upon coordination of the CO to the transition metal is convincing evidence for such d$\pi \rightarrow \pi^*$ bonding. In non-transition element carbonyl complexes and in carbon monoxide adsorbed on non-transition element solids, where no dπ valence electrons are available, the bonding to the carbonyl group has generally been described mainly or exclusively in terms of σ donor bonding from the lone pair of the carbon atom.[1-3] The slight increase in the C–O force constant in the latter cases has usually been ascribed to a slight antibonding character of the carbon lone pair orbital of CO.[2-4]

However, in a molecule such as borane carbonyl, $BH_3\cdot CO$, the possible effects of hyperconjugation must also be considered. The B–C bond in $BH_3\cdot CO$ has often been described as a combination of a σ donor–acceptor bond (from the carbon lone pair to the empty σ orbital of the BH_3 group) and a π donor–acceptor bond (from the bonding MO of the BH_3 group to the empty π^* orbital of CO).[5-7] This picture of the bonding, in which the strengthening of the σ C–O bond tends to cancel the weakening of the π C–O bond, rationalizes the fact that the C–O force constant of $BH_3\cdot CO$ is only slightly greater than that of free CO.[8] However, the ionization potential of the B–C σ-bonding MO of $BH_3\cdot CO$ is 14.13 eV, only slightly greater than that of the CO carbon lone pair, 14.01 eV.[9] This fact has been interpreted[7,10] as evidence for an exceedingly weak σ B–C bond and thus implies that the not negligible dissociation energy of $BH_3\cdot CO$ is mainly due to π bonding.

We believe that shifts in valence ionization potential are best interpreted with core binding energies to correct for the effects of atomic charge and relaxation energy.[11] Therefore, to attempt clarification of the bonding in $BH_3\cdot CO$ and other borane adducts for which valence shell photoelectron spectra have been reported, we need the core binding energies of these molecules. The core binding energies are presented in Table I.[12] Most of these data are new; the experimental details are given in the Experimental Section.

π Bonding

In all of the borane adducts, the HOMO is the BH_3 bonding MO of e symmetry, which we shall refer to as e(BH_3). The only borane adduct in which the e(BH_3) orbital cannot conceivably interact with another MO of the molecule is the BH_4^- ion, for which the gas-phase core binding energy is unknown. In the absence of an ideal e(BH_3) reference, we have chosen the e(BH_3) orbital of $BH_3\cdot NH_3$ as a reference against which to measure the relative bonding or antibonding characters of the e(BH_3) orbitals in the other borane adducts. For example, the relative stabilization of the e(BH_3) orbital in $BH_3\cdot CO$ was calculated as follows.[14,15] To obtain the e(BH_3) ionization potential for $BH_3\cdot CO$ corresponding to the hypothetical situation in which the net stabilization or destabilization of the e(BH_3) orbital is equal to that in $BH_3\cdot NH_3$, we add eight-tenths of the B 1s binding energy difference between $BH_3\cdot CO$ and $BH_3\cdot NH_3$ to the e(BH_3) ionization potential of $BH_3\cdot NH_3$. This reference ionization potential, 11.71 eV, is 0.5 eV lower than the actual e(BH_3) ionization potential of $BH_3\cdot CO$. From the summary of such calculations for all the adducts, shown in Table II, we see that only in the cases of $BH_3\cdot CO$ and $BH_3\cdot PF_3$ is the e(BH_3) orbital stabilized significantly relative to the e(BH_3) orbital of $BH_3\cdot NH_3$.

The origin of this stabilization in $BH_3\cdot CO$ is probably back-bonding to the π^* orbital of CO. The subject of π bonding in $BH_3\cdot CO$ and $BH_3\cdot CNCH_3$ will be treated in more detail in a subsequent section.

The stabilization of the e(BH_3) orbital in $BH_3\cdot PF_3$ could arise from back-bonding to either the σ^*(P–F) or the P dπ orbitals of PF_3. We believe that our data strongly suggest that P dπ bonding is far more important than σ^*(P–F) bonding. π acceptance by the σ^*(P–F) orbital should lead to an increase in negative charge on the fluorine atoms of PF_3, which should result in a lowering of the F 1s binding energy on going from PF_3 to $BH_3\cdot PF_3$. In fact, the F 1s binding energy *increases* slightly on complex formation, indicating a net flow of electron density in the opposite direction. Further evidence for an increase in positive charge on the fluorine atoms comes from the multiplicity weighted average fluorine lone pair ionization potential of PF_3, which increases from 17.0 to 17.3 eV on complex formation.[16] The P–F bond of PF_3 also becomes slightly shorter[17] on adduct formation, also indicating little π acceptance by the σ^*(P–F) orbitals.

The phosphorus $2p_{3/2}$ binding energy[12,13] is unchanged on complex formation, indicating that the flow of electron density from the phosphorus lone pair is balanced by an increase in relaxation energy on complex formation and by the flow of electron density back into the empty P dπ orbitals.

σ Bonding

The core binding energies of the donor atom in the free Lewis base and in the borane adduct can be used to calculate the expected shift in the Lewis base lone pair ionization potential upon formation of the borane adduct, assuming no σ interaction between the base and the BH_3 group. Addition of this shift to the free-base lone pair ionization potential (column 2 of Table III) gives the reference ionization potential (column 3 of Table III) or hypo-

---

(1) Brown, T. L.; Darensbourg, D. J. *Inorg. Chem.* **1967**, *6*, 971.
(2) Tevault, D.; Nakamoto, K. *Inorg. Chem.* **1976**, *15*, 1282.
(3) D'Amico, K. L.; Trenary, M.; Shinn, N. D.; Solomon, E. I.; McFeely, F. R. *J. Am. Chem. Soc.* **1982**, *104*, 5102.
(4) DeKock, R. L.; Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1971**, *10*, 38.
(5) Burg, A. B. *Rec. Chem. Prog.* **1954**, *15*, 159.
(6) Graham, W. A. G.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1956**, *3*, 164.
(7) Ermler, W. C.; Glasser, F. D.; Kern, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 3799.
(8) Jones, L. H.; Taylor, R. C.; Paine, R. T. *J. Chem. Phys.* **1979**, *70*, 749.
(9) Lloyd, D. R.; Lynaugh, N. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 947.
(10) DeKock, R. L.; Gray, H. B. "Chemical Structure and Bonding"; Benjamin/Cummings: Menlo Park, CA, 1980; pp 322–324.
(11) Jolly, W. L. *Acc. Chem. Res.* **1983**, *16*, 370.
(12) Core binding energies for the free Lewis base molecules are given in ref 13.
(13) Jolly, W. L.; Bomben, K. D.; Eyermann, C. J. *At. Data Nucl. Data Tables*, in press.
(14) For a detailed description of the method, see ref 11 and 15.
(15) Jolly, W.; Eyermann, C. J. *J. Phys. Chem.* **1982**, *86*, 4834.
(16) Hillier, I. H.; Marriot, J. C.; Saunders, V. R.; Ware, M. J.; Lloyd, D. R.; Lynaugh, N. *J. Chem. Soc., Chem. Commun.* **1970**, 1586.
(17) Bock, H. *Pure Appl. Chem.* **1975**, *44*, 343.

0020-1669/85/1324-0567$01.50/0

Table I. Core Binding Energies and Full-Widths at Half-Maximum (eV) for Borane Adducts

	B 1s		Lewis base donor atom level		other levels	
	E_B	fwhm	E_B	fwhm	E_B	fwhm
$BH_3{\cdot}NH_3$	193.73 (4)[a]	1.64 (10)	408.41 (2)	1.61 (6)		
$BH_3{\cdot}N(CH_3)_3$[b]	193.37		406.68			
$BH_3{\cdot}CO$[c]	195.10 (6)	1.73 (16)	296.18 (4)	1.25 (17)	542.05 (2)[d]	1.50 (8)
$BH_3{\cdot}CNCH_3$	193.60 (3)	1.63 (10)	293.43 (3)	1.07 (7)	294.06 (7)[e] 407.13 (2)[f]	1.23 (15) 1.29 (8)
$BH_3{\cdot}PF_3$	194.69 (5)	1.49 (14)	141.79 (3)	1.37 (5)	694.30 (2)[g]	1.69 (6)
$BH_3{\cdot}P(CH_3)_3$[b]	192.93		137.17			

[a] 2σ value of least-squares fit of data indicated parenthetically. [b] Reference 13. [c] Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *J. Am. Chem. Soc.* 1984, *106*, 536. [d] O 1s level. [e] C 1s of CH_3 group. [f] N 1s level. [g] F 1s level.

Table II. Stabilization of the $e(BH_3)$ Orbital of $BH_3{\cdot}L$, Relative to $BH_3{\cdot}NH_3$ (eV)

	IP		
compd	$e(BH_3)$[a]	(calcd) ref $e(BH_3)$ level[b]	increase of IP over ref value
$BH_3{\cdot}NH_3$	10.61[c]	(10.61)	(0.0)
$BH_3{\cdot}N(CH_3)_3$	10.32[c]	10.32	0.0
$BH_3{\cdot}CO$	12.22[c]	11.71	0.5
$BH_3{\cdot}CNCH_3$	10.52[d]	10.51	0.0
$BH_3{\cdot}PF_3$	12.0[e]	11.38	0.6
$BH_3{\cdot}P(CH_3)_3$	10.0[f]	10.0	0.0

[a] Average of Jahn-Teller split bands. [b] Calculated with the B 1s core binding energies of $BH_3{\cdot}L$ and the reference compound, $BH_3{\cdot}NH_3$. [c] Reference 9. [d] Reference 24. [e] Reference 16. [f] Bock, H.; Elbel, S.; Schmidbaur, H.; Vornberger, W., unpublished results, quoted in ref 17.

Table III. Stabilization of the Lewis Base Lone Pair Orbitals in Borane Adducts (eV)

	IP			
compd	:L	(calcd) ref $\sigma(BH_3\text{-}L)$ level[a]	$\sigma(BH_3\text{-}L)$	increase of IP[$\sigma(BH_3\text{-}L)$] over ref value
$BH_3{\cdot}NH_3$	10.84[b]	13.09	13.92[c]	0.83
$BH_3{\cdot}N(CH_3)_3$	8.45[c]	9.95	11.51[c]	1.56
$BH_3{\cdot}CO$	14.01[d]	13.96	14.13[c]	0.17
$BH_3{\cdot}CNCH_3$	11.24[e]	12.09	12.70[e]	0.61
$BH_3{\cdot}PF_3$	12.29[f]	12.30	~12.9[g]	~0.6
$BH_3{\cdot}P(CH_3)_3$	8.6[h]	9.6	10.9[i]	1.3

[a] Calculated from IP(:L) and the donor atom core binding energies of L and $BH_3{\cdot}L$. Core binding energies of L taken from ref 13 and 19. [b] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* 1975, *97*, 4136. [c] Reference 9. [d] Reference 20. [e] Reference 24. [f] Bassett, P. J.; Lloyd, D. R. *J. Chem. Soc., Dalton Trans.* 1972, 248. [g] Reference 16. [h] Cradock, S.; Ebsworth, E. A. V.; Savage, W. J.; Whiteford, R. A. *J. Chem. Soc., Faraday Trans. 2* 1972, *68*, 934. [i] Table II, footnote *f*.

thetical ionization potential corresponding to no σ interaction. In the last column of Table III are listed the differences between the actual $\sigma(BH_3{\cdot}L)$ ionization potentials and the reference values. These values represent the stabilization of the base lone pairs due to σ donor interaction with the borane group. Fortuitously, the lone pair stabilization energies in $BH_3{\cdot}CO$ and $BH_3{\cdot}PF_3$ are approximately the same as would be calculated from the uncorrected ionization potentials of the free Lewis bases. However, this is not true for the other adducts, where errors as great as 2.2 eV would be made by using the uncorrected ionization potentials.

The only Lewis acid that has no π acceptor or π donor character is the proton. Therefore, one might expect a correlation of the lone pair stabilization energies in the borane adducts with the corresponding Lewis base proton affinities.[18,19] Indeed, a plot of the stabilization energies vs. proton affinities, shown in Figure 1, shows a positive correlation, with a correlation coefficient of 0.920. The stronger Lewis bases are more effective in transferring negative charge to the boron atom in the adduct. Thus, the plot of boron 1s binding energies (which are expected to be lower when the boron atom is more negatively charged) vs. proton affinities, shown in Figure 2, shows a negative correlation, with a correlation coefficient of −0.970.

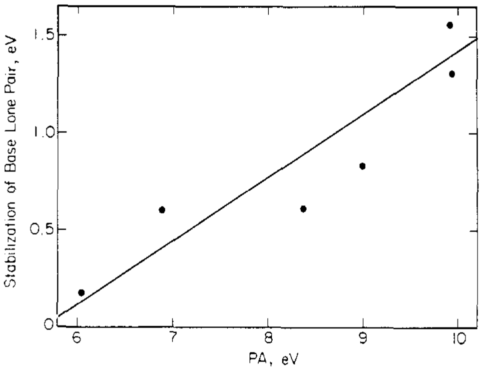

Figure 1. Plot of the stabilization energy of the base lone pair (from last column in Table III) vs. proton affinity of base.

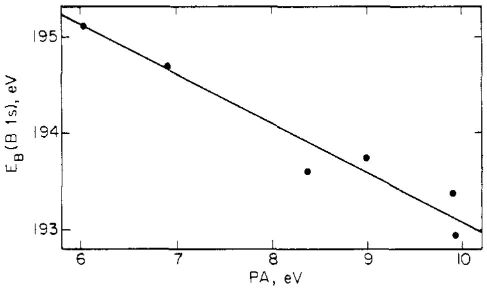

Figure 2. Plot of boron 1s binding energy of BH_3 adduct vs. proton affinity of base.

Bonding in $BH_3{\cdot}CO$ and $BH_3{\cdot}CNCH_3$

Using core binding energies, one can calculate the changes in the ionization potentials of CO and $CNCH_3$ due to changes in charge and relaxation energy that occur when these molecules form borane adducts. These corrected ionization potentials for the adducts may then be used to construct an energy diagram that illustrates the changes in the bonding character of the orbitals of CO and $CNCH_3$ when coordinated by a BH_3 group.

There are three bands in the He I photoelectron spectrum of CO.[20] These ionization potentials correspond to the 5σ carbon lone pair orbital, the 1π C–O π orbital, and the 4σ C–O σ orbital, which is largely oxygen in character. The carbon core binding energy difference between CO and $BH_3{\cdot}CO$ is used to correct the 5σ ionization potential; the average of the carbon and oxygen

---

(18) Jolly, W. L. "Modern Inorganic Chemistry"; McGraw-Hill: New York, 1984; p 174.

(19) For the PA of CH_3NC, see: Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 536.

(20) Turner, D. W.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: London, 1970.

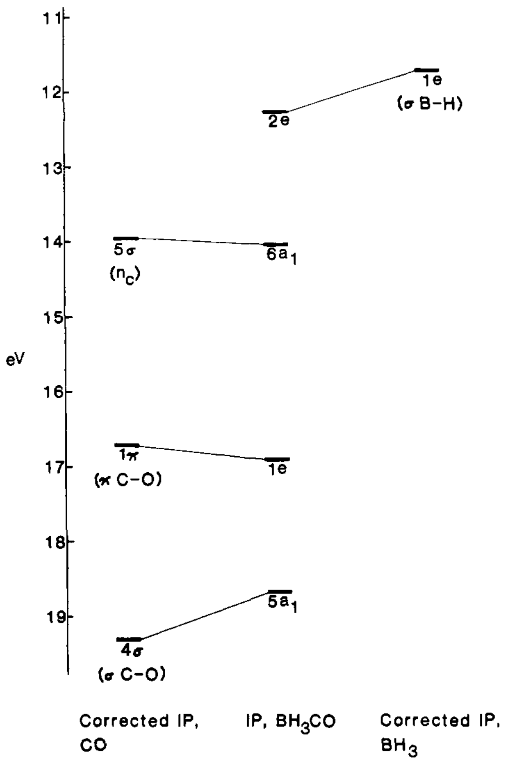

Figure 3. Energy level diagram showing the ionization potentials of CO (corrected for the charge and relaxation energy changes on going from free CO to BH_3·CO), the ionization potentials of BH_3·CO, and a corrected ionization potential of BH_3.

binding energy differences is used to correct the 1π ionization potential, and the oxygen binding energy difference is used to correct the 4σ ionization potential. An energy level diagram using these corrected ionization potentials, the ionization potentials of BH_3·CO, and the e(BH_3) ionization potential calculated with BH_3·NH_3 as a reference is shown in Figure 3.

In methyl isocyanide, four ionizations are observed in the He I spectrum,[20] corresponding to the $7a_1$ carbon lone pair orbital, the 2e C–N π orbital, the 1e pseudo π C–H σ orbital, and the $6a_1$ C–N σ orbital. The $7a_1$, 2e, and $6a_1$ ionization potentials were corrected analogously to their CO counterparts, and the 1e orbital was corrected with the methyl carbon binding energy difference between $CNCH_3$ and BH_3·$CNCH_3$. An energy level diagram for BH_3·$CNCH_3$ is shown in Figure 4.

The π-bonding interactions in BH_3·CO and BH_3·$CNCH_3$ are relatively straightforward. The filled 1π orbital of CO and the 2e orbital of $CNCH_3$ are both stabilized approximately 0.3 eV by interaction with a filled e(BH_3) orbital. In BH_3·$CNCH_3$, the C–N π* orbital stabilizes the e(BH_3) orbital by the same amount that it is destabilized by the filled C–N π orbital. The net effect is that the energy of the e(BH_3) orbital is unchanged, although electron density from this orbital has been delocalized into the $CNCH_3$ π orbitals, contributing to B–C bonding. The 1e orbital, which is localized on the methyl group, is unchanged in bonding character. In BH_3·CO, the CO π* orbital interacts more strongly with the e(BH_3) orbital, so that the latter orbital is significantly (0.5 eV) stabilized. This flow of negative charge back to the CO group is reflected in the decreased carbon and oxygen binding energies on going from CO to BH_3·CO.

The σ-bonding interactions are more complex. The 5σ orbital of CO is only slightly stabilized on coordination by the BH_3 group. If one only considered HOMO–LUMO interactions, one would conclude that σ bonding in BH_3·CO is negligible. However, it is possible that the $7a_1$ lone pair orbital of the complex is energetically poised about midway between the empty $8a_1$ orbital (the BH_3 "acceptor" orbital) and the $6a_1$ B 2s orbital. In such a situation, the $8a_1$ orbital would be destabilized about as much as the $6a_1$ orbital would be stabilized, with little net stabilization or destabilization of the $7a_1$ orbital. However, an overall stabilization of the system, corresponding to the σ bonding, would result because of the occupancy of the $6a_1$ orbital.

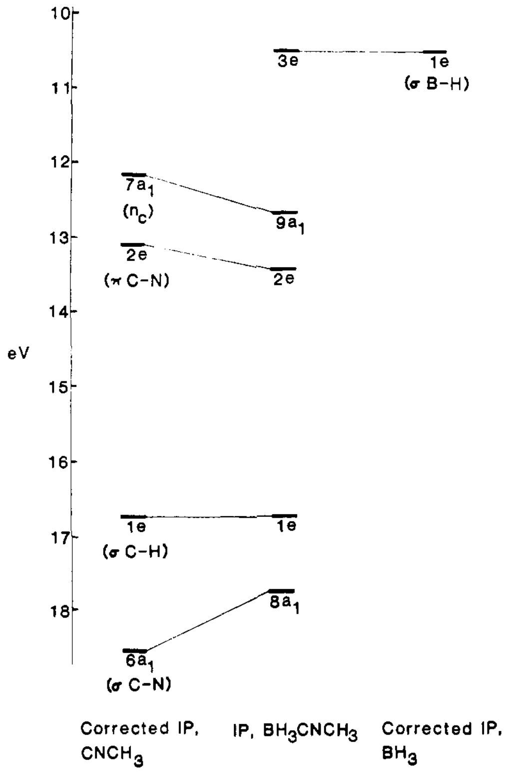

Figure 4. Energy level diagram showing the ionization potentials of $CNCH_3$ (corrected for charge and relaxation energy changes on going from free $CNCH_3$ to BH_3·$CNCH_3$), the ionization potentials of BH_3·$CNCH_3$, and the ionization potential of BH_3.

Further support for this explanation is found in the shift in the 4σ ionization potential of CO. On formation of the borane adduct, this orbital is significantly *destabilized.* This destabilization is undoubtedly due to a repulsive interaction with the orbital of mainly B 2s character, which lies just beyond the range of He I ionization. In the complexes studied by Lloyd and Lynaugh,[9] the only complex in which the "B 2s" ionization potential could be observed with any certainty (at 18.04 eV) was BH_3·$N(CH_3)_3$. In BH_3·$N(CH_3)_3$ it would be expected that there would be a very strong repulsive interaction between the "B 2s" and "N 2s" orbitals, causing the "B 2s" orbital ionization to be at a significantly lower ionization potential than in BH_3·CO. Hence, it is reasonable to propose that the ionization potential of the "B 2s" orbital in BH_3·CO lies slightly higher than 21 eV.

The σ-bonding interactions in BH_3·$CNCH_3$ are very similar. The $7a_1$ orbital of $CNCH_3$ lies higher in ionization potential than does its CO counterpart, so there is less repulsive interaction with the "B 2s" orbital and a greater net stabilization. Once again, the orbital at higher ionization potential, $6a_1$, is significantly destabilized by interaction with the "B 2s" orbital of BH_3.

Rehybridization

The strengthening of the C–O bond on going from CO to non-transition element adducts such as BH_3·CO has usually been ascribed to a withdrawal of electron density from the antibonding carbon lone pair orbital of CO. Unfortunately, whether this lone pair orbital is considered antibonding or bonding appears to depend on whether one uses Mulliken overlap population analysis[4] or orbital contour plots,[21] respectively, to determine the orbital character.

The fact that the vibrational frequency of CO increases from 2143 to 2160 cm^{-1} upon ionization of the lone pair orbital[20] suggests, but does not prove, that the orbital is slightly antibonding.

---

(21) Streitwieser, A.; Owens, P. H. "Orbital and Electron Density Diagrams"; Macmillan: New York, 1973; pp 92–96.

(22) Watari, F. *Inorg. Chem.* **1982**, *21*, 1442.

Undoubtedly the orbital is strongly modified by rehybridization either by removal of an electron from the orbital or by coordination to a Lewis acid. When the carbon lone pair loses an electron or becomes engaged in bonding, it acquires more p character, and the opposite carbon σ orbital (4σ, which is involved in the C–O σ bond) acquires more s character. This increase in s character increases the strength of the C–O bond. Theoretical work of Sherwood and Hall[23] has shown that, even in long-distance interactions of CO with a transition metal, σ rehybridization occurs, with a shift of the lone pair electron density toward the metal and a shortening of the C–O bond.

In the case of $BH_3 \cdot CO$, the extent to which the C–O bond is strengthened by such rehybridization cannot be simply determined from measures of the C–O bond strength (such as the C–O stretching frequency) because π back-bonding causes a simultaneous *weakening* of the bond. However, the situation is simpler in the case of the methyl isocyanide adduct of borane, $BH_3 \cdot CNCH_3$, because there is little π back-bonding in this molecule. The marked increase in the C–N stretching frequency of 150 cm^{-1} on going from CH_3NC to the adduct[22] must be due entirely to rehybridization of the σ N–C–B system. This conclusion is supported by an ab initio study of CH_3NC that shows that the HOMO has bonding character.[24]

Experimental Section

Diborane was prepared by the reaction of $NaBH_4$ and H_3PO_4.[25] Methyl isocyanide was prepared by the dehydration of *N*-methylformamide.[26] The borane–methyl isocyanide adduct[22] is relatively nonvolatile and was found to form higher oligomers when heated. In order to obtain an adequate flow of vapor into the spectrometer gas cell, the compound was prepared in a 2-l bulb attached to a 2.5-cm valve that led directly to the spectrometer inlet system. Excess methyl isocyanide was condensed over most of the interior surface of the bulb by slowly raising a liquid-nitrogen-filled Dewar around the bulb as the methyl isocyanide was admitted. Diborane was condensed in the flask, and it was allowed to warm to room temperature. The volatile residue was pumped off, leaving the adduct. Sufficient vapor evolved from the solid distributed over this large surface area to obtain spectra at room temperature. The infrared spectrum of the solid in the sample flask agreed with that in the literature.[22]

Borane–phosphorus trifluoride was prepared by the method of Parry and Bissot,[27] in which B_2H_6 is reacted with excess PF_3 (8 atm) for 3 days. The product was purified by fractional condensation, and its vapor pressure (23 mm at -111.8 °C) agreed with that in the literature. To minimize the dissociation of $BH_3 \cdot PF_3$, the sample was stored at -196 °C, fractionated immediately prior to use, and held at -111.8 °C during the collection of spectra. The B_2H_6 B 1s peak is separated from the B 1s peak of the adduct by more than 2 eV and was not observed. The measured phosphorus and fluorine binding energies of $BH_3 \cdot PF_3$ are very similar to those of PF_3, so that free PF_3 would not be readily observed. The absence of a peak attributable to diborane is our principal evidence that the compound does not dissociate under the conditions of measurement.

Borane–ammonia was obtained commercially (Alfa) and was sublimed before use. The spectrometer was heated to 50 °C, at which temperature a very weak signal was obtained. Attempts to use higher temperatures resulted in decomposition. The half-widths of the B 1s and N 1s lines were unusually broad, probably because of spectrometer drift during the 20 h necessary to obtain the spectra, even though a drift correction was applied every 30 min.

Gas-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 spectrometer utilizing a Mg anode. Nitrogen gas served as the internal calibrant, and the Ne 1s, N_2 1s, and Ne 2s photolines were used to determine the linearity of the spectrometer. Procedural details have been described elsewhere.[28]

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-A003-76SF00098.

Registry No. $BH_3 \cdot NH_3$, 13774-81-7; $BH_3 \cdot N(CH_3)_3$, 75-22-9; $BH_3 \cdot CO$, 13205-44-2; $BH_3 \cdot CNCH_3$, 62630-46-0; $BH_3 \cdot PF_3$, 14931-39-6; $BH_3 \cdot P(CH_3)_3$, 1898-77-7.

---

(23) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93.

(24) Bevan, J. W.; Sandorfy, C.; Pang, F.; Boggs, J. E. *Spectrochim. Acta, Part A* **1981**, *37A*, 601.

(25) Norman, A. D.; Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 15.

(26) Cassanova, J. C.; Parry, R. W. *J. Am. Chem. Soc.* **1963**, *85*, 4280.

(27) Parry, R. W.; Bissot, T. C. *J. Am. Chem. Soc.* **1956**, *78*, 1524.

(28) Chen, H. W.; Jolly, W. L.; Kopf, J.; Lee, T. H. *J. Am. Chem. Soc.* **1979**, *101*, 2607.

Contribution from the Istituto di Chimica Generale ed Inorganica, University of Padova, 35100 Padova, Italy, and Istituto di Chimica Generale ed Inorganica, University of Torino, Torino, Italy

UV Photoelectron and Theoretical Studies of Organometal Carbonyl Clusters of Ruthenium and Osmium. μ-Hydrido–μ_3-Allyl and μ-Hydrido–μ_3-Allenyl Triangulo Cluster Compounds

GAETANO GRANOZZI,*[1a] EUGENIO TONDELLO,[1a] RENZO BERTONCELLO,[1a] SILVIO AIME,[1b] and DOMENICO OSELLA[1b]

Received March 21, 1984

The electronic structures of μ-hydrido–μ_3-allyl and μ-hydrido–μ_3-allenyl triangulo clusters of ruthenium and osmium are discussed on the basis of both He I and He II gas-phase UV–PE spectra and CNDO quantum-mechanical calculations. The theoretical results contribute to the discussion of the PE data and to a deeper understanding of the bonding scheme in these very complex organometallic clusters. The description of the allyl cluster interactions in terms of one π and two σ bonds seems to be adequate. On the other hand, the formal distinction into one σ and two π bonds of the allenyl ligand cluster interaction is quite an oversimplification of the actual bonding scheme. The differences in thermodynamical stability between the allenyl and allyl derivatives are in agreement with the CNDO-computed total energies.

Introduction

It is now well established that many reactions involving $M_3(CO)_{12}$ clusters (M = Ru, Os) often afford hydrido–organometal clusters by oxidative addition of the incoming ligand.[2] In particular, in the thermal reactions of $M_3(CO)_{12}$ with alkynes (L–H) (contg. a hydrogen atom on the carbon in α position to the unsaturated sites) two isomeric compounds of formula $HM_3(CO)_9(L)$ are usually formed in good or moderate yields.[3–6]

---

(1) (a) University of Padova. (b) University of Torino.

(2) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.

(3) Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta* **1974**, *8*, 71.

(4) Aime, S.; Milone, L.; Osella, D.; Valle, M. *J. Chem. Res. Synop.* **1978**, *77*; *J. Chem. Res., Miniprint* **1978**, *77*, 785–797.

(5) Ferrari, R. P.; Vaglio, G. A. *J. Organomet. Chem.* **1979**, *182*, 245.

(6) Ferrari, R. P.; Vaglio, G. A. *Gazz. Chim. Ital.* **1975**, *105*, 939.