

adduct similar to **3**, the dihedral angle between the isopropylidene functions being  $52.3^\circ$ .<sup>6</sup>

Passage of the phenyl past the "inside" methyl results in racemization, a process that must possess a rather high activation energy barrier.<sup>7</sup> Adducts **3** and **5** show no tendency to undergo racemization over the course of several weeks at room temperature. The ease of preparation of chiral alkenylidenecyclopropanes containing a wide variety of functions attached to the cyclopropane and terminal allene carbon will allow the facile preparation of variously substituted chiral 1,2-alkylidenecyclopentanes related to **3** for structural and racemization kinetic studies. The results of such studies will complement and extend the results derived with chiral substituted biphenyls. Such studies have been initiated in our laboratories.

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(6) D. J. Pasto and W. R. Scheidt, unpublished observation.

(7) Kiefer and coworkers have measured the activation energies for the racemization of a 1,2-bis(isopropylidene)cyclobutane and -cyclohexane deriving values of <12 and 21.1 kcal/mol, respectively: see E. F. Kiefer, T. J. Levek, and T. T. Bopp, *J. Amer. Chem. Soc.*, **94**, 4751 (1972) and references cited therein.

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### Concerning the Ultraviolet Photoelectron Spectra of Osmium and Ruthenium Tetroxide

Sir:

McGlynn and coworkers<sup>1</sup> have recently reported He-I (21.21 eV) photoelectron (PE) spectra of the tetroxides, OsO<sub>4</sub> and RuO<sub>4</sub>. The spectra were interpreted in terms of an orbital ionization sequence  $3t_2 < 1t_1 < 2a_1 < 1e < 2t_2$  for OsO<sub>4</sub> and  $3t_2 < 1t_1 < 1e < 2a_1 < 2t_2$  in the case of RuO<sub>4</sub>. (The numbering scheme for the molecular orbitals ignores those correlating with the core orbitals of oxygen or the metal atom.) We wish to argue for an alternative assignment of the PE spectra, while pointing out that, in the case of RuO<sub>4</sub>, the He-I spectrum contains a strong impurity band incorrectly ascribed to the ruthenium compound.

The OsO<sub>4</sub> spectrum reproduced by McGlynn and coworkers is in good agreement with He-I spectra measured in Oxford<sup>2,3</sup> (though the band system commencing at ca. 16 eV is poorly characterized in the published spectrum). The He-I spectra of RuO<sub>4</sub> are in less good agreement, however. In particular, the spectrum reported by McGlynn, *et al.*,<sup>1</sup> shows a band that is absent in our spectrum (Figure 1).<sup>2b</sup> The position of this spurious structure is indicated by the arrow in the figure.<sup>3</sup> The same impurity (probably CO<sub>2</sub>) may also be responsible for a weak signal observed in the OsO<sub>4</sub>

(1) S. Foster, S. Felps, L. C. Cusachs, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **95**, 5521 (1973).

(2) (a) J. H. D. Eland, private communication, 1970; (b) S. Evans, A. Hamnett, and A. F. Orchard, unpublished work.

(3) The measurements on RuO<sub>4</sub> were less than straightforward since, as McGlynn and coworkers found,<sup>1</sup> the material has a damaging effect on channel electron multipliers. The spectra obtained on first admitting the RuO<sub>4</sub> vapor into the spectrometer did show the impurity band but this diminished in intensity as time progressed and eventually disappeared.

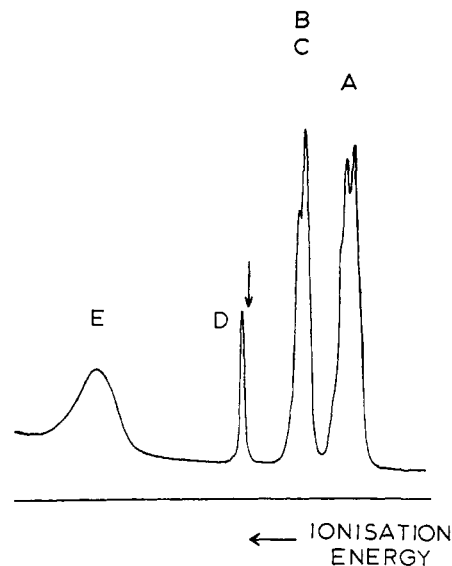


Figure 1. The He-I photoelectron spectrum of RuO<sub>4</sub>.

spectrum at 13.87 eV ionization energy. The He-I spectra of RuO<sub>4</sub> and OsO<sub>4</sub> have also been measured by Diemann and Müller.<sup>4</sup> The RuO<sub>4</sub> spectrum was not reproduced, but the tabulated ionization energy data indicate that it is also free from the spurious band observed by McGlynn and coworkers. However, both the RuO<sub>4</sub> and OsO<sub>4</sub> spectra show an impurity band at around 15.5 eV ionization energy, which was not recognized as such by the German workers.

Our own data for RuO<sub>4</sub> are summarized in Table I.

Table I. Ionization Energy Data (eV) for OsO<sub>4</sub> and RuO<sub>4</sub><sup>a</sup>

Band system	OsO <sub>4</sub>	RuO <sub>4</sub>	Assignment <sup>b</sup>
A <sup>c</sup>	12.35	12.15	1t <sub>1</sub>
	12.47	12.25	
	12.58	(12.35)	
	(12.68)	(12.45)	
	13.12		
B	13.24	12.92	3t <sub>2</sub>
	13.35	(13.01)	
		(13.10)	
C	13.53	(13.20)	1e
	13.64		
	13.74		
D	14.65	13.93	2a <sub>1</sub>
	14.76	0.5	
	16.40		
E	16.40	16.1	2t <sub>2</sub>
	16.76	1.7	

<sup>a</sup> The spectra, excited by He-I (21.2 eV) radiation, were measured on an instrument described by Evans, *et al.* (*Int. J. Mass Spectrom. Ion Phys.*, **7**, 261 (1971)). The most intense vibrational elements are indicated by the use of *italics*. The relative band intensities (band areas) for the various band systems, normalized with respect to band A (intensity = 3.0), are given after braces. <sup>b</sup> The assignment is specified in terms of the molecular subshell that is ionized. <sup>c</sup> Band in the OsO<sub>4</sub> spectrum contains additional, poorly resolved vibrational structure at 12.39, 12.42, 12.45, 12.51, 12.54, and 12.60 eV ionization energy.

The correspondence between the two spectra is not entirely obvious, but we believe that the counterparts of the well-separated band systems, B and C, in the OsO<sub>4</sub> spectrum are unresolved in the case of RuO<sub>4</sub>.

(4) E. Diemann and A. Müller, *Chem. Phys. Lett.*, **19**, 538 (1973).

The assignment ventured in Table I is necessarily different from those suggested by McGlynn, *et al.*,<sup>1</sup> and Diemann and Müller,<sup>4</sup> though we would infer the same sequence of orbital ionization as the latter workers, namely  $1t_1 < 3t_2 < 1e < 2a_1 < 2t_2$ . In the case of  $\text{OsO}_4$ , we differ from McGlynn and coworkers only with regard to the assignment of the first two PE bands. The identification of the first band with the  ${}^2T_2(3t_2^-)$  ion state was based on a detailed analysis of its vibrational fine structure and, in particular, on the discovery of a vibronic splitting of some  $50\text{ cm}^{-1}$  in the secondary vibrational progression associated with the  $\nu_2(e)$  mode. Yet it is by no means inconceivable that such fine structure might arise for the  $t_1$  ionizations, despite the non-bonding character of the  $t_1$  orbitals. We recall that a vibronic splitting of almost  $0.1\text{ eV}$  ( $\sim 800\text{ cm}^{-1}$ ) is observed in the  ${}^2T_1(t_1^-)$  band of  $\text{CBr}_4$ . We prefer to associate the first band in both the  $\text{OsO}_4$  and  $\text{RuO}_4$  spectra with the  ${}^2T_1$  ion state, an assignment based in part on analogy with the case history for  $\text{TiCl}_4$  and  $\text{TiBr}_4$  (also  $d^0$  molecules),<sup>5</sup> and in part on the currently accepted sequence of one-electron energy levels deduced from the electronic absorption spectra of both tetroxo ( $\text{MO}_4$ )<sup>6</sup> and tetrahalo ( $\text{MX}_4$ )<sup>7</sup>  $d^0$  species. Moreover, the sequence of orbital energies,  $1t_1 > 3t_2$ , implied by the assignments in Table I, is in agreement with the results of *ab initio* LCAO-MO SCF calculations on species such as  $\text{MnO}_4^-$ <sup>8</sup> (though we must of course recognize that differential relaxation effects may invalidate the qualitative trends expected from Koopmans' theorem).

The interpretation of their  $\text{RuO}_4$  spectrum favored by McGlynn and coworkers is naturally much confused by the impurity band. The same may be said of the discussion by Diemann and Müller of both their  $\text{OsO}_4$  and  $\text{RuO}_4$  spectra. Actually, the latter workers argue for the assignment of bands B and C in the  $\text{OsO}_4$  spectrum to split components of the  ${}^2T_2(3t_2^-)$  ion state. This would be barely conceivable unless the perturbing agency involved were spin-orbit coupling centered about the osmium atom, and this possibility may be ruled out simply on the grounds that the sequence of ion multiplet states,  $E''({}^2T_2) > U'({}^2T_2)$ , indicated by the relative intensities of bands B and C, is qualitatively incorrect for the  $t_2(d)^5$  configuration.<sup>5,9</sup>

(5) J. C. Green, M. L. H. Green, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Phil. Trans. Roy. Soc. London, Ser. A*, **268**, 111 (1970).

(6) A. Müller, E. Diemann, and C. K. Jorgensen, *Struct. Bonding (Berlin)*, **14**, 23 (1973), and references therein.

(7) B. D. Bird and P. Day, *J. Chem. Phys.*, **49**, 392 (1968).

(8) E.g., H. Johansen, *Chem. Phys. Lett.*, **17**, 569 (1972).

(9) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961

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## Preparation and Characterization of Copper(I) and Silver(I) Complexes of *O*-Ethylboranocarbonate

Sir:

The isoelectronic analogy between borane ( $\text{BH}_3$ ) and oxygen has been developed in detail for several systems including the carbonate ( $\text{CO}_3^{2-}$ )-boranocarbonate ( $\text{H}_3\text{BCO}_2^-$ ) system and the *O*-ethylcarbonate ( $\text{CO}_2^-$

$\text{OC}_2\text{H}_5^-$ )-*O*-ethylboranocarbonate ( $\text{H}_3\text{BCO}_2\text{C}_2\text{H}_5^-$ ) system.<sup>1,2</sup> Although suggestion of the coordination of the boranocarbonate species to transition metals has been made, no isolation or characterization of such complexes has been reported.<sup>3,4</sup> We wish to report the first metal complexes of the *O*-ethylboranocarbonate anion: *O*-ethylboranocarbonatobis(triphenylphosphine)copper(I),  $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$ , and *O*-ethylboranocarbonatotris(triphenylphosphine)silver(I),  $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$ . The compounds result from the reaction of  $(\text{Ph}_3\text{P})_3\text{CuCl}$  or  $(\text{Ph}_3\text{P})_3\text{AgNO}_3$  and  $\text{KH}_3\text{BCOOC}_2\text{H}_5$  in  $\text{CHCl}_3$  and ethanol using an excess of triphenylphosphine. The compounds have been identified using elemental analysis, molecular weight data, and ir and nmr spectral data.

Elemental analysis support the formulations given. *Anal.* Calcd for  $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$ : C, 69.42; H, 5.64; P, 9.18. Found: C, 69.66; H, 5.66; P, 9.16. Calcd for  $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$ : C, 69.74; H, 5.44; P, 9.47; Ag, 10.98. Found: C, 69.75; H, 5.54; P, 9.66; Ag, 9.95. Molecular weights in  $\text{CHCl}_3$  by vapor pressure osmometry resulted in the following values:  $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$  (0.0504 *M*) exptl 574, calcd 674.7;  $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$  (0.0428 + 0.0382 *M*  $\text{Ph}_3\text{P}$ ) exptl 501, calcd 981.7. The deviation of the experimental value from the calculated value is typical of complexes of this type and is attributed to the complex equilibria present due to dissociation by the phosphine when the compounds are dissolved in organic solvents.<sup>5,6</sup> Addition of the excess triphenylphosphine was necessary in the case of the silver complex to allow measurements to be carried out with a minimum of decomposition which is evidenced by the formation of metallic silver. Addition of triphenylphosphine to solutions of the copper and silver compounds increased the values for the molecular weights which is consistent with a depression of the dissociation by the phosphine ligands.

The infrared spectra of the copper and silver complexes in  $\text{CHCl}_3$  consist of the following absorption bands (only absorptions which directly pertain to the proposed structures are included):  $(\text{Ph}_3\text{P})_2\text{CuH}_3\text{BCOOC}_2\text{H}_5$  (absorption ( $\text{cm}^{-1}$ ), relative intensity, tentative assignment), 2990 (m)  $\nu_{\text{CH}_3(\text{asym})}$ , 2970 (m)  $\nu_{\text{CH}_2(\text{asym})}$ , 2940 (sh)  $\nu_{\text{CH}_3(\text{sym})}$ , 2900 (w)  $\nu_{\text{CH}_2(\text{sym})}$ , 2380 (m)  $\nu_{\text{terminal B-H}}$ , 1655 (vs)  $\nu_{\text{C=O}}$ ;  $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCOOC}_2\text{H}_5$  2980 (m)  $\nu_{\text{CH}_3(\text{asym})}$ , 2960 (sh, w)  $\nu_{\text{CH}_2(\text{asym})}$ , 2940 (w)  $\nu_{\text{CH}_3(\text{sym})}$ , 2900 (w)  $\nu_{\text{CH}_2(\text{sym})}$ , 2330, 2270 (m)  $\nu_{\text{terminal B-H}}$ , 2080 (m)  $\nu_{\text{bridge B-H}}$ , 1640 (vs)  $\nu_{\text{C=O}}$ .

The spectra of both complexes are characteristic of coordination *via* the hydrogens in the borane group since terminal B-H stretching absorptions near  $2400\text{ cm}^{-1}$  as well as bridging M-H-B absorptions near  $2000\text{ cm}^{-1}$  are observed. Moreover, the absorption near  $1630\text{ cm}^{-1}$  characteristic of the carbonyl stretching mode of the ethylboranocarbonate anion appears to undergo little change upon complexation. The positions of the B-H absorption bands in the copper as compared to

(1) L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).

(2) L. J. Malone, *Inorg. Chem.*, **7**, 1039 (1968).

(3) R. W. Parry, L. J. Malone, and K. W. Morse, *Proc. Int. Conf. Coord. Chem.*, **8th**, 117 (1964).

(4) (a) J. L. Mills, The Robert A. Welch Foundation Annual Report, 1972-1973. (b) J. L. Mills, private communication

(5) E. L. Muetterties and C. W. Aleganti, *J. Amer. Chem. Soc.*, **92**, 4114 (1970).

(6) S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, **11**, 753 (1972).