bonds (see Table I). In addition, the stability of the adduct formed by C–H insertion is less than those formed via C–O and C–C insertions. This is because $D(M^+-H)$ is usually smaller than $D(M^+-CH_3)$ or $D(M^+-R)^{21}$ where R is the alkyl group. It is intriguing that Cr^+ forms a large percentage of dehydrogenated products in its reactions with small alcohols in spite of its low reactivity. In a previous investigation,[3] it was found that Cr^+ prefers to form fragments with a high oxygen to carbon ratio. This may be an important factor in C–C bond insertion reactions (Table IV) in which the formation of $CrC_3H_6O^+$ appears very often and accounts for a high yield reaction channel.

The specificity exhibited by Mo^+ is not easily understood. While it is clear that Mo^+ is quite reactive, owing in part to its expanded-size d orbitals, it is unclear why it has such a large propensity for C–H insertion. These C–H insertions are the most energy demanding of the metal ion insertions, yet Mo^+ exclusively undergoes dehydrogenation and multiple dehydrogenations with alcohols having up to four carbons. This high specificity is surprising for such a reactive metal ion species. The formation of conjugated π-systems by multiple dehydrogenation has been postulated as a driving force for catalytic dehydrogenation in solution.[31] Interaction of Mo^+ with the multiple double bonds may lower the transition state energies for fragmentation of the initially formed adduct and channel most of the reactions along a dehydrogenation pathway. C–H activation followed by multiple dehydrogenation leading to stable aromatic ligands also occurs for reactions of molybdenum atoms.[32]

An interesting difference between Mo^+ and Cr^+ is that Mo^+ eliminates H_2 from methanol and Cr^+ does not. This may imply that Mo^+ inserts into the O–H bond, whereas the other metal ions do not. The loss of the first molecule of H_2 would then lead to formation of a C=O bond.

Conclusions

In conclusion, Fe^+ is the most reactive and least selective toward aliphatic alcohols having four or more carbon atoms. The chemistry of Cr^+ and alcohols having five or more carbons is quite similar to that of Fe^+ despite their different electronic configurations. Cr^+ is the least reactive species, and its reactions with alcohols that have four carbons or less are quite selective. Mo^+, on the other hand, is very reactive and specific in dehydrogenation or multidehydrogenation reactions. Dehydration and C–C bond insertion reactions appear as alternative reaction channels only when alcohols are branched or chain length is increased. It is important to note that although Mo^+ and Cr^+ have the same valance electronic configuration, their principal reactivities are distinctive.

The foci of this study are reactivity and reaction specificity. Only wide-ranging conclusions are possible at this stage. For example, reactivity and specificity may be discussed in terms of the energies of the bonds that need to be broken upon insertion, the energy released by bonding between the metal ion and its two ligands after insertion has occurred, and the stability of the product ions formed. The latter two factors affect the transition-state energies for decomposition reactions of the initially formed adduct. Specific details of reactions mechanisms must await studies of isotopic labeling and of comparisons of collisionally activated decomposition (CAD) spectra of product ions and reference compounds. We expect the CAD spectra to reveal, for example, whether Cr^+ simply attaches dissociatively to alcohols so that its d^5 electronic configuration is still retained despite its reactivity. These studies are underway.

(31) For a recent review, see: Crabtree, R. H. *Chem. Rev.* 1985, *85*, 245.
(32) Dam, E. M. V.; Brent, W. N.; Silvon, M. P.; Skell, P. S. *J. Am. Chem. Soc.* 1975, *98*, 465.

Reduction of Organic Carbonyl Compounds by the Cationic Dihydrido Carbonyl Species $(Cp_2Ta(CO)H_2)^+$. Synthesis of Alkoxy Tantalum(III) Derivatives

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The reaction of the monohydrides $(\eta^5$-$C_5H_4R)_2Ta(CO)H$ (**1**, R = H; **1'**, R = CMe_3) with HCl followed by treatment with NH_4PF_6 yields white salts $((\eta^5$-$C_5H_4R)_2Ta(CO)H_2)^+PF_6^-$ (**2**, R = H; **2'**, R = CMe_3) by protonation of the metal. Compound **2** reacts with carbonyl derivatives to give $((\eta^5$-$C_5H_5)_2Ta(CO)$-$HOCHRR')^+PF_6^-$ (**3a**, **3b**, and **3c**, respectively, with acetone, 2-butanone, and propanal). In basic medium these salts are deprotonated leading to $(\eta^5$-$C_5H_5)_2Ta(CO)(OCHRR')$ (**4a**, **4b**, and **4c**, respectively). Spectroscopic characterization of the complexes have included measurement of their ^1H NMR, IR, and mass spectra.

The dihydrides Cp_2MH_2 (M = Mo, W) possess well-known basic properties owing to an electron lone pair situated in a low-lying molecular orbital. In acidic medium, the dihydrides can be protonated, yielding $(Cp_2MH_3)^+$, and can react with Lewis acids such as BF_3 and AlR_3^1 or with

unsaturated organometallic fragments leading to donor-acceptor bimetallic systems.[2] An electronic similarity

(1) Muetterties, E. L. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971; p 152.

Chart I

$$(C_5H_4R)_2 \, Ta \, (CO) \, H \xrightleftharpoons[OH^\ominus]{HCl \, ; \, NH_4PF_6} \left[(C_5H_4R)_2 \, Ta \, (CO) \, H_2 \right]^\oplus PF_6^\ominus \quad (1)$$

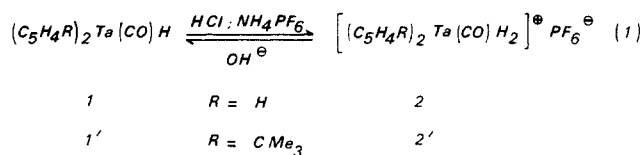|		
1	R = H	2
1'	R = CMe_3	2'

Chart II

A   B

exists in the niobium or tantalum monohydrides Cp₂M-(CO)H (M = Nb, Ta). We have recently shown the ability of these d² complexes to associate with Lewis acid organometallic moieties.[3] Moreover, upon reaction of Cp₂Nb(CO)H with HCl, the protonated species (Cp₂Nb-(CO)H₂)⁺ has been reported by Brintzinger et al., but full characterization of the cation was precluded due to a fast reductive H₂ elimination giving Cp₂Nb(CO)Cl.[4,5] Since an enhanced stability is a general trend of the tantalum series, we have investigated the behavior of the Cp₂Ta-(CO)H and Cp'₂Ta(CO)H (Cp' = C₅H₄CMe₃) monohydrides in acidic medium. We report our results obtained in this paper and describe the unexpected reactivity of the dihydrido cationic species toward organic carbonyl compounds.

Results and Discussion

Upon treatment of Cp₂Ta(CO)H (1) or Cp'₂Ta(CO)H (1') with aqueous HCl in THF solution, the initial purple color slowly disappeared, and after anion exchange with NH₄⁺PF₆⁻, a white solid was obtained in ca. 70% yield.

The regeneration of the starting hydrides was immediate and quantitative when the salts 2 and 2' were treated with a basic reagent.

The high value of the CO IR absorption (Table I) showed that the protonation has occurred at the metallic nucleus and not at the oxygen atom of the carbonyl ligand. The very poor solubility of the salt 2 did not allow an NMR study.

With the more soluble *tert*-butyl derivative 2', NMR data could be obtained. The ¹H of 2' spectrum (Table I) displayed two triplets for the four cyclopentadienyl hydrogen atoms and one singlet for the two hydride ligands. In the ¹³C spectrum (Table II) the four unsubstituted ring carbon atoms gave rise to two resonances (doublets, $^1J_{^1H-^{13}C}$ = 185 Hz), whereas the carbonyl carbon atom appeared as a triplet ($^2J_{^1H-^{13}C}$ = 25 Hz). These spectroscopic data suggest a symmetrical coordination about Ta with the CO ligand in the central equatorial position mutually cis to both hydride ligands (type A). A lateral approach of H⁺, in keeping with the location of the lone pair outside the H–M–CO angle (1a¹ orbital[6]), may thus account for this C_{2v} molecular symmetry.

An identical structure, based on similar spectroscopic observations, has been proposed by Bercaw et al. for the
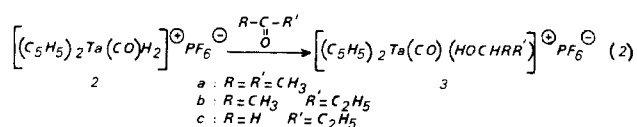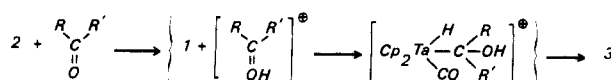
Chart III

$$\left[(C_5H_5)_2 Ta(CO)H_2 \right]^\oplus PF_6^\ominus \xrightarrow{\overset{R-C-R'}{\underset{O}{\parallel}}} \left[(C_5H_5)_2 Ta(CO)(HOCHRR') \right]^\oplus PF_6^\ominus \quad (2)$$

a	R = R' = CH₃	
b	R = CH₃	R' = C₂H₅
c	R = H	R' = C₂H₅

    2   3

Chart IV

Chart V

C   D

Chart VI

red   green
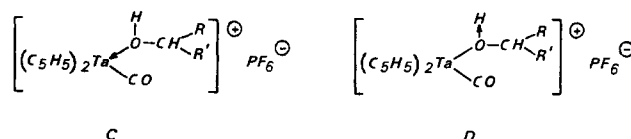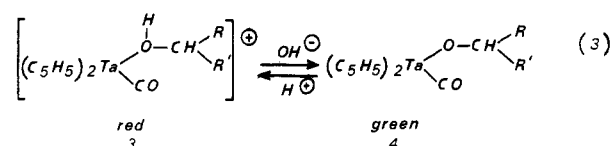3   4

isoelectronic complexes (C₅Me₅)₂Zr(CO)H₂[7] and (C₅Me₅)₂Hf(CO)H₂.[8] It has been assumed that these adducts A, afforded after treatment of the zirconium or hafnium dihydrides with CO, were the thermodynamic products. The kinetic and highly unstable adducts B, arising from a lateral coordination of CO, were formed in a preliminary step.[9]

Upon dissolution of the salt 2 in acetone, a fast reaction occurred as shown by a color change from white to red. No gas evolution was detected, and after solvent evaporation 3a was obtained as a red solid in a nearly quantitative yield. The CO IR frequency was shifted to 1918 cm⁻¹, and the ¹H NMR spectrum consisted of a set of three resonances (two doublets and a double heptet) related to each other: this spin system corresponds to the isopropyl alcohol ligand. Similar reactions were performed with 2-butanone and propanal and give 3b and 3c, respectively.

The mechanism depicted in Chart IV can be put forward to explain these results. It implies acidic properties of the cation (Cp₂Ta(CO)H₂)⁺ (2) which lead in a preliminary step to the protonation of the carbonyl substrate followed by a donor–acceptor association between the basic monohydride Cp₂Ta(CO)H and the electrophilic carbon center.[10]

A reductive elimination from the cationic intermediate and subsequent coordination of the alcohol RR'CHOH by the unsaturated 16e species (Cp₂Ta(CO))⁺ give rise to the complexes 3.

Support for this mechanism comes from the immediate formation of 3a when Cp₂Ta(CO)H is allowed to react with acetone containing a stoichiometric amount of HPF₆. The

(2) Deubzer, B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1986**, *90*, 3276.

(3) Leblanc, J. C.; Reynoud, J. F.; Moïse, C. *J. Organomet. Chem.* **1983**, *244*, C24.

(4) Otto, E. E. H.; Brintzinger, H. H. *J. Organomet. Chem.* **1978**, *148*, 29.

(5) In contrast, the dihydrido phosphine cation (Cp₂Nb(PR₃)H₂)⁺ is rather stable: Lucas, C. R.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1005.

(6) Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1972**, 421. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(7) Manriquez, J. M.; Mc Alister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733.

(8) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

(9) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. Kerrie, I. G.; Barry, P.; Schwartz, J.; Williams G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

(10) Leblanc, J. C.; Moïse, C.; Tirouflet, J. *J. Organomet. Chem.* **1985**, *292*, 225. Moïse, C.; Reynoud, J. F.; Leblanc, J. C.; Broussier, R. *J. Organomet. Chem.* **1982**, *240*, C15.

Table I. IR and ^{1}H NMR Data

compd	IR		^{1}H NMR^a			
	$\nu_{CO}{}^b$	$\nu_{Ta-H}{}^c$	Cp or Cp'	O-H	O-CH or O-CH$_2$-	other assigns
(C$_5$H$_5$)$_2$Ta(CO)H (1)	1890	1750	4.48 (d, 10, J = 0.75 Hz)			Ta-H -6.78 (m, 1)
((C$_5$H$_5$)$_2$Ta(CO)H$_2$)$^+$PF$_6^-$ (2)	2112	1782	d			
(C$_5$H$_4$CMe$_3$)$_2$Ta(CO)H (1')	1887	1780	4.96 (m, 2), 4.74 (m, 2), 4.60 (m, 2), 4.36 (m, 2)			Ta-H -6.88 (s, 1), CMe$_3$ 1.20 (s, 18)
((C$_5$H$_4$CMe$_3$)$_2$Ta(CO)H$_2$)$^+$PF$_6^-$ (2')	2103	1772	6.13 (t, 4),^{e} 5.56 (t, 4, J = 2.5 Hz)			Ta-H$_2$ -1.62 (s, 2), CMe$_3$ 1.38 (s, 18)
((C$_5$H$_5$)$_2$Ta(CO){O(H)CH(CH$_3$)$_2$})$^+$PF$_6^-$ (3a)	1918		5.76 (s, 10)	6.32 (d, 1, J = 6.6 Hz)	3.64 (m, 1)	CH$_3$ 1.12 (d, 6)
(C$_5$H$_5$)$_2$Ta(CO){OCH(CH$_3$)$_2$} (4a)	1877		4.80 (s, 10)		3.37 (h, 1)	CH$_3$ 0.97 (d, 6)
((C$_5$H$_5$)$_2$Ta(CO){O(H)CH(CH$_3$)(C$_2$H$_5$)})$^+$PF$_6^-$ (3b)	1919		5.76 (s, 5), 5.75 (s, 5)	6.21 (d, 1, J = 6.8 Hz)	3943 (m, 1)	CH$_2$-CH$_3$ 1.44 (m, 2), CH-CH$_3$ 1.10 (d, 3), CH$_2$-CH$_3$ 0.82 (t, 3)
(C$_5$H$_5$)$_2$Ta(CO){OCH(CH$_3$)(C$_2$H$_5$)} (4b)	1872		4.81 (s, 5), 4.80 (s, 5)		3.12 (m, 1)	CH$_2$-CH$_3$ 1.23 (m, 2), CH-CH$_3$ 0.97 (d, 3), CH$_2$-CH$_3$ 0.87 (t, 3)
((C$_5$H$_5$)$_2$Ta(CO){O(H)CH$_2$C$_2$H$_5$})$^+$PF$_6^-$ (3c)	1919		5.74 (s, 10)	6.88 (t, 1, J = 4.8 Hz)	3.48 (m, 2)	CH$_2$-CH$_3$ 1.44 (m, 2), CH$_2$-CH$_3$ 0.77 (t, 3)
(C$_5$H$_5$)$_2$Ta(CO){OCH$_2$C$_2$H$_5$} (4c)	1874		4.80 (s, 10)		3.38 (t, 2)	CH$_2$-CH$_3$ 1.31 (m, 2), CH$_2$CH$_3$ 0.89 (t, 3)

^{a} ^{1}H NMR spectra recorded in benzene-d_6 (compounds 1, 4a-c), in acetone-d_6 (compounds 3a-c), or in THF-d_8, (compounds 1', 2'). Chemical shifts in δ measured from internal Me$_4$Si. ^{b} IR spectra (cm-3) recorded in THF (compounds 1, 2, 1', 2', 3a-c) or in toluene (compounds 4a-c). ^{c} Nujol mull. ^{d} Too poorly soluble in THF-d_8 or in dichloromethane-d_2. ^{e} In dichloromethane-d_2: δ 5.77 (t, 4), 5.12 (t, 4), 1.19 (s, 18), -1.7 (s, 2).

Table II. ^{13}C NMR Data of 1, 1', and 2'^{a}

compd	Cp	CMe$_3$	CO
(C$_5$H$_5$)$_2$Ta(CO)H (1)	83.5 (d, J = 179 Hz)		262 (d, J = 5.8 Hz)
(C$_5$H$_4$CMe$_3$)$_2$Ta(CO)H (1')	77 (d), 80.5 (d), 81.5 (d), 82.5 (d, J = 175 Hz), 128.65 (s)	32.3 (s), 32.7 (q, J = 126 Hz)	263 (d, J = 4.5 Hz)
((C$_5$H$_4$CMe$_3$)$_2$Ta(CO)H$_2$)$^+$- PF$_6^-$ (2')	87 (d), 92 (d, J = 185 Hz), 139.5 (s)	32.7 (s), 32.4 (q, J = 125 Hz)	201 (t, J = 25 Hz)

^{a} NMR spectra (ppm) recorded in benzene-d_6 (1), THF-d_8 (1'), and dichloromethane-d_2 (2'). Chemical shifts in δ.

reduction of the carbonyl derivatives by a molecule of hydrogen evolving from the cationic complex 2 can be therefore ruled out.

The two extreme representations shown in C and D may account for the structure of the compounds 3. Both include an 18-electron configuration about the tantalum atom.

In structure C, the oxygen atom n donation allows the closed shell of electrons to be reached. Structure D can be viewed as an oxonium salt of a tantalum alkoxy derivative. Support for representation D was found in the behavior of the complexes 3 in basic medium. When a benzene suspension of 3 was treated with few drops of 1 N NaOH, the deprotonated complexes 4 were formed and isolated as green solids.

IR and ^{1}H NMR data of 3 and 4 are listed in Table I. The nonequivalence of the Cp rings due to the chiral center of the alcohol or alkoxy ligand was observed in 3b and 4b. Reactions 2 and 3 provide a convenient route to the yet unknown alkoxy Ta(III) derivatives. Another route involving a nucleophilic substitution between Cp$_2$Ta(CO)Cl and an alkoxide ion was unsuccessful because of the high inertness of the chloro compound.[11]

Upon reaction of 4 with HPF$_6$, the reverse reaction occurred and the salts 3 were cleanly regenerated. It is noteworthy that no tantalum-oxygen bond cleavage took place during this protonation reaction. Under analogous conditions, titanium- or vanadium-oxygen bonds were immediately broken.[12]

For examination of the catalytic potential of the reduction depicted in eq 2, the reaction of the dihydrido cationic species (Cp$_2$M(CO)H$_2$)$^+$ with acetone was carried out under a H$_2$ atmosphere. No formation of isopropyl alcohol was detected even at 60 °C, and only complex 3a was characterized. This failure is in keeping with the postulated oxonium structure D which involves a strong tantalum-oxygen bond.

Other reducible functional groups such as nitriles are under current investigation since the weaker Ta-N bond might provide the opportunity of a catalytic reduction process. In addition, studies on the chemio- and regioselectivity of this reduction reaction are in progress.

Experimental Section

General Procedures. All manipulations of air-sensitive products were performed under a purified argon atmosphere using Schlenk techniques. The solvents were distilled under argon from sodium benzophenone immediately before use. The starting complexes (η^5-C$_5$H$_5$)$_2$Ta(CO)H (1) and (η^5-C$_5$H$_4$CMe$_3$)$_2$Ta(CO)H (1') were prepared by the reported methods.[13,14]

(11) The chloro carbonyl Cp$_2$Ta(CO)Cl was not affected by alkylating reagents such as CH$_3$Li or RMgX. Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *165*, 31.

(12) Moïse, C.; Leblanc, J. C.; Tirouflet, J. *J. Am. Chem. Soc.* **1975**, *97*, 6272. Martin, J.; Moïse, C. *J. Organomet. Chem.* **1980**, *193*, C57.

$((\eta^5\text{-}C_5H_5)_2Ta(CO)H_2)^+PF_6^-$ (2). A molar solution of HCl (3 mL) was added at room temperature to a suspension of $Cp_2Ta(CO)H$ (1.18 mmol) in water (15 mL) and THF (5 mL). After 0.5 h the mixture was filtered and a solution of NH_4PF_6 (1.23 mmol) in water (5 mL) was added dropwise to the filtrate at 0 °C. The THF was then removed; the white precipitate was filtered, washed with cold water, and dried under vacuum. Crude white solid was obtained 0.45 g, 79% yield. Anal. calcd for $C_{11}H_{12}OF_6PTa$: C, 27.18; H, 2.49. Found: C, 26.92; H, 2.73.

$((\eta^5\text{-}C_5H_4CMe_3)_2Ta(CO)H_2)^+PF_6^-$ (2'). Following the procedure for the preparation of **2** and starting with 200 mg (0.44 mmol) of $(\eta^5\text{-}C_5H_4CMe_3)_2Ta(CO)H$, 190 mg of the crude white solid product **2'** was isolated (72% yield). Anal. Calcd for $C_{19}H_{28}OF_6PTa$: C, 38.14; H, 4.72. Found: C, 38.32; H, 4.86.

$((\eta^5\text{-}C_5H_5)_2Ta(CO)\{HOCH(CH_3)_2\})^+PF_6^-$ (3a). A solution of **2** (1.03 mmol) in CH_3COCH_3 (3 mL) was stirred for 2 h at room temperature. The resulting red solution was then evaporated to dryness. Recrystallization of the crude solid from THF–heptane afforded an analytically pure sample as red crystals (68% yield). Anal. Calcd. for $C_{14}H_{18}O_2F_6PTa$: C, 30.90; H, 3.33. Found: C, 31.05; H, 3.45.

We have carried out another efficient synthesis of this red compound as follows. Acetone (20 mL) and HPF_6 (1 mL of a 60% aqueous solution) was stirred for 0.5 h; 0.6 mL (0.2 mmol) of this solution was added to $Cp_2Ta(CO)H$ (0.2 mmol) dissolved in acetone (10 mL). The color turned immediately from violet to brown-red, and the resulting solution was evaporated. The crude product was then purified as described above.

$((\eta^5\text{-}C_5H_5)_2Ta(CO)\{HOCH(CH_3)(C_2H_5)\})^+PF_6^-$ (3b). The reaction was carried out at room temperature by dissolving compound **2** (0.21 mmol) in $CH_3COC_2H_5$ (2 mL). The mixture

was stirred for 1.5 h and evaporated. The crude red solid **2b** was recrystallized from THF–heptane (65% yield). Anal. Calcd for $C_{15}H_{20}O_2F_6PTa$: C, 32.27; H, 3.61. Found: C, 31.94; H, 3.93.

$((\eta^5\text{-}C_5H_5)_2Ta(CO)\{HOCH_2CH_2CH_3\})^+PF_6^-$ (3c). A solution of **2** (0.25 mmol) in CH_3CH_2CHO (2 mL) was stirred for 2 h. The solvent was then removed, and the red solid was purified by recrystallization from THF–heptane (72% yield). Anal. Calcd for $C_{14}H_{18}O_2F_6PTa$: C, 30.90; H, 3.33. Found: C, 30.27; H, 3.91.

$(\eta^5\text{-}C_5H_5)_2Ta(CO)(OCH(CH_3)_2)$ (4a). A molar solution of NaOH was added dropwise to a stirred suspension of **2a** (0.44 mmol) in toluene (10 mL) until a green organic layer was obtained. The toluene layer was decanted and solvent evaporated leading to a green crude solid (53% yield). Mass fragments: m/e (assignment, relative intensity) 370 ($M^+ - CO$, 10), 369 ($M^+ - CO - H$, 18), 355 ($Cp_2TaOC_2H_4^+$, 18), 341 ($Cp_2TaOCH_2^+$, 5). Anal. Calcd for $C_{14}H_{17}O_2Ta$: C, 42.22; H, 4.30. Found: C, 42.71; H, 4.51.

$(\eta^5\text{-}C_5H_5)_2Ta(CO)(OCH(CH_3)(C_2H_5))$ (4b). Treatment of the salt **3b** (0.09 mmol) with a molar solution of NaOH by the above procedure afforded **4b** as a green solid (48% yield). Mass fragments: m/e (assignment, relative intensity) 384 ($M^+ - CO$, 15), 355 ($Cp_2TaOC_2H_4^+$, 9), 341 ($Cp_2TaOCH_2^+$, 4), 312 (Cp_2TaH^+, 28), 311 (Cp_2Ta^+, 15). Anal. Calcd for $C_{15}H_{19}O_2Ta$: C, 43.70; H, 4.65. Found: C, 44.07; H, 4.43.

$((\eta^5\text{-}C_5H_5)_2Ta(CO)(OCH_2CH_2CH_3)$ (4c). Complex **4c** was prepared (60% yield) by the same method starting from **3c** (0.13 mmol). Mass fragments: m/e (assignment, relative intensity) 370 ($M^+ - Co$, 35), 327 (Cp_2TaO^+, 7), 312 (Cp_2TaH^+, 37), 311 (Cp_2Ta^+, 28). Anal. Calcd for $C_{14}H_{17}O_2Ta$: C, 42.22; H, 4.30. Found: C, 41.88; H, 4.09.

(13) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.
(14) Reynoud, J. F.; Leblanc, J. C.; Moïse, C. *Organometallics* **1985**, *4*, 1059.

He I and He II Photoelectron Spectra and Pseudopotential ab Initio Calculations of Some Tetracoordinated Tin(IV) Derivatives

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The gas-phase UV photoelectron (PE) spectra of $Sn(CH_3)_nCl_{4-n}$ (n = 0–4) and of $Sn(CH_3)_m(NCS)_{4-m}$ (m = 2, 3) are discussed with the aid of the results of pseudopotential ab initio calculations (extended basis sets with inclusion of 5d polarization functions and relativistic corrections for tin). The excellent numerical agreement between experimental and computed (Koopmans) ionization energies has allowed a reassignment of some published PE data and the discussion of the new spectra. The actual involvement of tin 5s, 5p, and 5d atomic orbitals into the valence MOs is also discussed. Both the theoretical and experimental data suggest the presence of strong π_{Sn-Cl} interactions with significant contribution from Sn 5d AOs. As far as the NCS derivatives are concerned, both PE and theoretical data are in agreement with a largely ionic bond.

Introduction

The electronic structures of many organotin compounds have been studied extensively by means of gas-phase UV photoelectron spectroscopy.[2–10] Up to now, however, the

assignment of the various PE bands has been accomplished mainly by using experimental criteria. Among them, however, He I vs. He II intensity changes have rarely aided the interpretation of the PE spectra of tin compounds. In

(1) (a) University of Padova. (b) Université P. Sabatier, Toulouse.
(2) Green, J. C.; Green, M. L. H.; Joachim, P. J.; Orchard, A. F.; Turner, D. W. *Philos. Trans. R. Soc. London, A* **1970**, *268*, 111.
(3) Evans, S.; Green, J. C.; Joachim, P. J.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *2*, 905.
(4) Boschi, R.; Lappert, M. F.; Pedley, J. B.; Schmidt, W.; Wilkins, B. T. *J. Organomet. Chem.* **1973**, *50*, 69.
(5) Flamini, A.; Semprini, E.; Stefani, F.; Sorriso, S.; Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1976**, 731.

(6) Cauletti, C.; Furlani, C.; Piancastelli, M. N. *J. Organomet. Chem.* **1978**, *149*, 289.
(7) Egdell, R. G.; Fragalà, I.; Orchard, A. F. *J. Electron Spectrosc.* **1979**, *17*, 267.
(8) Fragalà, I.; Ciliberto, E.; Egdell, R. G.; Granozzi, G. *J. Chem. Soc., Dalton Trans.* **1980**, 145.
(9) Bancroft, G. M.; Pellach, E.; Tse, J. S. *Inorg. Chem.* **1982**, *21*, 2950.
(10) Fragalà, I.; Ciliberto, E.; Finocchiaro, P.; Recca, A. *J. Chem. Soc., Dalton Trans.* **1979**, 240.