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Gas-Phase Photoelectron Studies of Bis(cyclopentadienyl)titanium(III) Halides

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The He I and He II photoelectron spectra of a series of Cp'_2TiX complexes (X = Cl, Br; Cp′ = $C_5H_{5-n}(CH_3)_n$, n = 0, 1, 3–5) are reported. The assignments are made on the basis of ionization energy trends and variations of relative band intensities with the energy of the excitation radiation. The monomeric Cp'_2TiX species are present in the gas phase. The order of ionizations is d(Ti) < π(Cp) < p(X) < σ(Ti–X). The photoelectron data suggest a strong interaction between the orbitals of the Cp'_2Ti moiety and halogen p orbitals. The effect of cyclopentadienyl methylation on the particular ionization energies is additive within the series.

Introduction

The chemistry of Cp_2ML_n complexes has been of considerable interest in recent years.[1-4] The UV photoelectron (PE) spectroscopic studies on group 4B metallocenes dealt with d^0 species having halogen,[5-7] sulfur and selenium,[8,9] and NCO, NCS, and phenolate ligands[10] L and with d^2 $Cp_2Ti(CO)_2$ complexes.[11] Information on the properties of the 15-electron d^1 complexes of the general formula Cp'_2TiL is scarce. The cyclopentadienyl and methylcyclopentadienyl species form dimeric halides $(Cp'_2TiX)_2$ (X = Cl, Br, I) exhibiting an antiferromagnetic behavior;[12,13] however, the dimers dissociate in the presence of Lewis bases to give the monomeric electron-donor complexes.[14-17] The THF adducts are the only products of the electrochemical reduction of the Cp_2TiX_2 complexes in THF.[18] On the other hand, the permethylated $(Me_5Cp)_2TiX$ species are monomeric in the condensed phase.[19] Of other simple Cp'_2TiL species, the Cp_2Ti(alkyl) compounds are unstable at ambient temperature[20,21] and $(Me_5Cp)_2$(alkyl) derivatives decompose at elevated temperatures to form $(Me_5Cp)(Me_4C_5CH_2)Ti$.[22] The Cp_2Ti(aryl) compounds are stable to a maximum of 100 °C, depending on the structure of the aryl substituent.[23] To our knowledge there is no experimental evidence on the electronic structure of the Cp_2TiL complexes.

The general bonding scheme for bent metallocenes can be constructed from molecular orbitals (MO's) of the bent bis(cyclopentadienyl)metal fragment and p orbitals of the ligand X[24-26] (Figure 1). According to the X-ray diffraction data for monomeric $(Me_5Cp)_2TiCl$ the halogen atom is coordinated in the equatorial plane and the molecule exhibits an approximate C_{2v} symmetry.[19] The quantification of this bonding scheme for d^0 Cp_2MX_2 complexes was the subject of both experimental and theoretical studies.[6,27-29]

We report here an ultraviolet PE study on series of Cp'_2TiCl and Cp'_2TiBr complexes (Cp′ = C_5H_5 (Cp), $CH_3C_5H_4$ (MeCp), $(CH_3)_3C_5H_2$ (Me_3Cp), $(CH_3)_4C_5H$ (Me_4Cp), $(CH_3)_5C_5$ (Me_5Cp)). The localized electron structure perturbation proved to be an efficient tool for the translation of the photoelectron spectral data into the MO picture independent of quantum-chemical calculations.[30] The photoelectron band displacements upon cyclopentadienyl methylation provide an approximate measure of the localization of MO's. Within the simple MO concept the sensitivity to such a substitution is proportional to the square of atomic orbital coefficients.[31] The replacement of chlorine by the less electronegative

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Table I. Vertical Ionization Energies and Assignments for Bis(cyclopentadienyl)titanium Halides

	ionization energy,[a] eV						
band	Cp′ = Cp	Cp′ = MeCp	Cp′ = Me_3Cp	Cp′ = Me_4Cp	Cp′ = Me_5Cp	ΔIE per Me,[b] eV	assignt
				Cp'_2TiCl			
a	6.81 (1.00)[c]	6.55	6.18	6.00	5.88	0.22	d(Ti)
b	8.25 (0.23)	8.04	7.69	7.49	7.31	0.20	π(Cp + Cl)
c	9.17 (0.38)	8.82	8.34	8.01	7.72	0.30	π(Cp)
d	9.46 (0.34)	9.16	8.58	8.26		0.31	π(Cp)
e	10.41 (0.08)	10.25	9.99	9.84	9.69	0.15	p(Cl)
f	10.93 (0.10)	10.82	10.68	10.50	10.44	0.10	σ(Ti–Cl)
				Cp'_2TiBr			
a	6.79 (1.00)	6.58	6.22	6.05 (1.00)	5.90	0.19	d(Ti)
b	8.15 (0.33)	7.97	7.62	7.51 (0.35)	7.27	0.19	π(Cp + Br)
c	9.19 (0.35)	8.81	8.31	8.01	7.83	0.33	π(Cp)
d	9.64	9.20	8.50	8.33		0.38	π(Cp)
e	9.85	9.54	9.34	9.27 (0.16)	9.13	0.19	p(Br)
f	10.43	10.31	10.13	10.03 (0.04)	9.90	0.11	σ(Ti–Br)

[a] Estimated error 0.05 eV. [b] Mean value of ΔIE per methyl group for MeCp through Me_5Cp. [c] Values in parentheses are the He II/He I intensity ratios related to that for the d ionization.

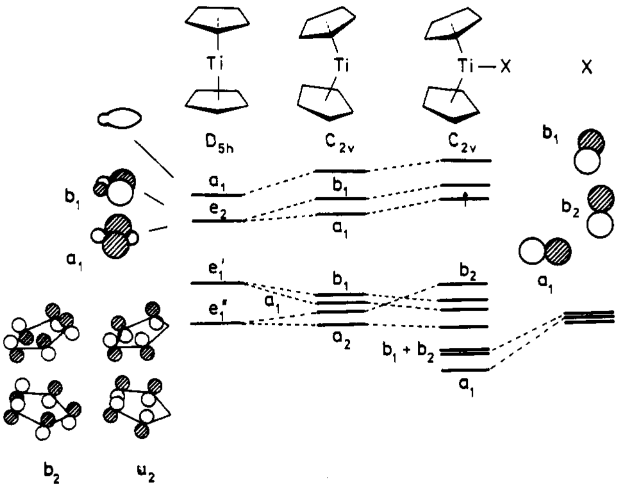

Figure 1. Interaction diagram for bis(cyclopentadienyl)titanium halides. Only the components of the e_1'' level are depicted. The components of the e_1' level are obtained simply by changing the phase on one cyclopentadienyl ligand.

bromine brings about band shifts revealing ionization events localized predominantly on the halogen atom. The observed ionization energies (IE's) are influenced by the Coulombic effect of substituents. Therefore, the MO localization can be estimated from the relative band shifts within a series rather than from the absolute IE changes.

Experimental Section

The bis(cyclopentadienyl)titanium halides were prepared from the corresponding dihalides.[27] The preparations were performed under vacuum using an entirely sealed glass device. Dimeric $(Cp_2TiX)_2$ and $((MeCp)_2TiX)_2$ were obtained by reduction with aluminum powder in THF.[32] The reaction solutions were evaporated, and solid residues were extracted with diethyl ether to remove aluminum halides. After about half of the solid product was transferred into washings, the solid residues were dried in vacuo and then dissolved in toluene; dirty green solutions of the chloro species and yellow-brown solutions of the bromo compounds were evaporated in vacuo to give samples for PE measurements. The $(Me_3Cp)_2TiX$ and $(Me_4Cp)_2TiX$ compounds were obtained by controlled reduction of the dihalide derivatives by $LiAlH_4$ in boiling toluene. The reduction was stopped by cooling to ambient temperature after the reaction solutions turned blue. The blue products were purified by crystallization from hexane. The $(Me_5Cp)_2TiX$ compounds were obtained by adding 1.2 equiv of *i*-PrMgX in ether to the dihalide. After evaporation to dryness the blue $(Me_5Cp)_2TiCl$ and green $(Me_5Cp)_2TiBr$ were extracted with hexane and crystallized by cooling. The $(Me_5Cp)_2TiX$ compounds are known to be monomeric in the solid state and in hydrocarbon solutions;[19] the very similar ESR and electronic absorption spectra recently obtained for the toluene solutions of all the Me_5Cp, Me_4Cp, and Me_3Cp complexes[33] imply their monomeric structure. The purity of all compounds was checked by mass spectrometry: the loss of HX, Cp′ and Cp′H from the molecular ion was the characteristic fragmentation pattern. No ion signals from the dimerized species and their fragmentation were observed.

The samples were transferred into the spectrometer under an inert atmosphere. The photoelectron spectrometer used was a Perkin-Elmer PE 18 instrument. The working resolution (full width at half-maximum, fwhm) was 50 meV for the Ar $2p_{3/2}$ peak. A good signal to noise ratio was attained at temperatures of 200–240 °C. The PE spectra were calibrated by simultaneous addition of an Ar/Xe mixture. The integral intensities of the overlapping bands were obtained by the numeric procedure by Hughes and Sexton[34] using Gauss–Lorentz product functions.

Results and Discussion

The low-IE parts of He I and He II photoelectron spectra are shown in Figures 2 and 3. The PE spectra of the Cp'_2TiX complexes can be divided into two parts. The broad, poorly resolved band system approximately above 12 eV comes from the ionization events related to σ(C–C) and σ(C–H) orbitals and the highest cyclopentadienyl π levels. With an increasing number of methyl groups the onset of the σ band envelope shifts to lower IE, as is observed generally in the PE spectra of hydrocarbons.[35] The low-IE features are from the cyclopentadienyl π orbitals of e_1 symmetry, the MO's involving the halogen p orbitals, and the singly occupied central atom d level. Vertical IE's below 12 eV are summarized in Table I.

Bis(cyclopentadienyl)titanium Chlorides. Six ionization events can be resolved in the low-IE range of the PE spectrum of Cp_2TiCl (Figure 2). The fwhm of the first band (a) amounts to 0.35 eV and indicates a nonbonding or a weakly bonding character of the corresponding MO. The He II/He I intensity ratio decreases in the order a > c ≈ d > b > e ≈ f. Within the simple Gelius[36] model the cross sections are directly related to the cross sections of the atomic orbitals contributing to the appropriate mo-

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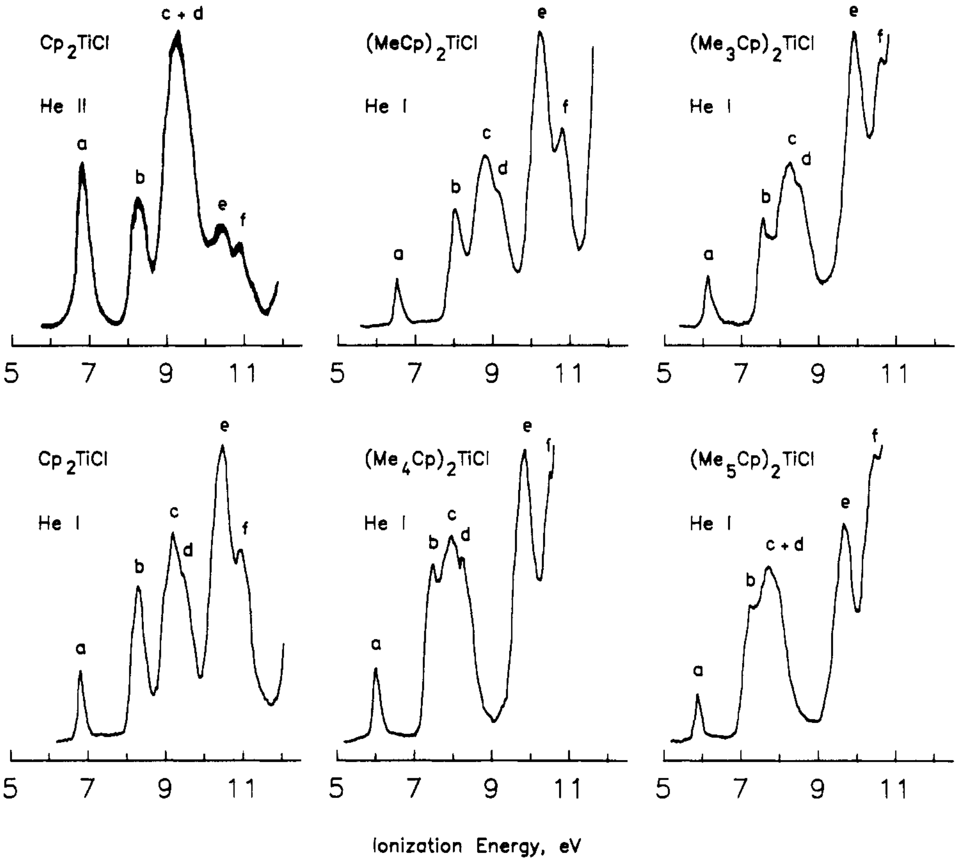

Figure 2. He I and He II photoelectron spectra for Cp′$_2$TiCl complexes.

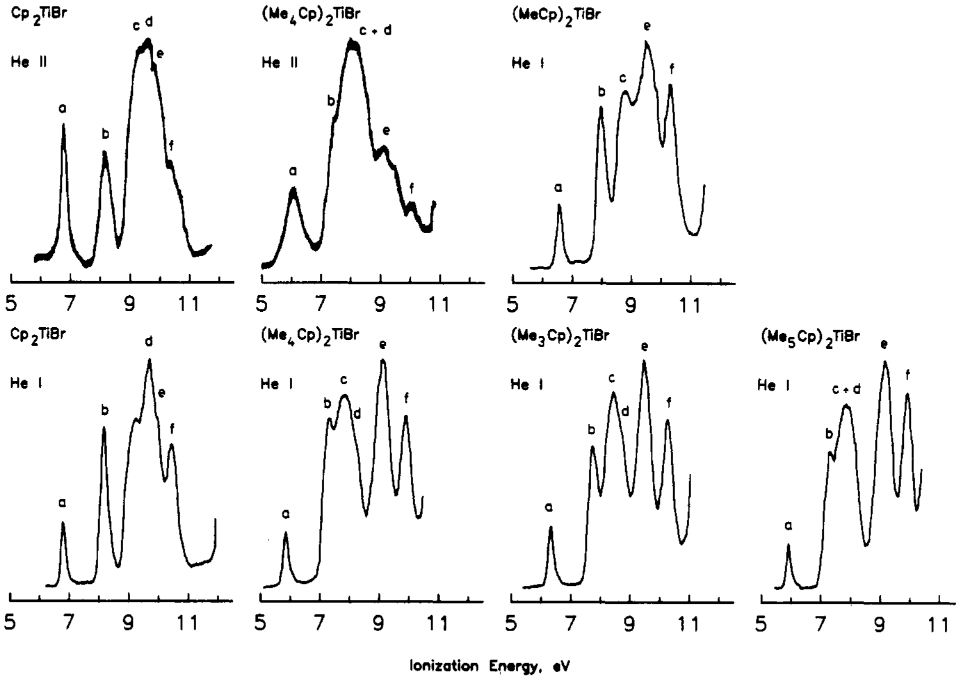

Figure 3. He I and He II photoelectron spectra for Cp′$_2$TiBr complexes.

lecular orbital. The intensity changes of particular bands are influenced by two effects which act in opposite directions. The halogen p orbitals have a lower He II cross section relative to that of the carbon-based p orbitals, whereas the relative intensity of the metal 3d ionizations increases with the energy of the exciting radiation. Thus, band a can be assigned to the predominantly d-based singly occupied level. The dramatic decrease of the intensity of bands e and f indicates a large contribution from the halogen-based orbitals. Bands b–d, whose intensity ratio is between these extreme values, can be assigned to the cyclopentadienyl π orbitals. The greater decrease of the intensity of band b relative to the intensities of bands c and d can indicate a higher halogen contribution or a weaker interaction with d orbitals. Both the stronger interaction with the deeper lying halogen p orbitals and a weaker mixing with the central atom d orbitals tend to destabilize the b level.

The PE spectrum does not provide any information concerning the symmetry species of the single d electron.

According to the EPR study of the monomeric Me_3Cp and Cp* complexes the molecular ground state is $^2A_1$.[33]

The introduction of one methyl group into the Cp ligand brings about a general low-IE shift of PE bands. Ionizations c and d exhibit the largest shift, amounting to 0.35 and 0.3 eV, respectively. Features a and b are destabilized by 0.21–0.26 eV. Bands e and f exhibit the lowest sensitivity to methylation (ΔIE = 0.11–0.16 eV).

The substitution of Cp by Me_3Cp brings about an earlier onset of the envelope of σ ionizations on which band f is superimposed. The low-IE shifts of bands c and d amount to 0.83 and 0.88 eV with respect to the parent non-methylated complex. Ionizations a and b exhibit medium sensitivity (ΔIE = 0.63 and 0.56 eV). Bands e and f are shifted by only 0.42 and 0.25 eV. The introduction of four and five methyl groups brings about an overall change of the appearance of the PE spectra. Due to the lower sensitivity of band b to cyclopentadienyl methylation, this band overlaps with features c and d and forms only a shoulder on the low-IE side in the spectrum of the permethylated complex. The permethylation of the cyclopentadienyl ligand destabilizes bands a and b by 0.93 eV. Ionization c exhibits the largest IE shift (1.45 eV). Band e is destabilized by 0.72 eV, and feature f is the least sensitive to permethylation (0.49 eV).

The average value of ΔIE per methyl is 0.3 eV for ionization features c and d. The sensitivity of bands a and b is approximately 0.2 eV per methyl. Ionizations e and f are shifted by 0.15 and 0.1 eV per methyl, respectively. The cyclopentadienyl methylation affects the Cp–Ti–Cp angle due to the steric congestion of the methyl groups. No X-ray diffraction data are available for the monomeric Cp_2TiCl for a comparison with the bending in the permethylated species. For the related Cp'_2TiCl_2 complexes the permethylation brings about the opening of the Cp–Ti–Cp angle from 130.97 to 137.4°.[37,38] A slight destabilization of the cyclopentadienyl levels due to the ligand bending was observed in PE spectra of Cp'_2TiCl_2, in agreement with the EHT calculations.[27] No spectral features indicating significant changes in orbital mixing were observed. The EHT study of the Cp_2M moiety[26] shows that a change in the Cp–Ti–Cp angle lower than 10° brings about no switching of orbital ordering. Thus, the prevailing effect of the methyl groups is of electronic nature rather than due to the steric congestion. The band displacements indicate that the orbitals correlating with ionizations c and d have the largest cyclopentadienyl character. The smallest intensity drop of these bands in the He II spectrum agrees with the assignment of these bands to components of the $e_1(\pi)$ levels of cyclopentadienyl ligands.

The dramatic decrease in the intensity of bands e and f and their low sensitivity to the methylation indicate a halogen p character. The Ti–Cl σ interaction is obviously stronger than the interaction of the halogen $p(\pi)$ lone pairs ($b_1 + b_2$ symmetry species) with the Cp_2Ti moiety (Figure 1). Thus, the higher IE band f is assigned to the a_1 σ-(Ti–Cl) ionization having a predominant contribution from the a_1 halogen p orbital. The halogen lone pairs of π symmetry can be assigned to band e. The gap between bands e and f is 0.52 eV for the non-methylated species and increases to a value of 0.85 for Cp^*_2TiCl. The increasing gap between the σ(Ti–Cl) and $p(\pi)$ halogen orbitals upon methylation may indicate some delocalization of the halogen lone pairs on the cyclopentadienyl ligands. In terms of orbital interaction, despite its through-space or through-bond nature the destabilization of the higher lying cyclopentadienyl orbitals induces some low-IE shift of the deeper lying halogen $p(\pi)$ orbitals. The slight opening of the Cp–Ti–Cp angle may also affect the Cl–Cp interaction.

The low-IE shifts of band b upon methylation show a decreased localization on the Cp ligand in comparison to that for ionizations c and d. The value of the He II/He I intensity ratio is approximately between those of cyclopentadienyl- and halogen-based orbitals. The lower localization of level b on the cyclopentadienyl ligands is thus due to an interaction with halogen p orbitals rather than with the central atom d orbitals. The b_2 halogen $p(\pi)$ orbital perpendicular to the equatorial plane has the most feasible orientation for an overlap with the cyclopentadienyl π orbitals as depicted in Figure 1.

The gradual changes of PE spectra in the series are explained by the electronic effects of the methyl groups. The $(Me_5Cp)_2TiCl$ species is obviously monomeric in the vapor phase, as no dimer was detected in the condensed phase.[19] A splitting of the d band was found in the PE spectrum of the binuclear complex (μ-η^5:η^5-fulvalene)bis(μ-chloro)bis((η^5-cyclopentadienyl)titanium), where d electrons are weakly coupled.[39] An analogous splitting or some broadening would be observed if dimerized species were populated, and a more complex shape of halogen-based ionizations would result from the interaction of halogen p orbitals. No such spectral feature was found in the PE spectra of the lower members of the series. This indicates that under the conditions of PE measurement, i.e. a pressure of approximately 10 Pa and a temperature of ~500 K, the complexes are monomeric rather than dimeric. The mass spectra support the presence of monomeric units in the gas phase. No signal corresponding to the molecular ion of the dimer or its fragmentation was observed in the mass spectra.

Bis(cyclopentadienyl)titanium Bromides. The shape of the PE spectrum of the parent Cp_2TiBr complex is slightly different from that of the chloro derivative (Figure 3) due to the overlap of bands e and f with the band system c + d. Bands e and f are shifted by 0.5–0.7 eV to lower IE in comparison to those of the chloro species. The shifts of bands a–d do not exceed twice the experimental error. The lower electronegativity of bromine brings about the low-IE shifts of levels rich in halogen character. The increase of the relative intensity of band a in a switch from He I to He II is observed. Due to an extensive overlap of bands and a poorer resolution of He II spectra no quantitative estimation of the He II/He I intensity ratio can be drawn for particular bands in the 8.5–10.5-eV range. For band b the He II/He I relative intensity ratio is slightly higher than for the Cl derivative. However, the ratio of He II/He I intensity for $p(\pi)$ orbitals was found to be approximately 1.4 times higher for bromine.[40,41] Thus, the higher intensity ratio for band b in comparison to that for Cp_2TiCl cannot be simply interpreted in terms of different orbital mixing.

Due to the higher sensitivity of bands c and d toward methylation, features e and f are better resolved in the spectra of higher members of the series. The sharp intensity drop of bands e and f in the He II spectrum of

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$(Me_4Cp)_2TiBr$ corroborates their assignment to halogen-localized orbitals.

The average values ΔIE of methyl group are (within the experimental error) identical with those for the chloro derivatives. Thus, the same assignment of the PE bands is adopted as for the Cp'_2TiCl species.

No spin–orbital splitting of bromine p(π) ionizations has been resolved in the above PE spectra, in spite of the atomic spin–orbit coupling parameter of 0.305 eV for bromine. Reduction of the spin–orbit splitting is approximately proportional to the decrease of the electron density on the atomic center. Bonding interactions bring about broadening of the vibrational envelope of lone-pair ionizations. Thus, unresolved spin–orbit components within band e indicate some interaction of bromine p(π) orbitals with the Cp'_2Ti fragment. This interaction seems to be of comparable extent for the two symmetry species of p(π) orbitals. No spectral feature indicating the presence of the dimerized species was detected in the PE spectra.

Conclusions

The effect of methyl groups upon ionization energies is additive. Variations of photoionization cross sections with photon energy and band shifts provide a consistent assignment. According to the classification of the bonding situation in bis(cyclopentadienyl)metal halides introduced by Cauletti and co-workers,[6] the Cp'_2TiX complexes adhere to the class A systems; i.e., the cyclopentadienyl $e_1(\pi)$ orbitals lie above the halogen lone pairs. The extent of the delocalization of the halogen p orbitals seems to be comparable for Cl and Br. No dimer species were detected in the PE spectra of the Cp_2TiX and $(MeCp)_2TiX$ complexes.

Registry No. Cp_2TiCl, 60955-54-6; $(MeCp)_2TiCl$, 32698-18-3; $(Me_3Cp)_2TiCl$, 120325-58-8; $(Me_4Cp)_2TiCl$, 120325-59-9; $(Me_5Cp)_2TiCl$, 73348-99-9; Cp_2TiBr, 128467-43-6; $(MeCp)_2TiBr$, 137045-86-4; $(Me_3Cp)_2TiBr$, 140167-91-5; $(Me_4)_2TiBr$, 140167-90-4; $(Me_5Cp)_2TiBr$, 107495-35-2.

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Synthesis, Molecular Structure, and Reactivity of Octahedral Alkylhydridoosmium(II) Complexes $[OsH(R)(CO)_2(PR'_3)_2]$

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In contrast to the reaction of $[OsH(\eta^2\text{-}BH_4)(CO)(PR'_3)_2]$ (**2a,b**) with methanol under reflux, which gives the dihydrides *cis,cis,trans*-$[OsH_2(CO)_2(PR'_3)_2]$ (**4a,b**), the corresponding reaction with ethanol or 2-methoxyethanol under the same conditions leads to the formation of the alkylhydridoosmium(II) complexes $[OsH(R)(CO)_2(PR'_3)_2]$ (**5a,b** (R = CH_3), **6a,b** (R = $MeOCH_2$)) in good yields. The X-ray structural analysis of **5a** reveals an octahedral coordination sphere around the osmium center with the CO ligands in cis and the phosphines in trans positions. Reactions of **5a,b** with electrophiles preferentially leads to cleavage of the Os–CH_3 bond; thus, on treatment with HX (X = Cl, CH_3CO_2, CF_3CO_2) the monohydrides $[OsHX(CO)_2(PR'_3)_2]$ (**11**, **12**, **13a,b**) are formed. Protonation of **5a** with HBF_4 in ether/acetone yields quantitatively the cationic hydrido complex $[OsH(acetone)(CO)_2(P^iPr_3)_2]BF_4$ (**15**) whereas from **5a,b** and HBF_4 in the presence of water the compounds $[OsH(H_2O)(CO)_2(PR'_3)_2]BF_4$ (**16a,b**) are obtained. Complex **15** reacts with acetonitrile, trimethyl phosphite, or pyrazole by displacement of the acetone ligand to give the compounds $[OsH(L)(CO)_2(P^iPr_3)_2]BF_4$ (**17**–**19**). Subsequent reaction of **19** (L = pyrazole) with the dimers $[M(\mu\text{-}OMe)(diolefin)]_2$ (**20**, **22**, M = Rh; **21**, M = Ir) produces the heterobinuclear complexes **23**–**25**; in these the metal centers (Os and Rh or Ir) are bridged by a hydride and a pyrazolyl group. Treatment of **15** with methyl vinyl ketone and CO_2Me-substituted alkynes $RC{\equiv}CO_2Me$ gives cationic four- and five-membered metallacycles **26**–**29** which are formed by a Markovnikov or an anti-Markovnikov type of insertion of the unsaturated substrate into the Os–H bond.

We have recently reported that the five-coordinate hydridoosmium complex $[OsHCl(CO)(P^iPr_3)_2]$ (**1a**) under hydrogen not only catalyzes the reduction of cyclohexene, 1,3- and 1,4-cyclohexadiene, styrene, and diphenyl- and phenylacetylene[1,2] but in presence of $NaBH_4$ also serves as a catalyst for hydrogen transfer from 2-propanol to cyclohexanone, acetophenone, benzylideneacetone, benzylideneacetophenone, and phenylacetylene.[3-5] It was shown that compound **1a** reacts with $NaBH_4$ to give initially the tetrahydridoborate complex **2a**, which in the presence of 2-propanol decomposes to the tetrahydride **3a** (Scheme I).[6] If $[OsHCl(CO)(PMe^tBu_2)_2]$ is used as starting material, in a similar reaction sequence complex

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