www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 593–594 (2000) 19–26

Carbon monoxide and tertiary phosphines as ligands in cyclopentadienyl derivatives of Group 4 elements in high oxidation state

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Received 4 March 1999; accepted 20 April 1999

Dedicated to our 'maestro', Professor Fausto Calderazzo, on the occasion of his 70th birthday.

Abstract

The titanocene dicarbonyl dication $[TiCp_2(CO)_2][BPh_4]_2$, (**1**) has been obtained in toluene under carbon monoxide by double protonation of $TiCp_4$ with $[NH^nBu_3][BPh_4]$ or by two-electron oxidation of $TiCp_2(CO)_2$ with $[FeCp_2][BPh_4]$. Protonation reactions on $ZrCp_4$ and $HfCp_4$ proceed with elimination of 1 mol of cyclopentadiene independently on the ammonium salt/MCp_4 molar ratio used. By this route the high electrophilic, solvent-free $[ZrCp_3]^+$ cation has been isolated and characterized by IR, ^{1}H-NMR and elemental analysis. In the case of hafnium, the isolation has not been possible; nevertheless, in the presence of CO a rare example of a carbonyl derivative of hafnium(IV), $[HfCp_3(CO)][BPh_4]$, has been isolated and characterized.

Keywords: Titanium; Zirconium; Hafnium; Carbonyl; Cyclopentadienyl

1. Introduction

Metal carbonyl chemistry is dominated by low valent metal compounds (metals with d^2–d^8 electronic configurations) in which $d \rightarrow \pi^*$ back-bonding contributes significantly to the M–CO bond. However, metal carbonyl derivatives are known which exhibit $\tilde{\nu}_{CO}$ values higher than that of the free CO (2143 cm^{-1} in the gas phase), suggesting that those M–CO bonds are primarily σ-donor in character and that the $d \rightarrow \pi^*$ back-bonding is well reduced. To this regard, much attention has been paid to late transition element species [neutral or cationic derivatives of Pd(II), Pt(II), Cu(I), Ag(I), Au(I) and Hg(II) have been prepared [1]]. Moreover, hexacarbonyl cations of Fe(II), Ru(II), Os(II) and Ir(III) have been recently added [1] to the isostructural M(I) species, M = Mn, Tc, Re, obtained by Fischer and coworkers [2] and by Hieber and coworkers [3] more than 30 years ago.

On the other hand, electrophilic, high oxidation state, early transition metals are capable of coordinating carbon monoxide and examples of such carbonyl derivatives of Group 4 metals have been previously reported [4].

In the framework of our research projects on organometallic derivatives of early transition elements, we recently described [5] a high yield procedure for the preparation of MCp_4, M = Ti, Zr, Hf. These species are reactive towards proton sources so that one or two cyclopentadienyl rings are protonated to give $MCp_3(O_3SCF_3)$ or MCp_2L_2 (L = Cl, O_3SCF_3, CF_3-COO, Ph_3SiO) and cyclopentadiene [5].

It is known that the highly electrophilic organyl cations $[MCp_2R]^+$ can be obtained, inter alia, by protonation of the corresponding MCp_2R_2 compounds with trialkylammonium salts of weakly coordinating anions [6]. For this reason, we decided to examine the reactivity of the tetracyclopentadienyl derivatives of Group 4 elements with $[N^nBu_3H][BPh_4]$ in the presence or absence of donor molecules.

Dealing with carbonyl derivatives and, in particular, with the synthesis and the characterization of the first dicationic metallocene dicarbonyl species,

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0022-328X/00/$ - see front matter
PII: S0022-328X(99)00233-8

$[TiCp_2(CO)_2][BPh_4]_2$, this paper wishes to be a contribution [7] to a field in which Professor Fausto Calderazzo has made many important contributions.

2. Results and discussion

2.1. Titanium

By reaction of $TiCp_4$ with $[N^nBu_3H][BPh_4]$ in toluene under a CO atmosphere, the ionic species $[TiCp_2(CO)_2][BPh_4]_2$, (**1**), (Eq. (1)) was isolated [8]. Compound **1** has also been synthesized by oxidizing $TiCp_2(CO)_2$ with two equivalents of $[FeCp_2][BPh_4]$ in toluene under a CO atmosphere (Eq. (2)) [9]:

$$TiCp_4 + 2[N^nBu_3H][BPh_4] + 2CO \rightarrow [TiCp_2(CO)_2][BPh_4]_2 + 2CpH + 2N^nBu_3 \quad (1)$$

$$TiCp_2(CO)_2 + 2[FeCp_2][BPh_4] \rightarrow [TiCp_2(CO)_2][BPh_4]_2 + 2FeCp_2 \quad (2)$$

$[TiCp_2(CO)_2][BPh_4]_2$ is an exceedingly moisture-sensitive brown solid, whose IR spectrum in the solid state shows two strong carbonyl absorptions at 2119 and 2099 cm^{-1}, besides the bands typical of the carbocyclic groups (Cp^- and phenyl). Compound **1** is thermally stable and does not lose CO at room temperature (r.t.) even under high vacuum. On the other hand, rapid evolution of gas and sublimation of BPh_3 is observed by heating the complex in vacuo at ca. 50°C.

Instability to moisture and to basic solvents (CO is promptly evolved on treatment of **1** with THF or acetone) and limited solubility in hydrocarbon solvents did not allow single crystals of **1** to be grown. Nevertheless, a pseudotetrahedral structure of the $[TiCp_2(CO)_2]^{2+}$ cation can be proposed on the basis of its spectral pattern in the carbonyl stretching region, similar to that of $MCp_2(CO)_2$, M = Ti, Zr, Hf [10], and $[VCp_2(CO)_2]^+$ [11], i.e. two carbonyl stretching vibrations of approximate equal intensity ($A_1 + B_1$ symmetry). The OC–M–CO angle of the $[TiCp_2(CO)_2]^{2+}$ cation, calculated on the basis of the integrated areas of the symmetric and asymmetric carbonyl stretching vibrations [12] is 86.8°, compared with 88° [13] as obtained from the Nujol mull spectrum of $TiCp_2(CO)_2$ [CO = 1962 and 1874 cm^{-1}]. The decreased interligand angle for **1** is qualitatively in agreement with the increased oxidation state on going from titanium(II) to titanium(IV).

Compound **1** is the first dicationic metallocene dicarbonyl derivative to be described; moreover, $[TiCp_2(CO)_2][BPh_4]_2$ adds to the still restricted family of the dicationic carbonyl compounds of recent acquisition in the literature [14].

The reactivity of the new dicarbonyl derivative **1** has been examined.

Carbon monoxide is readily lost from $[TiCp_2(CO)_2][BPh_4]_2$ in the presence of chloride ions: the reactions with [PPN]Cl or $[NH_2Et_2]_2[ZrCl_6]$ in toluene give quantitative yields of $TiCp_2Cl_2$ and $[PPN][BPh_4]$ or $[NH_2Et_2][BPh_4]$ and $ZrCl_4$, respectively (Eqs. (3) and (4)). Gas-volumetric controls of the reactions showed the treatment of **1** with [PPN]Cl or $[NH_2Et_2]_2[ZrCl_6]$ in toluene at 26.8°C causes CO evolution corresponding to a CO/Ti molar ratio of 1.98 and 1.96, respectively:

$$[TiCp_2(CO)_2][BPh_4]_2 + 2[PPN]Cl \rightarrow TiCp_2Cl_2 + 2[PPN][BPh_4] + 2CO \quad (3)$$

$$[TiCp_2(CO)_2][BPh_4]_2 + [NH_2Et_2]_2[ZrCl_6] \rightarrow TiCp_2Cl_2 + ZrCl_4 + 2CO + 2[NH_2Et_2][BPh_4] \quad (4)$$

Carbon monoxide displacement is also observed in the reaction of **1** with $NHEt_2$ or dmpe. In both cases, the products consist of dicationic derivatives of titanocene (see Eq. (5)):

$$[TiCp_2(CO)_2][BPh_4]_2 + L_2 \rightarrow [TiCp_2L_2][BPh_4]_2 + 2CO \quad (5)$$

$L_2 = 2NHEt_2$, dmpe.

$[TiCp_2(NHEt_2)_2][BPh_4]_2$ is a brown solid, substantially insoluble in all hydrocarbon solvents. Its IR spectrum in the solid state shows the bands typical of the carbocyclic groups (Cp^- and phenyl: 3096 m, 3052 m-s, 3038 m-s, 862 m, 848 m-s, 806 s, 743 s, 710 s). A medium intensity absorption at 3141 cm^{-1} has been assigned to the N–H stretching vibration of the coordinated amine; the lower wavenumber of this band with respect to both the free or coordinated amine [15] suggests that some H-bond interaction is involved. Noticeable is that, in reaction 5, $NHEt_2$ does not react by nucleophilic attack on the coordinated CO [16], but it behaves as a better donor ligand with respect to CO and displaces it from the coordination sphere of the metal.

$[TiCp_2(dmpe)][BPh_4]_2$ has been characterized by elemental analysis, IR and ^{31}P-NMR spectra. The Nujol mull IR spectrum shows some very intense bands at 867 m, 848 m, 800 s, 748 s, 732 s, 707 vs cm^{-1} assigned to the C–H bending vibrations of the aromatic rings. $[TiCp_2(dmpe)][BPh_4]_2$ is slightly soluble in toluene and is soluble in THF, where it is stable over short periods of time. This higher solubility with respect to $[TiCp_2(CO)_2][BPh_4]_2$ and $[TiCp_2(NHEt_2)_2][BPh_4]_2$ has to be attributed to the presence of coordinated dmpe, because of its increased stability in basic solvents. The ^{31}P-NMR spectrum presents the resonance of the coordinated phosphine at −9.1 ppm in toluene and at −8.1 ppm in THF, to be compared with the peak of free PEt_3 at −18.8 ppm.

The oxidation state IV of titanium in **1** was further confirmed by the reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with

$CoCp_2$ in toluene under an argon atmosphere which gives quantitative yields of $TiCp_2(CO)_2$ and $[CoCp_2][BPh_4]$ (Eq. (6)):

$$[TiCp_2(CO)_2][BPh_4]_2 + 2CoCp_2 \rightarrow TiCp_2(CO)_2 + 2[CoCp_2][BPh_4] \quad (6)$$

Noteworthy is the reaction of **1** with water. A suspension of **1** in toluene promptly reacts with water to give $TiCp_2(CO)_2$ (90%, IR analysis), biphenyl (GC-MS analysis), suggesting that the Ti(IV) → Ti(II) reduction is promoted by the BPh_4^- anion [17]. Some benzene was observed in solution (GC-MS analysis) probably due to hydrolysis of the triphenylboron formed during the reduction.

2.2. Zirconium and hafnium

Whereas $TiCp_4$ decomposes and $HfCp_4$ does not react in toluene or decomposes in CH_2Cl_2 when treated with $[N^nBu_3H][BPh_4]$ (vide infra), $ZrCp_4$ promptly and cleanly reacts with $[N^nBu_3H][BPh_4]$ in CH_2Cl_2 to give $[ZrCp_3][BPh_4]$ (**2**) (Eq. (7)):

$$ZrCp_4 + [N^nBu_3H][BPh_4] \rightarrow [ZrCp_3][BPh_4] + CpH + N^nBu_3 \quad (7)$$

The $[ZrCp_3]^+$ cation was not previously isolated as a pure material; nevertheless its presence in solution [as obtained by reaction of $ZrCp_3Me$ with $B(C_6F_5)_3$] has been deduced on the basis of the reactivity of the freshly prepared solutions with Lewis bases [4j, 18].

We have observed that when solutions of $ZrCp_4$ in CH_2Cl_2 are treated with $[N^nBu_3H][BPh_4]$, a yellow solid forms which is not stable in the reaction medium [19]; in order to isolate **2** in reasonable yields, it has to be separated quickly from the solution (see Section 3). The lower solubility of $[ZrCp_3][BPh_4]$ in CH_2Cl_2 with respect to $[ZrCp_3][MeB(C_6F_5)_3]$, may be the reason for the successful isolation of **2**. $[ZrCp_3][BPh_4]$ is a pale-yellow solid extremely sensitive to moisture either in the solid state and in solution [20]. The Nujol mull IR spectrum shows, among the others, a weak band at 3116 cm^{-1} due to the C–H stretching vibration of the Cp rings, some weak absorptions at 3094, 3077 and 3048 cm^{-1} attributed to the C–H stretching vibrations of the aromatic rings and some very intense bands at 846, 810, 746, 735 and 707 cm^{-1} assigned to the C–H bending vibrations of the aromatic rings. The ^1H-NMR spectrum of **2** in CD_2Cl_2, registered immediately after mixing the components, has peaks at 7.6, 7.5, 7.4, 7.1 and 6.9 ppm assigned to the protons of the $[BPh_4]^-$ anion and a singlet at 6.07 ppm due to the Cp protons.

As a confirmation of its identity, $[ZrCp_3][BPh_4]$ is quantitatively carbonylated to $[Cp_3Zr(CO)][BPh_4]$ (see Eq. (8)), which can also be obtained by direct protonolysis of $ZrCp_4$ under a CO atmosphere in CH_2Cl_2 or toluene as solvent (Eq. (9)). Gas volumetric controls of the carbonylation reactions have shown that the amount of CO absorbed corresponds to a Zr/CO molar ratio of 1. The same product is formed when using an $[N^nBu_3H][BPh_4]/ZrCp_4$ molar ratio of 2 [21]:

$$[ZrCp_3][BPh_4] + CO \rightarrow [Cp_3Zr(CO)][BPh_4] \quad (8)$$

$$ZrCp_4 + [N^nBu_3H][BPh_4] + CO \rightarrow [ZrCp_3(CO)][BPh_4] + CpH + N^nBu_3 \quad (9)$$

The solid state IR spectrum of $[ZrCp_3(CO)][BPh_4]$ presents, besides the absorptions due to the aromatic rings (3070, 3052, 841, 819, 764, 736, 707 cm^{-1}), a carbonyl band at 2132 cm^{-1} (Nujol mull) slightly below that of the free CO (2143 cm^{-1} in the gas phase). Noteworthy is the fact that the reported value of the carbonyl stretching frequency of $[ZrCp_3(CO)][CH_3B(C_6F_5)_3]$ [4j] is 2150 cm^{-1} (KBr), slightly above that of the free CO, 2143 cm^{-1}.

Even though dichloromethane solutions of $HfCp_4$ do not react with $[N^nBu_3H][BPh_4]$ even after prolonged reaction times [22], in the presence of CO a fast reaction is observed with precipitation of $[HfCp_3(CO)][BPh_4]$ (Eq. (10)), the third member of the restricted family of d^0 carbonyl species of hafnium [4d, 4k]:

$$HfCp_4 + [N^nBu_3H][BPh_4] \xrightarrow[CH_2Cl_2]{CO} [HfCp_3(CO)][BPh_4] + CpH + N^nBu_3 \quad (10)$$

In the solid state IR spectrum, it presents, besides the absorptions due to the Cp (3121 cm^{-1}) and to the phenyl rings (3070, 3052, 844, 799, 773, 744, 701 cm^{-1}), a carbonyl band at 2132 cm^{-1}. The ^1H-NMR spectrum in CD_2Cl_2 presents aromatic peaks at 7.6, 7.5 and 7.1 ppm assigned to the protons of the $[BPh_4]^-$ anion and a singlet at 6.3 ppm due to the Cp protons.

Also PEt_3 has been used to stabilize the $[MCp_3]^+$, M = Zr, Hf, cations. The complexes MCp_4, M = Zr, Hf, react in CH_2Cl_2 with $[N^nBu_3H][BPh_4]$ in the presence of PEt_3 giving the new phosphino complexes $[MCp_3(PEt_3)][BPh_4]$, M = Zr, Hf, (Eq. (11)):

$$MCp_4 + [N^nBu_3H][BPh_4] \xrightarrow[CH_2Cl_2]{PEt_3} [MCp_3(PEt_3)][BPh_4] + CpH + N^nBu_3 \quad (11)$$

M = Zr, Hf.

$[ZrCp_3(PEt_3)][BPh_4]$ has been synthesized also by directly treating $[ZrCp_3][BPh_4]$ with an excess of PEt_3 in CH_2Cl_2. The compound has been characterized by elemental analysis, IR and ^1H and ^{31}P-NMR spectra [23,24]. In particular, the ^{31}P-NMR spectrum presents the resonance of the coordinated phosphine at 13.9 ppm, to be compared with the peak of free PEt_3 at -18.8 ppm. Under a CO atmosphere, $[ZrCp_3(PEt_3)][BPh_4]$ does not undergo displacement of the phosphine ligand by the CO as is observed for the bis(cyclopentadienyl)diphosphine derivatives $MCp_2(PR_3)_2$ [25]. The highly electrophilic nature of zirconium in the oxidation state +IV can be invoked to explain its higher affinity for a stronger electron-donor ligand, such as PEt_3, with respect to a better π-acceptor ligand, such as CO.

3. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were recorded on an FT-1725X instrument, on solutions or Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air.

^1H-(200 MHz, TMS as reference) and ^{31}P-NMR (81 MHz, H_3PO_4 in H_2O as reference) spectra were measured on a Varian Gemini 200BB instrument.

PEt_3 (Argus Chemicals) and dmpe (Aldrich) were commercially available and were used with no further purification. PPNCl (Strem) was commercially available and was freed from oxygen and moisture before use by recrystallization from H_2O followed by drying in vacuo.

The following reagents were prepared according to literature procedures: MCp_4, M = Ti, Zr, Hf [5], $TiCp_2(CO)_2$ [26], $[NH_2Et_2]_2[ZrCl_6]$ [27], $[FeCp_2][BPh_4]$ [28], $CoCp_2$ [29].

$[N^nBu_3H][BPh_4]$ was prepared from equimolar amounts of $[N^nBu_3H][Cl]$ and $Na[BPh_4]$ in H_2O. The resulting suspension was filtered and the colorless solid was dried over P_4O_{10} in vacuo for 24 h and then stored in flame-sealed vials. IR (Nujol and PCTFE): $\tilde{\nu} = 3563$ s, 3506 s, 3108 m, 3050 s, 3034 s, 2962 vs, 2931 s, 2873 m, 1945 w, 1884 w, 1820 w, 1767 w, 1600 m-w, 1580 m, 1469 s, 1426 m-s, 1403 m, 1384 m-s, 1305 w, 1267 m, 1183 m, 1153 m, 1096 w, 1067 m, 1033 m, 973 w, 924 m-w, 861 w, 848 m, 797 w, 745 vs, 734 vs, 711 vs, 626 w, 615 m, 606 m-s cm^{-1}. ^1H-NMR (CD_2Cl_2, 25°C): $\delta = 7.5$ (m, 4H, ar), 7.1 (t, 8H, ar), 6.9 (t, 8H, ar), 3.8 (s, 1H, NH), 2.2 (m, 6H, CH_2), 1.7 (m, 12H, CH_2), 0.9 (t, 9H, CH_3) ppm.

3.1. Synthesis of $[TiCp_2(CO)_2][BPh_4]_2$ (**1**)

3.1.1. A. From $TiCp_4$ and $[N^nBu_3H][BPh_4]$ under a CO atmosphere

A suspension of $[N^nBu_3H][BPh_4]$ (0.35 g, 0.7 mmol) in toluene (10 ml) was saturated with CO at atmospheric pressure and $TiCp_4$ (0.10 g, 0.32 mmol) was then added. After 6 h stirring at r.t., a suspension of a brown solid in an almost colorless solution was obtained. The suspension was filtered and the solid was dried in vacuo and identified as $[TiCp_2(CO)_2][BPh_4]_2$, (0.22 g, 79% yield). Anal. Found: C, 82.5; H, 6.0; CO, 6.3. Calc. for $[TiCp_2(CO)_2][BPh_4]_2$ ($C_{60}H_{50}B_2O_2Ti$): C, 82.6; H, 5.8; CO, 6.4. IR (Nujol and PCTFE): $\tilde{\nu} = 3093$ m, 3053 m-s, 2119 s, 2099 s, 1951 v w, 1880 v w, 1772 v w, 1591 m, 1582 m-w, 1480 m, 1430 m-s, 1376 m, 1332 m, 1263 m, 1240 m, 1185 w, 1157 w, 1108 w, 1068 w, 1031 m, 1019 m, 885 m-w, 834 s, 817 s, 773 w, 746 s, 735 s, 708 vs, 675 m, 639 w, 614 w, 604 m cm^{-1}. The same product is formed when using an $[N^nBu_3H][BPh_4]/TiCp_4$ molar ratio of 1.

3.1.2. B. From $TiCp_2(CO)_2$ and $[FeCp_2][BPh_4]$

A suspension of $[FeCp_2][BPh_4]$ (2.54 g, 5.0 mmol) in toluene (50 ml) was saturated with CO at atmospheric pressure, and solid $TiCp_2(CO)_2$ (0.59 g, 2.5 mmol) was added. After 72 h stirring at r.t., a suspension of a brown solid in an orange solution was obtained. An IR spectrum of the solution showed no absorptions due to $TiCp_2(CO)_2$. The suspension was filtered, and the brown solid was washed with toluene until almost colorless washings (5 × 5 ml). The solid was then dried in vacuo at r.t. and identified as $[TiCp_2(CO)_2][BPh_4]_2$ (0.17 g, 78% yield). Anal. Found: C, 82.5; H, 6.0; CO, 6.3. Calc. for $[TiCp_2(CO)_2][BPh_4]_2$ ($C_{60}H_{50}B_2O_2Ti$): C, 82.6; H, 5.8; CO, 6.4. IR (Nujol and PCTFE): $\tilde{\nu} = 3093$ m, 3053 m-s, 2119 s, 2099 s, 1951 v w, 1880 v w, 1772 v w, 1591 m, 1582 m-w, 1480 m, 1430 m-s, 1376 m, 1332 m, 1263 m, 1240 m, 1185 w, 1157 w, 1108 w, 1068 w, 1031 m, 1019 m, 885 m-w, 834 s, 817 s, 773 w, 746 s, 735 s, 708 vs, 675 m, 639 w, 614 w, 604 m cm^{-1}. The orange solution was evaporated to dryness under reduced pressure at r.t., and the residue afforded $FeCp_2$ (0.66 g, 71% yield) after sublimation (0.05 mmHg, 40°C).

3.2. Reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with [PPN]Cl

A suspension of [PPN]Cl (0.59 g, 1.0 mmol) in toluene (25 ml) was treated with solid $[TiCp_2(CO)_2][BPh_4]_2$ (0.46 g, 0.5 mmol). From the initially brown suspension, a colorless solid precipitated out and the solution turned red–orange after 15 h stirring at r.t. The suspension was filtered, the solid was washed with toluene (6 × 3 ml), dried in vacuo and identified as $[PPN][BPh_4]$ (0.60 g, 70% yield) from its IR spectrum. The solution was dried in vacuo at r.t. affording 0.11 g (88% yield) of $TiCp_2Cl_2$, identified by IR and ^1H-NMR spectra. A gas-volumetric control of the reaction showed that the treatment of $[TiCp_2(CO)_2][BPh_4]_2$ with [PPN]Cl in toluene at 26.8°C causes CO evolution corresponding to a CO/Ti molar ratio of 1.98.

3.3. Reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with $[NH_2Et_2]_2[ZrCl_6]$: gas-volumetric study

A suspension of $[NH_2Et_2]_2[ZrCl_6]$ (0.21 g, 0.46 mmol) in toluene (25 ml) was saturated with CO, thermostated at 20.9°C, connected to a gas-volumetric apparatus and then contacted with solid $[TiCp_2(CO)_2][BPh_4]_2$ (0.41 g, 0.47 mmol) contained in a sealed glass ampoule. Evolution of CO corresponding to a CO/Ti molar ratio of 1.96 was observed. The resulting suspension was filtered. The solvent was removed in vacuo at r.t. and the solid washed with heptane (2 × 10 ml), dried in vacuo and identified as $TiCp_2Cl_2$ (0.06 g, 51% yield) by elemental analysis (Ti, Cl), IR and ^1H-NMR spectra.

3.4. Reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with $NHEt_2$: preparation of $[TiCp_2(NHEt_2)_2][BPh_4]_2$

To a suspension of $[TiCp_2(CO)_2][BPh_4]_2$ (0.43 g, 0.48 mmol) in toluene (25 ml) $NHEt_2$ (0.3 ml, 2.9 mmol) was added. Evolution of gas was observed. After ca. 16 h stirring at r.t., the suspension of a red–brown solid in a pale-orange solution was obtained. After filtration, the solid was washed with toluene (5 ml) and dried in vacuo, obtaining $[TiCp_2(NHEt_2)_2][BPh_4]_2 \cdot C_7H_8$ as a red–brown solid (0.32 g, 63% yield). Anal. Found: C, 83.5; H, 11.1; N, 2.5. Calc. for $C_{73}H_{80}B_2N_2Ti$: C, 83.1; H, 7.6; N, 2.5. IR (Nujol and PCTFE): $\tilde{\nu} = 3141$ m (ν_{NH}), 3096 m, 3052 m-s, 3038 m-s, 1954 v w, 1881 v w, 1816 v w, 1776 v w,1579 m-w, 1565 m-w, 1478 m-s, 1428 m-s, 1413 m, 1308 m-w, 1262 m, 1184 w, 1155 w, 1148 w, 1068 w, 1031 m, 862 m, 848 m-s, 806 s, 743 s, 710 s, 662 m cm^{-1}.

3.5. Reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with dmpe: preparation of $[TiCp_2(dmpe)][BPh_4]_2$

To a suspension of $[TiCp_2(CO)_2][BPh_4]_2$ (0.36 g, 0.41 mmol) in toluene (10 ml), dmpe (0.07 ml, 0.42 mmol) was added. After ca. 24 h stirring at r.t., the suspension of a brown solid in a pale-orange solution was obtained. After filtration, the solid was washed with toluene (5 ml) and dried in vacuo, obtaining $[TiCp_2(dmpe)][BPh_4]_2$ as a brown solid (0.25 g, 63% yield). Anal. Found: C, 80.1; H, 7.1; Ti, 4.8. Calc. for $[TiCp_2(dmpe)][BPh_4]_2$ ($C_{64}H_{66}B_2P_2Ti$): C, 79.5; H, 6.9; Ti, 4.9. IR (Nujol): $\tilde{\nu} = 3043$ m, 1579 w, 1302 m, 1286 m, 1262 m, 1194 m, 1182 w, 1150 w, 1030 m, 1071 w, 1030 m, 1019 m, 939 w, 903 w, 867 m, 848 m, 800 s, 748 s, 732 s, 707 vs cm^{-1}. ^{31}P-NMR (THF): −8.1 ppm.

3.6. Reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with $CoCp_2$

A suspension of $[TiCp_2(CO)_2][BPh_4]_2$ (0.38 g, 0.43 mmol) in toluene (10 ml) was treated with solid $CoCp_2$ (0.17 g, 0.90 mmol). After 1 h stirring at r.t., an IR spectrum of the solution showed the presence of $TiCp_2(CO)_2$ (98% yield, calculated on the basis of the intensity of the carbonyl stretching vibration at 1885 cm^{-1}, $\varepsilon_{1885} = 2200$ M^{-1} cm^{-1}). The suspension was filtered and the yellow solid was washed with toluene (3 ml), dried in vacuo, and identified as $[CoCp_2][BPh_4]$ (0.32 g, 69% yield) from its IR spectrum.

3.7. Reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with H_2O

Degassed H_2O (0.015 ml, 0.83 mmol) was added to a suspension of $[TiCp_2(CO)_2][BPh_4]_2$ (0.38 g, 0.43 mmol) in toluene (10 ml). An IR spectrum of the solution showed the presence of $TiCp_2(CO)_2$ (90% yield calculated on the basis of the absorbance of the carbonyl stretching vibration at 1885 cm^{-1}; $\varepsilon_{1885} = 2200$ M^{-1} cm^{-1}). A gas-chromatographic analysis of the solution showed the presence of C_6H_6 and diphenyl in solution.

*3.8. Reaction of $ZrCp_4$ with $[N^nBu_3H][BPh_4]$: synthesis of $[ZrCp_3][BPh_4]$ (**2**)*

A solution of $[N^nBu_3H][BPh_4]$ (1.05 g, 2.04 mmol) in CH_2Cl_2 (50 ml) was treated with $ZrCp_4$ (0.72 g, 2.05 mmol). The precipitation of a yellow solid was observed after some minutes from the mixing of reagents. After an additional 30 min stirring at r.t., the resulting yellow suspension was filtered, the solid washed with heptane (5 ml), dried in vacuo and identified as $[ZrCp_3][BPh_4]$ (0.63 g, 51% yield). IR (Nujol and PCTFE): $\tilde{\nu} = 3116$ m, 3094 m, 3077 m, 3048 m, 1592 m-w, 1580 m-w, 1478 m-s, 1457 m-w, 1427 s, 1368 m-s, 1313 w, 1266 m, 1242 m, 1183 w, 1147 w, 1133 w, 1067 m, 1030 m-s, 1010 m-s, 932 w, 888 w, 846 s, 810 vs, 746 s, 735 s, 707 s, 644 m, 626 w, 606 m cm^{-1}. ^1H-NMR (CD_2Cl_2, 25°C): $\delta = 7.6$ (t, 4H, ar), 7.5 (m, 6H, ar), 7.4 (s, 6H, ar), 7.1 (t, 2H, ar), 6.9 (t, 2H, ar), 6.07 (s, 15H, Cp) ppm.

3.9. Reaction of MCp_4, M = Zr, Hf, with $[N^nBu_3H][BPh_4]$ under CO

3.9.1. A. In CH_2Cl_2

M = Zr: synthesis of $[ZrCp_3(CO)][BPh_4]$. A solution of $[N^nBu_3H][BPh_4]$ (0.41 g, 0.8 mmol) in CH_2Cl_2 (25 ml) was saturated with CO at atmospheric pressure. Then, $ZrCp_4$ (0.28 g, 0.8 mmol) was added. The precipitation of a yellow solid was observed after some minutes from the mixing of the reagents. After an additional 30 min stirring at r.t., the resulting yellow suspension was filtered, the solid dried in vacuo and identified as $[ZrCp_3(CO)][BPh_4]$, (0.16 g, 31% yield). IR (Nujol and PCTFE): $\tilde{\nu} = 3120$ m-w, 3070 m, 3052 m-s, 2132 s, 1951 w, 1884 w, 1817 w, 1592 m-w, 1581 m-w, 1479 m, 1447 m-w, 1428 s, 1370 m, 1309 w, 1266 m, 1240 m, 1184 w, 1154 w, 1127 w, 1068 w, 1023 m-s, 976 w, 841 s, 819 vs, 764 s, 736 vs, 707 vs, 675 m, 643 w, 627 w, 605 m cm^{-1}. ^1H-NMR (CD_2Cl_2, 25°C): $\delta = 7.6$ (m, 8H, ar), 7.5 (m, 8H, ar), 7.1 (t, 4H, ar), 6.4 (s, 15H, Cp) ppm.

M = Hf: synthesis of $[HfCp_3(CO)][BPh_4]$. A solution of $[N^nBu_3H][BPh_4]$ (0.26 g, 0.5 mmol) in CH_2Cl_2 (10 ml) was saturated with CO. Then $HfCp_4$ (0.22 g, 0.5 mmol) was added. After 10 min stirring at r.t., the resulting yellow suspension was filtered, the solid was washed with heptane (3 ml), dried in vacuo and identified as $[HfCp_3(CO)][BPh_4]$ (0.14 g, 39% yield). IR (Nujol and PCTFE): $\tilde{\nu} = 3121$ m-w, 3070 m, 3052 m-s, 2126 s, 1591 m, 1581 m-w, 1479 m, 1430 s, 1372 m, 1315 w, 1287 m, 1262 m, 1240 s, 1185 w, 1155 w, 1127 w, 1069 w, 1017 m-s, 885 m, 844 s, 799 vs, 773 s, 763 s, 744 vs, 701 vs, 676 m, 639 w, 626 w, 604 m cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 25°C): $\delta = 7.6$ (m, 8H, ar), 7.5 (m, 8H, ar), 7.1 (t, 4H, ar), 6.3 (s, 15H, Cp) ppm.

3.9.2. B. In toluene

M = Zr. (i) Synthesis of $[ZrCp_3(CO)][BPh_4]$. A suspension of $[N^nBu_3H][BPh_4]$ (0.58 g, 1.1 mmol) in toluene (25 ml) was saturated with CO at atmospheric pressure. Then $ZrCp_4$ (0.40 g, 1.1 mmol) was added. After 10 h stirring at r.t., the yellow suspension was filtered, the solid was washed with heptane (5 ml), dried in vacuo and identified as $[ZrCp_3(CO)][BPh_4]$ (0.62 g, 89% yield). IR (Nujol and PCTFE): $\tilde{\nu} = 3120$ m-w, 3070 m, 3052 m-s, 2132 s, 1951 w, 1884 w, 1817 w, 1592 m-w, 1581 m-w, 1479 m, 1447 m-w, 1428 s, 1370 m, 1309 w, 1266 m, 1240 m, 1184 w, 1154 w, 1127 w, 1068 w, 1023 m-s, 976 w, 841 s, 819 vs, 764 s, 736 vs, 707 vs, 675 m, 643 w, 627 w, 605 m cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 25°C): $\delta = 7.6$ (m, 8H, ar), 7.4 (t, 8H, ar), 7.1 (t, 4H, ar), 6.4 (s, 15H, Cp) ppm. The same product forms even if the reaction is performed with an $[N^nBu_3H][BPh_4]/ZrCp_4$ molar ratio of 2.

(ii) Gas-volumetric study. A suspension of $[N^nBu_3H][BPh_4]$ (0.25 g, 0.5 mmol) in toluene (10 ml) was saturated with CO at atmospheric pressure, thermostated at 20.7°C and connected to a gas-volumetric apparatus. Then, $ZrCp_4$ (0.16 g, 0.45 mmol), in a thin-walled glass ampoule, was added. The reaction was over in about 2 h: 4×10^{-4} mol of CO were absorbed corresponding to a $CO/ZrCp_4$ molar ratio of 0.87.

3.10. Reaction of $[ZrCp_3][BPh_4]$ with CO: synthesis of $[ZrCp_3(CO)][BPh_4]$

A suspension of $[ZrCp_3][BPh_4]$ (0.04 g, 0.07 mmol) in CH_2Cl_2 (5 ml) was saturated with CO. After 2 h stirring at r.t., the yellow suspension was evaporated to dryness under reduced pressure at r.t. and the yellow solid identified as $[ZrCp_3(CO)][BPh_4]$ by IR spectroscopy.

3.11. Reaction of MCp_4, M = Zr, Hf, with $[N^nBu_3H][BPh_4]$ and PEt_3

3.11.1. A. In CH_2Cl_2

M = Zr: synthesis of $[ZrCp_3(PEt_3)][BPh_4]$. To a solution of $[N^nBu_3H][BPh_4]$ (0.24 g, 0.46 mmol) and PEt_3 (0.07 ml, 0.47 mmol) in CH_2Cl_2 (10 ml), $ZrCp_4$ (0.17 g, 0.48 mmol) was added. After 1 h stirring at r.t., a ^{31}P-NMR of the solution (to which some C_6D_6 was added) showed a peak at 11.8 ppm. The remaining yellow solution was evaporated to dryness under reduced pressure at r.t. and heptane was added (5 ml). The suspension was filtered and the yellow solid was dried in vacuo affording $[ZrCp_3(PEt_3)][BPh_4]$ (0.30 g, 86%). Anal. Found: C, 72.4; H, 7.4. Calc. for $[ZrCp_3(PEt_3)][BPh_4]$ ($C_{45}H_{50}BPZr$): C, 74.7; H, 7.0. IR (Nujol and PCTFE): $\tilde{\nu} = 3112$ m-w, 3051 m, 3012 m-w, 1945 w, 1878 w, 1752 w, 1580 m-w, 1561 w, 1479 m, 1456 m, 1438 s, 1426 m, 1377 m, 1307 w, 1262 m, 1183 w, 1149 w, 1134 w, 1097 w, 1068 m, 1034 m-s, 1011 m, 919 w, 848 s, 813 vs, 735 vs, 707 vs, 626 w, 608 m cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 25°C): $\delta = 7.4$ (m, 8H, ar), 7.1 (t, 8H, ar), 6.9 (t, 4H, ar), 5.8 (s, 15H, Cp), 2.1 (quintet, 6H, CH_2), 1.4 (d t, 9H, CH_3) ppm. ^{31}P-NMR (CD_2Cl_2, 25°C): $\delta = 13.9$ (s) ppm. No displacement of the phosphine ligand was observed by treating $[ZrCp_3(PEt_3)][BPh_4]$ with CO at atmospheric pressure in toluene.

M = Hf. To a solution of $[N^nBu_3H][BPh_4]$ (0.19 g, 0.37 mmol) and PEt_3 (0.05 ml, 0.34 mmol) in CH_2Cl_2 (10 ml), $HfCp_4$ (0.16 g, 0.36 mmol) was added. After 3 h stirring at r.t., a ^{31}P-NMR spectrum of the solution presented a peak at -18.8 ppm (non-coordinated PEt_3) and a peak at 8.44 ppm. The remaining yellow solution was evaporated to dryness under reduced pressure at r.t. and heptane was added (2 ml). The suspension was filtered and the yellow solid (0.30 g), dried in vacuo, was spectroscopically identified as a mixture of $HfCp_4$, $[N^nBu_3H][BPh_4]$ and $[HfCp_3(PEt_3)][BPh_4]$.

3.11.2. B. In toluene

M = Zr. A suspension of $[N^nBu_3H][BPh_4]$ (0.03 g, 0.06 mmol) and PEt_3 (0.01 ml, 0.07 mmol) in toluene (5 ml) was treated with $ZrCp_4$ (0.02 g, 0.06 mmol). After 3 h stirring at r.t., the yellow suspension was evaporated to dryness under reduced pressure at r.t. and the yellow solid was spectroscopically (IR, ^{1}H-NMR) identified as $[ZrCp_3(PEt_3)][BPh_4]$.

3.12. Reaction of $[ZrCp_3][BPh_4]$ with PEt_3: synthesis of $[ZrCp_3(PEt_3)][BPh_4]$

3.12.1. A. In CH_2Cl_2

To a suspension of $[ZrCp_3][BPh_4]$ (0.15 g, 0.25 mmol) in CH_2Cl_2 (5 ml), PEt_3 (0.04 ml, 0.27 mmol) was added. After 3 h stirring at r.t., a ^{31}P-NMR of the solution showed absence of the free phosphine and complete conversion of the reagents to $[ZrCp_3(PEt_3)][BPh_4]$.

3.12.2. B. In toluene

PEt_3 (0.08 ml, 0.54 mmol) was added to a suspension of $[ZrCp_3][BPh_4]$ (0.35 g, 0.58 mmol) in toluene (10 ml). After 3 h stirring at r.t., a ^{31}P-NMR of the solution presented a peak at −18.8 ppm due to non-coordinated PEt_3. The remaining yellow suspension was evaporated to dryness under reduced pressure at r.t. and the yellow solid was identified as a mixture of $[ZrCp_3][BPh_4]$ and $[ZrCp_3(PEt_3)][BPh_4]$ (^1H and ^{31}P-NMR spectra).

4. Conclusions

This paper has shown that the tetracyclopentadienyl derivatives of Group 4 elements are useful starting materials for the preparation of cyclopentadienyl cations of titanium(IV), zirconium(IV) and hafnium(IV). In particular, the unsolvated species $[ZrCp_3][BPh_4]$ has been isolated from the reaction of $ZrCp_4$ and $[N^nBu_3H][BPh_4]$ in CH_2Cl_2. The nature of the counterion appears to be decisive in the isolation of the unsolvated species: as a matter of fact, $[ZrCp_3][BPh_4]$ can be isolated, whereas $[ZrCp_3][CH_3B(C_6F_5)_3]$ decomposes during the isolation procedure [4j].

We have demonstrated that single (M = Zr, Hf) or double (M = Ti) protonation of the tetracyclopentadienyl derivatives may occur; the size of the central atom and the nature of the cyclopentadienyl ligand determining the nature of the product [29]. In the presence of donor ligands, cationic adducts of formula $[MCp_3(L)][BPh_4]$ (M = Zr, L = CO, PEt_3; M = Hf, L = CO) or $[TiCp_2(CO)_2][BPh_4]_2$ can be prepared. The latter can also be obtained by a two-electron oxidation of $TiCp_2(CO)_2$ with $[FeCp_2][BPh_4]$. Noteworthy are the titanium and the hafnium derivatives, due to the fact that $[TiCp_2(CO)_2][BPh_4]_2$ represents the first example of a metallocene dicarbonyl dication and $[HfCp_3(CO)][BPh_4]$ is a new member of the class of the carbonyl derivatives of hafnium(IV) which, at the best of our knowledge, consists of just two members [4d, 4k].

Acknowledgements

The authors wish to thank the Consiglio Nazionale delle Ricerche (C.N.R., Roma), Progetto Strategico Metodologie Innovative for financial support and the Scuola Normale Superiore, Pisa, for a fellowship to G.T.

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