PHYSICAL METHODS OF INVESTIGATION

Edge-Shared [M₂Cl₁₀]²⁻ Complexes of Reaction between Oxophilic Group 4 Metal and Phosphorus Ylides¹

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Abstract—The reactions between oxophilic group 4 metal chlorides, α -keto ylides in THF, led to the formation of titanium, zirconium and hafnium edge-shared $[M_2Cl_{10}]^{2-}$ complexes (1a-3f). We describe that the reaction between MCl₄ (M = Ti, Zr and Hf) with phosphorus ylides produce edge-shared $[M_2X_{10}]^{2-}$ complexes instead of O-coordination previously reported complexes. Adding dimethyl sulfoxide (DMSO) to these complexes in room temperature crystalline solid $[M(DMSO)_8] \cdot 4Cl \cdot mH_2O \cdot DMSO]$ ($\dot{M} = Ti$ (1g), Zr (2g) and Hf (3g); m = 0-3) together with phosphonium salts in mother liquid were formed. The compounds were characterized by elemental analysis, IR and ¹H, ¹³C and ³¹P NMR spectroscopy.

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The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [1, 2]. Phosphorus ylides are remarkable ligands which have attracted much attention in synthetic, catalytic and theoretical fields of transition metal chemistry [3]. The complexes of α -keto-stabilized phosphorus ylides with late transition-metal ions are thoroughly investigated [4, 27]; there are a few examples of such complexes with early transition metals [7, 8].

We attend to the oxophilic group 4 metals, Ti, Zr and Hf that can be classified as a hard metal. The extent of the interaction between the metal centers is clearly dependent on the electronic properties of the constituent metals but the nature of the bridging ligand framework can also play a significant role. Among the species displaying metal-metal interactions, the dinuclear compounds represented by the face-shared $[M_2X_9]^{2-}$ and edge-shared $[M_2X_{10}]^{2-}$ (dimer) species are particularly noteworthy as they are formed by many transition metals [7]. The decahalodimetallate $[M_2Cl_{10}]^{2-}$ anions of zirconium(IV) and hafnium(IV) within the second and third row of the transition d elements have been prepared as their triphenylmethyl derivatives $[Ph_3C]_2[M_2Cl_{10}]$ and the structural data of the hafnium derivative have been reported. The structure of the hafnium dinuclear anion is similar to that of the corresponding titanium derivative, with PCl_4^+ as counterion [11a]. The bonding parameters of the $[Hf_2Cl_{10}]^{2-}$ anion and also the crystal structure of [Me₂SCH₂Cl]₂[Zr₂Cl₁₀], have been reported [11b, 12]. In view of these observations we have initiated an investigation of the chemistry of $TiCl_4$, $ZrCl_4$ and $HfCl_4$ with phosphorus ylides as a ligand. As part of these studies, we report the preparation and characterization complexes of the type $(Ar_3PCH_2COR)_2[M_2Cl_{10}]$ (R = OCH_2C_6H_5, C_4H_3S, $C_6H_4NO_2$ and C_6H_4Cl , Ar = Ph; $R = C_6H_4NO_2$, C_6H_4Cl , Ar = PhMe). But the most interesting point of our study is the coordination center of DMSO in solution. The reaction of DMSO with metals plays an important role in biological and catalytic processes, and also in the chemistry of complex compounds [13]. The nature of dimethyl sulfoxide as a monodentate ligand is explored in this set of experiments [14, 15]. In each particular case, the problem for study is the determination of the coordination center of DMSO (S- or O-coordination respectively). Dimethyl sulfoxide is a polar aprotic solvent, thus allowing studies of its coordination properties. It is an ambidentate ligand, usually coordinating via the oxygen atom [16], but to a number of soft electron-pair acceptors, it is also coordinating via the sulfur atom [17]. The dominating coordination figures of zirconium(IV) and hafnium(IV) complexes are the square antiprism [18], very often distorted octahedron and distorted sevencoordinated complexes are fairly common [19, 20]. We prepared crystalline solid $[M(DMSO)_8] \cdot 4Cl \cdot$ $mH_2O \cdot DMSO(1g-3g; m = 0-3)$ together with phosphonium salt of the type Ar_3PCH_2COR (R = $OCH_2C_6H_5$, C_4H_3S , $C_6H_4NO_2$ and C_6H_4Cl , Ar = Ph; $R = C_6H_4NO_2$, C_6H_4Cl , Ar = PhMe) in mother liquid were formed.

¹ The article is published in the original.

EXPERIMENTAL

General

All reactions were carried out under a nitrogen atmosphere. THF and diethyl ether were distilled from sodium benzophenone just before use. All other solvents were reagent grade and used without further purifications. All glassware was dried for 2 h (150°C) prior to use. Metal halide salts were purchased and used as received from Aldrich Chemical Co. The phosphorous ylides Ph₃P=CHCOOCH₂C₆H₅ (**Y**¹)^{4a}, Ph₃P=CHCOC₄H₃S (**Y**²)^{4b}, Ph₃P=CHCOC₆H₄NO₂ (**Y**³)⁵, Ph₃P=CHCOC₆H₄Cl (**Y**⁴)⁶, (*p*-tolyl)₃P= CHCOC₆H₄NO₂ (**Y**⁵)^{4b} and (*p*-tolyl)₃P= CHCOC₆H₄Cl (**Y**⁶)^{4b} were synthesized according to the published procedures.

Instrumentation

Elemental analysis for C, H and N were performed using a Perkin-Elmer 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer in the region 350-4000 cm⁻¹ and the measurements were made by the KBr disk method. Melting points were measured on a SMP3 apparatus. Solutionstate ¹H, ³¹P and ¹³C NMR spectra at ambient temperature were obtained in DMSO-*d*₆ or CDCl₃ using a FT-NMR Bruker 300 (300 MHz) and FT-NMR JEOL FX 90 Q (90 MHz) spectrometers. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid.

Preparation of Phosphorus Ylides

 α -Bromo ketone (1 mmol) was dissolved in 20 mL of acetone and then a solution of triphenylphosphine (PPh₃) or paratolylphosphine (P(*p*-tolyl)₃) (1 mmol) in the same solvent (5 mL) was added dropwise to the above solution. The resulting solution was stirred for 13 h. The solid product (phosphonium salt), was filtered off, washed with diethyl ether and dried under reduced pressure. Addition of the phosphonium salt (1 mmol) to an aqueous solution of NaOH (0.5 M) led to the elimination of HBr and gave the free ligand (Scheme 1).



M = Ti, Zr and Hf Ar = Ph (phenyl); PhMe (paratolyl)

i = ipso; o = ortho; m = meta; p = para





Preparation of Complexes

Complexes of Titanium

Synthesis of bis[benzoylacetatetriphenylphosphonium]di-µ-chloro-bis[tetrachlorotitanate(IV)] (1a). General procedure. A 100-mL Schlenk tube was charged with (0.53 mL, 0.53 mmol of TiCl₄ (1 M solution in CH₂Cl₂) and 20 mL of THF. To this yellow solution was added Y¹ (0.20 g, 0.53 mmol) in 15 mL of THF and stirred for 20 min. The pale yellow solution was concentrated to 2 mL, and diethyl ether (15 mL) added to precipitate the moisture-sensitive white complex. Ylied (0.21 g, 70%); mp 69-70°C; IR (KBr) v: 1731 (C=O), 921 (P-C), cm⁻¹; ¹H NMR (DMSO) δ: 5.5 (d, J = 13.35 Hz, 2H, CH), 5.0 (s, 2H, CH₂), 7.01-7.95 (m, 20H, Fh); ³¹P NMR (DMSO) δ: 20.77 (s), 26.37 (s, triphenylphosphoxide); ¹³C NMR (DMSO) δ : 31.0 (d, J = 56.0 Hz, CH₂), 67.9 (s, 1C, CH_2), 126.4 (s, 1C, COPh(i)), 131.4 (s, 2C, COPh(o)), 129.3 (s, 2C, COPh(m)), 131.8 (s, 1C, COPh(p), 118.3 (d, J = 88.5 Hz, 3C, $PPh_3(i)$), 133.8 $(d, J = 10.58 \text{ Hz}, 6C, \text{PPh}_3(0)), 130.3 (d, J = 12.70 \text{ Hz},$ 6C, PPh₃(m)), 135.2 (s, 3C, PPh₃(p)), 164.8 (s, CO). Anal. calcd. for C₅₄H₄₈Cl₁₀O₄P₂Ti₂: C 50.94, H 3.80; Found C 50.90, H 3.32.

Data for bis[(4-thionylmethyl)triphenylphosphonium]di- μ -chloro-bis[tetrachlorotitanate(IV)] (1b). *Pale brown solid.* Ylied (0.21 g, 70%); mp 225–228°C (decomp); IR (KBr) δ : 1654 (C=O) 938(P-C) cm⁻¹; ¹H NMR (DMSO) δ : 6.34 (d, J = 13.3 Hz, 2H, CH₂); 7.32–8.37 (m, 18H, arom.). ³¹P NMR (DMSO): 21.51 (s). ¹³C NMR (DMSO) δ : 35.39 (d, J = 58.7, CH₂); 137.52 (s, C(2)); 134.51 (s, C(3)); 137.52 (s, C(4)); 141.75 (d, J = 6.6, C(5)); 119.05 (d, J = 88.2 Hz, 3C, PPh₃(i)); 133.66 (d, J = 10.2 Hz, 6C, PPh₃(o)); 129.82 (d, J = 13.0 Hz, 6C, PPh₃(m)); 129.09 (s, 3C, PPh₃(P)); 184.73(d, J = 4.5, CO). Anal. calcd. for C₄₈H₄₀Cl₁₀O₂P₂S₂Ti₂: C 47.06, H, 3.29; Found C 47.22, H 3.20.

Data for bis[(p-nitrophenylmethylene)triphenylphosphonium]di-µ-chloro-bis[tetrachlorotitanate(IV)] (1c). Orange solid. 0.27 g (94%). mp 153-155°C decomp. IR (KBr) v: 1685 (C=O), 995 (P-C) cm⁻¹. ¹H NMR (DMSO) δ : 6.43 ((d, J=13.7, 2H, CH₂); 7.76-8.34 (m, 19H, arom.). ³¹P NMR (DMSO) δ: 21.32 (s). ¹³C NMR (DMSO) δ: 36.65 (d, J = 58.5 Hz, CH₂); 140.07 (s, COPh(i)); 135.24 (s, COPh(o)); 124.35 (s, COPh(m)); 151.15 (s. COPh(p)): 119.39 (d. J = 89.8 Hz, PPh₂(i)): 134.21 $(d, J = 8.7, PPh_3(o)); 130.49 ((d, J = 11.5, PPh_3(m));$ 131.19 (s, PPh₃(p)); 192.39 (s, CO). Anal. calcd. for C₅₂H₄₂Cl₁₀N₂O₆P₂Ti₂: C 47.93, H 3.25, N 2.15; Found C 47.16, H 3.21, N 2.11.

Data for bis[(p-chlorophenylmethylene)triphenylphosphonium]di- μ -chloro-bis[tetrachlorotitanate(IV)] (1d). Cream solid. 0.14 g (72%). mp 98– 100°C. IR (KBr) v: 1674 (C=O), 990 (P-C) cm⁻¹. ¹H NMR (DMSO) δ : 6.47 (d, J = 13.62 Hz, 2H, CH₂); 7.21–8.33 (m, 19H, arom.). ³¹P NMR (DMSO) δ : 21.50 (s). ¹³C NMR (DMSO) δ : 36.20 (d, J = 61.4 Hz, CH₂); 140.26 (s, COPh(i)); 135.11 (s, COPh(o)); 129.47 (s, COPh(m)); 119.59 (d, J = 88.6 Hz, PPh₃(i)); 134.17 (d, J = 10.3 Hz, PPh₃(o)); 130.42 (d, J = 12.68 Hz, PPh₃(m)); 131.64 (s, PPh₃(p)); 192.27 (s, CO). Anal. calcd. for C₅₂H₄₂Cl₁₂O₂P₂Ti₂: C 48.72, H 3.30. Found C 48.56, H 3.25.

Data for bis[(p-nitrophenylmethylene)triparatolylphosphonium]di-µ-chloro-bis[tetrachlorotitanate(IV) (1e). Orange solid. Ylied (0.3 g, 92%); mp $124^{\circ}C$ (decomp); IR(KBr) v: 1686 (C = O), 995 $(P-C) \text{ cm}^{-1}$; ¹H NMR (DMSO) δ : 2.5 (s, 9H, CH₃), 6.4 (d, J = 9.82 Hz, 2H, CH), 7.33-8.36 (m, 16H, Ph); ${}^{31}P$ NMR (DMSO) δ : 20.41 (s); ${}^{13}C$ NMR (DMSO) δ : 21.6 (s, 3C, CH₃), 37.3 (d, J = 65.2 Hz, CH₂), 145.7 (s, 1C, COPh(i)), 140.2 (s, 2C, COPh(o)), 124.2 (s, 2C, COPh(m)), 151.0 (s, 1C, COPh(p)), 116.3 (d, J = 90.8 Hz, 3C, $P(p-tolyl)_3(i)$), 134.0 (d, J = 12.21 Hz, 6C, P(*p*-tolyl)₃(o)), 130.9 (d, J = 11.4 Hz, 6C, P(p-tolyl)₃(m)), 131.0 (s, 3C, P(p $tolyl_3(p)$, 192.6 (s, CO). Anal. calcd. for C₅₈H₄₆Cl₁₀N₂O₆P₂Ti₂: C 50.51, H 3.36, N 2.03; Found C 50.41; H 3.32, N 2.19.

Data for bis[(p-chlorophenylmethylene)triparatolylphosphonium]di- μ -chloro-bis[tetrachlorotitanate(IV)] (1f). Cream solid. Yield (0.22 g, 77%); m.p. 112–114°C; IR(KBr) v: 1674 (C=O), 1589, 991 (P–C) cm⁻¹; ¹H NMR (DMSO) δ : 2.4 (s, 9H, CH₃), 6.2 (d, J = 13.0 Hz, 2H, CH), 7.29–8.25 (m, 16H, Ph); ³¹P NMR (DMSO) δ : 20.7 (s); ¹³C NMR (DMSO) δ : 21.7 (s, 3C, CH₃), 36.2 (d, J = 61.4 Hz, CH₂), 140.1 (s, 1C, COPh(i)), 145.7 (br, 4C, COPh(o) and COPh(p)), 129.4 (s, 1C, COPh(m)), 116.5 (d, J = 91.6 Hz, 3C, P(p-tolyl)₃(i)), 134.0 (d, J =10.9 Hz, 6C, P(p-tolyl)₃(o)), 130.9 (d, J = 13.2 Hz, 6C, P(p-tolyl)₃(m)), 131.6 (s, 3C, P(p-tolyl)₃(p)), 192.1 (s, CO). Anal. calcd. for C₅₈H₅₄Cl₁₂O₂P₂Ti₂: C 50.99, H 3.98; Found C 50.54, H 3.81.

Complexes of Zirconium

Synthesis of bis[benzovlacetatetriphenvlphosphonium]di-µ-chloro-bis[tetrachlorozirconate(IV)] (2a). General procedure. A 100-mL Schlenk tube was charged with (0.12 g, 0.53 mmol) of ZrCl₄ and 20 mL of THF. To this colorless solution was added Y^1 (0.20 g. 0.53 mmol) in 8 mL of THF. The solution, which remained colorless, was stirred for 2 h. The colorless solution was concentrated to 2 mL, and diethyl ether (15 mL) added to precipitate the moisture-sensitive pale yellow complex. Ylied (0.19 g, 58%); mp 82-84°C; IR(KBr) v: 1732 (C=O), 996 (P-C) cm⁻¹; ¹H NMR (DMSO) δ : 5.5 (d, J = 13.75 Hz, 2H, CH), 5.1 (s, 2H, CH₂), 6.97–8.12 (m, 20H, Ph); ³¹P NMR (DMSO) δ: 20.85 (s), 26.35 (s, triphenylphosphoxide); ¹³C NMR (DMSO) δ : 29.7 (d, J = 55.1 Hz, CH₂), 67.6 (s, 1C, CH₂), 126.3 (s, 1C, COPh(i)), 131.2 (s, 2C, COPh(o)), 129.0 (s, 2C, COPh(m)), 131.6 (s, 1C, COPh(p)), 118.1 (d, J = 88.9 Hz, 3C, $PPh_3(i)$), 133.6 (d, J = 10.80 Hz, 6C, PPh₃(o)), 130.0 (d, J = 12.83 Hz, 6C, PPh₃(m)), 134.9 (s, 3C, PPh₃(p)), 164.6 (s, CO). Anal. calcd. for C₅₄H₄₈Cl₁₀O₄P₂Zr₂: C 47.69, H 3.56; Found C 47.50, H 3.50.

Data for bis[(4-thionylmethyl)triphenylphosphonium]di- μ -chloro-bis[tetrachlorozirconate(IV)] (2b)). *Pale yellow solid.* Ylield (0.19 g, 58%); mp 286–288°C decomp. IR (KBr) v: 1654 (C=O), 937 (P–C) cm⁻¹. ¹H NMR (DMSO) δ : 6.35 (d, J = 12.5 Hz, 2H, CH₂); 7.33–8.35 (m, 18H, arom.). ³¹P NMR (DMSO) δ : 21.49 (s). ¹³C NMR (DMSO) δ : 35.60 (d, J = 51.4 Hz, CH₂); 138.00 (s, C(2)); 134.95 (s, C(3)); 137.54 (s, C(4)); 142.13 (d, J = 7.6 Hz, C(5)); 119.37 (d, J = 88.7 Hz, PPh₃(i)); 133.98 (d, J = 10.6 Hz, PPh₃(o)); 130.19 (d, J = 12.6 Hz, PPh₃(m)); 129.09 (*s*, PPh₃(p)); 185.14 (d, J = 5.8, CO). Anal. calcd. for C₄₈H₄₀Cl₁₀O₂P₂S₂Zr₂: C 43.95, H 3.07; Found C 44.15, H 3.22.

Data for bis[(p-nitrophenylmethylene)triphenylphosphonium]di- μ -chloro-bis[tetrachlorozirconate(IV)] (2c). *Orange solid.* 0.11 g (35%). mp 140–143°C decomp. IR (KBr) v: 1686 (C=O), 994 (P–C) cm⁻¹. ¹H NMR (DMSO) δ : 6.56 (d, J = 11.6, 2H, CH₂); 7.75–8.38 (m, 19H, arom.). ³¹P NMR (DMSO) δ : 21.02 (s). ¹³C NMR (DMSO) δ : 36.6 ((d, J = 55.7, CH₂); 140.06 (s, COPh(i)); 135.23 (s, COPh(o)); 124.36 (s, COPh(m)); 151.18 (s, COPh(p)); 119.38 (d, J = 88.1, PPh₃(i)); 134.20 ((d, J = 8.5, PPh₃(o)); 130.47 ((d, J = 10.1, PPh₃(m)); 131.17 (s, PPh₃(p)); 192.44 (s, CO). Anal. calcd. for C₅₂H₄₂Cl₁₀N₂O₆P₂Zr₂: C 44.94, H 3.05, N, 2.02; Found C 44.71, H, 3.13, N 2.08.

Data for bis[(p-chlorophenylmethylene)triphenylphosphonium]di- μ -chloro-bis[tetrachlorozirconate(IV)] (2d). White solid. 0.24 g (77%). mp 103– 105°C. IR (KBr) v: 1674 (C=O), 989 (P-C) cm⁻¹. ¹H NMR (DMSO) δ : 6.41 (d, J = 13.8 Hz, 2H, CH₂); 7.21–8.26 (m, 19H, arom.). ³¹P NMR (DMSO) δ : 21.52 (s). ¹³C NMR (DMSO) δ : 36.29 (d, J = 61.8, CH₂); 140.27 (s, COPh(i)); 135.11 (s, COPh(o)); 129.46 (s, COPh(m)); 119.64 (d, J = 88.9 Hz, PPh₃(i)); 134.20 (d, J = 10.5 Hz, PPh₃(o)); 130.42 (d, J = 12.7 Hz, PPh₃(m)); 131.66 (s, PPh₃(p)); 192.30 (s, CO). Anal. calcd. for C₅₂H₄₂Cl₁₂O₂P₂Zr₂: C 45.63, H 3.09; Found C 45.37, H 3.20.

for bis[(p-nitrophenylmethylene)tripara-Data tolylphosphonium]di-µ-chloro-bis[tetrachlorozirconate(IV)] (2f). Orange solid. Ylied (0.15 g, 49%); mp 160°C (decomp); IR(KBr) v: 1688 (C=O), 994 (P-C) cm⁻¹; ¹H NMR (DMSO) δ: 2.4 (s, 9H, CH₃), 6.3 (d, J = 13.9 Hz, 2H, CH), 7.61-8.36 (m, 16H, Ph);³¹P NMR (DMSO) δ: 20.42 (s); ¹³C NMR (DMSO) δ: 21.7 (s, 3C, CH₃), 35.8 (d, J = 60.5 Hz, CH₂), 145.8 (s, 1C, COPh(i)), 140.2 (s, 2C, COPh(o)), 124.2 (s, 2C, COPh(m)), 151.1 (s, 1C, COPh(p)), 116.3 (d, J= 90.9 Hz, 3C, $P(p-tolyl)_3(i)$, 134.0 (d, J = 10.5 Hz, 6C, $P(p-tolyl)_{3}(0)$, 135.8 (d, J = 12.5 Hz, 6C, $P(p-tolyl)_{3}(0)$ $tolyl_{3}(m)$, 131.0 (s, 3C, P(*p*-tolyl)₃(p)), 192.7 (s, CO). Anal. calcd. for C₅₈H₄₆Cl₁₀N₂O₆P₂Zr₂: C 47.52, H 3.16, N 1.91; Found C 46.93, H 3.02, N 2.02.

Data for bis[(p-chlorophenylmethylene)triparatolylphosphonium]di- μ -chloro-bis[tetrachlorozirconate(IV)] (2g). White solid. Yield (0.12 g, 79%); mp 118–120°C; IR (KBr) v: 1674 (C=O), 990 (P–C) cm⁻¹; ¹H NMR (DMSO) δ : 2.5 (s, 9H, CH₃), 6.2 (d, J = 13.0 Hz, 2H, CH), 7.23–8.30 (m, 16H, Ph); ³¹P NMR (DMSO) δ : 20.7 (s); ¹³C NMR (DMSO) δ : 21.7 (s, 3C, CH₃), 36.0 (d, J = 62.9 Hz, CH2), 140.2 (s, 1C, COPh(i)), 145.8 (br, 4C, COPh(o) and COPh(p)), 129.5 (s, 1C, COPh(m)), 116.5 (d, J = 91.7 Hz, 3C, P(*p*-tolyl)₃(i)), 134.0 (d, J = 10.9 Hz, 6C, P(*p*-tolyl)₃(o)), 130.9 (d, J = 13.2 Hz, 6C, P(*p*tolyl)₃(m)), 131.5 (s, 3C, P(*p*-tolyl)₃(p)), 192.1 (s, CO). Anal. calcd. for C₅₈H₅₄Cl₁₂O₂P₂Zr₂: C 47.95, H 3.75; Found C 47.80, H 3.69.

Complexes of Hafnium

Data for bis[benzoylacetatetriphenylphosphonium]di-µ-chloro-bis[tetrachlorohafnate(IV)] (3a). Pale brown solid. Ylied (0.20 g, 61%); mp 90-92°C; IR(KBr) v: 1732 (C=O), 1625, 1601, 1587, 1486, 1438, 1379, 1263, 1127, 1072, 968 (P-C), 906, 805, 746, 728, 695 cm⁻¹; ¹H NMR (DMSO) δ : 5.6 (d, J = 14.51 Hz, 2H, CH), 5.1 (s, 2H, CH₂), 6.93–7.92 (m, 20H, Ph); ³¹P NMR (DMSO) δ: 20.83 (s), 26.20 (s, triphenylphosphoxide); ${}^{13}CNMR$ (DMSO) δ : 67.6 (s, 1C, CH₂), 128.4 (s, 1C, COPh(i)), 131.2 (s, 2C, COPh(o)), 129.0 (s, 2C, COPh(m)), 131.7 (s, 1C, COPh(p)), 118.2 (d, J = 88.9 Hz, 3C, $PPh_3(i)$), 133.7 $(d, J = 10.56 \text{ Hz}, 6C, \text{PPh}_2(0)), 130.0 (d, J = 12.84 \text{ Hz},$ 6C, PPh₃(m)), 135.0 (s, 3C, PPh₃(p)), 164.6 (s, CO). Anal. calcd. for C₅₄H₄₈Cl₁₀O₄P₂Hf₂: C 42.27, H 3.15; Found C 42.18, H 3.10.

Data for cis[(4-thionylmethyl)triphenylphosphonium]di- μ -chloro-bis[tetrachlorohafnateIV)] (3b). *Pale brown solid.* 0.22 g (59%). mp 297–299°C decomp. IR (KBr) v: 1655 (C=O), 939 (P–C) cm⁻¹. ¹H NMR (DMSO) δ : 6.15 (d, J = 13.8 Hz, 2H, CH₂); 7.08–8.15 (*m*, 18H, arom.). ³¹P NMR (DMSO) δ : 21.38 (s). ¹³C NMR (DMSO) δ : 137.73 (s, C(2)); 134.71 (s, C(3)); 137.32 (s, C(4)); 141.82 (d, J = 7.5 Hz, C(5)); 118.96 (d, J = 88.6 Hz, PPh₃(i)); 133.68 (d, J = 10.5 Hz, PPh₃(o)); 129.96 (d, J = 12.9 Hz, PPh₃(m)); 129.23 (s, PPh₃(p)); 184.50 (s, CO). Anal. calcd. for C₄₈H₄₀Cl₁₀Hf₂O₂P₂S₂: C 38.79, H 2.71; Found C 38.65, H 2.84.

Data for bis[(p-nitrophenvlmethylene)triphenylphosphonium]di- μ -chloro-bis[tetrachlorohafnate(IV)] (3c). *Orange solid.* 0.12 g (45%). mp 136–138°C decomp. IR (KBr) v: 1683 (C=O), 994 (P–C) cm⁻¹. ¹H NMR (DMSO) δ : 6.56 (d, J = 13.7 Hz, 2H, CH₂); 7.77– 8.35 (m, 19H, arom.). ³¹P NMR (DMSO) δ : 21.26 (s). ¹³C NMR (DMSO) δ : 36.71 (d, J = 62.0 Hz, CH₂); 140.08 (s, COPh(i)); 135.25 (s, COPh(o)); 124.34 (s, COPh(m)); 151.10 (s, COPh(p)); 119.40 (d, J = 89.3 Hz, PPh₃(i)); 134.22 (d, J = 9.1 Hz, PPh₃(o)); 130.50 (d, J = 12.1 Hz, PPh₃(m)); 131.12 (s, PPh₃(p)); 192.36 (s,



Fig. 1. The molecular structure of 3g.



Fig. 2. The molecular structure of 2g.

CO). Anal. calcd. for $C_{52}H_{42}Cl_{10}Hf_2N_2O_6P_2$: C 39.92, H 2.71, N 1.79; Found C 39.42, H 2.62, N 1.92.

Data for bis[(p-chlorophenylmethylene)triphenylphosphonium]di- μ -chloro-bis[tetrachlorohafnate(IV)] (3d). *White solid*. 0.26 g (75%). mp 107–109°C. IR (KBr) v: 1673 (C=O), 990 (P–C) cm⁻¹. ¹H NMR (DMSO) δ: 6.42 (*d*, *J* = 13.6 Hz, 2H, CH₂); 7.38–8.41 (m, 19H, arom.). ³¹P NMR (DMSO) δ: 21.53 (s). ¹³C NMR (DMSO) δ: 36.20 (d, *J* = 60.4 Hz, CH₂); 140.28 (*s*, COPh(i)); 135.12 (s, COPh(o)); 129.48 (s,

Complexes ylides	$v_{C=O} (cm^{-1})$	$v_{p^+-C^-}$ (cm ⁻¹)	Ref.	
APPY ^a	1530	—	24	
BPPY ^b	1525	—	25	
\mathbf{Y}^{1}	1610	887	4a	
Y^2	1527	879	4b	
Y^3	1529	884	5	
Y^4	1579	882	6	
Y ⁵	1600	886	4b	
Y ⁶	1581	882	4b	
la	1731	923	This work	
2a	1732	996	This work	
3a	1732	968	This work	
1b	1654	938	This work	
2b	1654	937	This work	
3b	1655	939	This work	
1c	1685	995	This work	
2c	1686	994	This work	
3c	1683	994	This work	
1d	1674	990	This work	
2d	1674	989	This work	
3d	1673	990	This work	
1e	1686	995	This work	
2e	1688	994	This work	
3e	1690	992	This work	
lf	1674	991	This work	
2f	1674	990	This work	
3f	1675	991	This work	

Table 1. v(CO) and $v(P^+-C^-)$ of phosphoranes and their metal complexes

^a acetylmethylmetriphenylphosphorane.

^b benzoylmethylenephenylphosphorane.

COPh(m)); 119.59 (d, J = 89.0 Hz, PPh₃(i)); 134.18 (d, J = 10.7 Hz, PPh₃(o)); 130.43 (d, J = 12.9 Hz, PPh₃(m)); 131.63 (s, PPh₃(p)); 192.24 (s, CO). Anal. calcd. for C₅₂H₄₂Cl₁₂Hf₂O₂P₂: C 40.47, H 2.74; Found C 40.35, H 2.50.

Data for bis[(p-nitrophenylmethylene)triparatolylphosphonium]di- μ -chloro-bis[tetrachlorohafnate(IV)] (3e). Orange solid. Ylied (0.12 g, 45%); mp 153°C (decomp); IR(KBr) v: 1690 (C=O), 992 (P-C) cm⁻¹; ¹H NMR (DMSO) δ : 2.4 (s, 9H, CH₃), 6.2 (d, J = 12.7 Hz, 2H, CH), 7.56–8.41 (m, 16H, Ph); ³¹P NMR (DMSO) δ : 20.38 (s); ¹³C NMR (DMSO) δ : 21.6 (s, 3C, CH₃), 36.5 (d, J = 61.4 Hz, CH₂), 140.1 (s, 1C, COPh(i)), 145.9 (s, 2C, COPh(o)), 124.3 (s, 2C, COPh(m)), 151.1 (s, 1C, COPh(p)), 116.2 (d, J = 91.6 Hz, 3C, P(*p*-tolyl)₃(i)), 134.0 (d, J = 10.8 Hz, 6C, P(*p*-tolyl)₃(o)), 131.0 (d, J = 13.2 Hz, 6C, P(*p*-tolyl)₃(m)), 131.1 (s, 3C, P(*p*-tolyl)₃(p)), 192.3 (s, CO). Anal. calcd. for C₅₈H₄₆Cl₁₀N₂O₆P₂Hf₂: C 42.47, H 2.83, N 1.71; Found C 42.32, H 2.80, N 1.65.

Data for bis[(p-chlorophenylmethylene)triparatolylphosphonium]di-µ-chloro-bis[tetrachlorohafnate(IV)] (**3f**). White solid. Yield (0.27, 80%); mp 125–127°C; IR(KBr) v: 1675 (C=O), 991 (P-C) cm⁻¹; ¹H NMR $(DMSO) \delta: 2.4 (s, 9H, CH_3), 6.3 (d, J = 13.5 Hz, 2H,$ CH), 7.11–8.24 (m, 16H, Ph); ³¹P NMR (DMSO) δ: 20.6 (s); ¹³C NMR (DMSO) δ: 21.6 (s, 3C, CH₃), 36.0 $(d, J = 60.6 \text{ Hz}, \text{CH}_2), 140.1 \text{ (s, 1C, COPh(i))}, 145.8$ (br, 4C, COPh(o) and COPh(p)), 129.3 (s, 1C, COPh(m)), 116.5 (d, J = 91.6 Hz, 3C, $P(p-tolyl)_3(i)$), 134.0 (d, J = 11.0 Hz, 6C, P(p-tolyl)₃(o)), 131.0 (d, J = 13.3 Hz, 6C, P(p-tolyl)₃(m)), 131.6 (s, 3C, P(p-tolyl)₃(m)) tolyl)₃(p)), 192.2 (s, CO). Anal. calcd. for C₅₈H₅₄Cl₁₂O₂P₂Hf₂: C 42.81, H 3.34; Found C 42.73, H 3.51.

Preparation of Octakis(dimethyl sulfoxide)titanium(IV) (1g)

General procedure. With 0.1of $(\text{RCOCH}_2\text{PAr}_3)_2[\text{Ti}_2\text{Cl}_{10}] \ (\text{R} = \text{OCH}_2\text{C}_6\text{H}_5, \ \text{C}_4\text{H}_3\text{S},$ $C_6H_4NO_2$ and C_6H_4Cl ; Ar = Ph and $(R = C_6H_4NO_2)$ and C_6H_4Cl ; Ar = PhMe) was added DMSO in room temperature. The solution, which remained colorless. so 5 day crystalline solid was formed. The colorless solution contain two product, one of the product $[Ti(DMSO)_{8}]$ in crystalline solid and another product, phosphonium salt in mother liquid, mp 140–142°C, IR(KBr) v: 1020 (S=O, symmetric stretch), 950 (S=O, asymmetric stretch), 488 (Ti–O, symmetric stretch), 448 (Ti–O, asymmetric stretch) cm⁻¹. Anal. calcd. for C₁₆H₄₈O₈S₈Ti: C 28.56, H 7.19; Found C 28.02, H 6.88.

Data for octakis(dimethyl sulfoxide)zirconium(IV) (2g). mp 153–155°C, IR(KBr) v: 1030 (S=O, symmetric stretch), 953 (S=O, asymmetric stretch), 484 (Ti–O, symmetric stretch), 436 (Ti–O, asymmetric stretch) cm⁻¹. Anal. calcd. for $C_{16}H_{48}O_8S_8Zr$: C 26.83, H 6.75; Found C 26.51, H 6.63.

Data for octakis(dimethyl sulfoxide)hafnium(IV) (3g). mp 168–170°C, IRv_{max}/cm^{-1} 1024 (S=O, symmetric stretch), 952 (S=O, asymmetric Mstretch), 483 (Ti–O, symmetric stretch), 441 (Ti–O, asymmetric stretch). Anal. calcd. for $C_{16}H_{48}HfO_8S_8$: C 23.92, H 6.02; Found C 23.12, H 5.78.

RESULTS AND DISCUSSION

The reaction between the group 4 metal halide salts and the α -keto ylides Y¹, Y², Y³, Y⁴, Y⁵ and Y⁶ in THF led to the formation of complexes of the type (Ar₃PCH₂COR)₂[M₂Cl₁₀] (**la**-3**f**). The anionic

No	1a	1b	1c	1d	1e	lf	2a	2b	2c
R	OCH ₂ C ₆ H ₅	C_4H_3S	$C_6H_4NO_2$	C ₆ H ₄ Cl	$C_6H_4NO_2$	C ₆ H ₄ Cl	$OCH_2C_6H_5$	C_4H_3S	C ₆ H ₄ NO ₂
R'	Н	Н	Н	Н	Me	Me	Н	Н	Н
Μ	Ti	Ti	Ti	Ti	Ti	Ti	Zr	Zr	Zr
No	2d	2e	2f	3a	3b	3c	3d	3e	3f
R	C ₆ H ₄ Cl	C ₆ H ₄ NO ₂	C ₆ H ₄ Cl	OCH ₂ C ₆ H ₅	C_4H_3S	C ₆ H ₄ NO ₂	C ₆ H ₄ Cl	$C_6H_4NO_2$	C ₆ H ₄ Cl
R'	Н	Me	Me	Н	Н	Н	Н	Me	Me
Μ	Zr	Zr	Zr	Hf	Hf	Hf	Hf	Hf	Hf



Fig. 3. Suggested structure of 1a–3f.

 $[M_2Cl_{10}]^{2-}$ and the cationic $(RCOCH_2PAr_3)^+$ units are held together by electrostatic forces. The M_1 and M_2 atoms in the $[M_2Cl_{10}]^{2-}$ dimer environment are sixcoordinate with a distorted octahedral configuration. The reaction of APPY and BPPY with MCl₄ (M = Ti, Zr and Hf) produced O-coordination complexes [7]. In this work, the reaction of MCl₄ with α -keto phosphorus ylides edge-shared $[M_2Cl_{10}]^{2-}$ complexes are formed. The decahalogenodimetalate(IV) dianions as their phosphorus ylides are well soluble in DMSO. After five day in room temperature crystalline solid **1g–3g** together with phosphonium salts in mother liquid were formed.

Proton decoupled ³¹P-NMR spectra in room temperature showed only one sharp singlet around 21 ppm for 1a-3f. As we described earlier the reaction between MCl_4 (M = Ti, Zr and Hf) with phosphorus ylides produce edge-shared $[M_2X_{10}]^{2-}$ complexes instead of O-coordination that previously reported [7]. The ³¹P chemical shift values for these complexes appear to be downfield by about $\delta \approx 6-7$ ppm with respect to the parent ylides. Gutmann and co-workers [26] suggest the existence of the $[Zr_2X_{10}]^{2-}$ anion in the reaction between $ZrCl_4$ and Ph_3CCi in acetonitrile solution. These complexes are soluble in DMSO and crystalline solid of 1g-3g were formed gradually in room temperature. The structure of this crystal indicated that DMSO coordinated from oxygen into metal center. This is similar to the structures of the octakis(dimethyl sulfoxide)zirconium (IV) chloride dimethyl sulfoxide trihydrate [18] and octakis(dimethyl sulfoxide)hafnium(IV) chloride dimethyl sulfoxide dihydrate [17] (Fig. 1) were built up of discrete octakis(dimethyl sulfoxide)zirconium(IV) and hafnium(IV) complexes, chloride ions and with an additional dimethyl sulfoxide molecule and two or three water molecules in the lattice. This work also showed that the zirconium(IV) ions are surrounded by eight oxygen atoms from the dimethyl sulfoxide molecules in a fairly regular square antiprism (Fig. 2). The v (CO) and v (P⁺-C⁻) in **1a-3f** are compared, in Table 1.

As mentioned earlier, in each particular case, the problem for study is the determination of the coordination center of DMSO (the S or O atoms; S- or O-coordination respectively). This problem is traditionally solved from the displacement of the band due to the stretching vibration v_{SO} , lying in the near infrared range. Among other possible methods of determining the coordination centers of DMSO, this method

Table 2. M-O and S=O symmetric and asymmetric stretching vibration frequencies in 1g-3g

Complexes	S=O symmetric stretch	S=O asymmet- ric stretch	M–O symmet- ric stretch	M–O asymmet- ric stretch
DMSO	1054	954	_	_
Ti(DMSO) ₈	1020	950	488	448
Zr(DMSO) ₈	1030	953	484	436
Hf(DMSO) ₈	1024	952	483	441

Parameters	${}^{1}J_{\mathrm{P-C}}$	$^{2}J_{\mathrm{P-H}}$
Complexes/Ligands	(CH ₂)	(CH ₂)
Y ¹	124.89	_
la	56.00	13.35
2a	55.10	13.75
3a	—	14.51
Y^2	112.73	23.12
1b	58.75	13.26
2b	51.45	13.35
3b	—	13.81
Y^3	110.20	22.85
lc	57.15	13.70
2c	55.77	11.58
3c	62.04	13.73
Y^4	110.30	23.75
1d	61.44	13.62
2d	61.82	13.81
3d	60.42	13.62
Y^5	113.47	22.67
le	65.20	9.82
2e	60.05	13.90
3e	61.40	12.70
Y ⁶	112.00	23.12
1f	61.40	13.00
2f	62.90	13.00
3f	60.60	14.50

Table 3. Compared J_{P-CH} of the complexes 1a-3f with ylides

occupies essentially a monopoly position. It is not applicable, however, in those cases where the range in which v_{SO} appears is overlapped by the bands due to other vibrations [13]. Attempts to improve the situation by means of an analysis of the spectra in the range in which the metal-DMSO stretching vibrations appear (tentatively, $v_{M-S} = 500-260$, $v_{M-O} = 530-380$ cm⁻¹) [13, 21, 22], have generally had little success, because of the indefinite nature of the assignments and the overlap of the corresponding spectral intervals. Preliminary results from normal coordinate analysis show that there are major contributions from S–O stretching in the IR bands at 927 and 897 cm⁻¹ [23]. The MO and SO stretching vibration frequencies **1g–3g** are listed in Table 2.

The ¹H NMR spectrum of **1a–3f** in room temperature showed resonances associated with the aromatic phenyl groups around 7–8 ppm and resonances corresponding to the methinic protons around 6–7 ppm as a doublet. The suggested structure for these complexes (Fig. 3) shows that involving a phosphonium cation and a μ -dichloro M₂Cl₁₀ dianion. The ¹³C NMR spectra of **1a**–**3f** in room temperature are the up field shift of the signals due to ylidic carbon. High solubility of ylides in CDCl₃ allowed us to record the spectrum in this solvent but for the complexes we had to use DMSO- d_6 and presence of a septet pick due to solvent at 39.5 ppm in the CH resonance region caused that some of these signals were not seen. The ¹³C-NMR spectrum revealed resonances only in the range of 127–130 ppm, associated with the phenyl groups. Table 3 contains the coupling constant of **1a–3f** compared with parent ylides. This indicates interaction between $[M_2Cl_{10}]$ with counterion showed in Scheme 1.

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Supplementary Information

Supplementary data contains three figures, the molecular structure of octakis(dimethyl sulfoxide)hafnium(IV) chloride dimethyl sulfoxide dihydrate (Fig. 1) the molecular structure of octakis(dimethyl sulfoxide)zirconium(IV) chloride dimethyl sulfoxide (Fig. 2).

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