

## Edge-Shared $[M_2Cl_{10}]^{2-}$ Complexes of Reaction between Oxophilic Group IV Metal and Phosphorus Ylides

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The reactions between oxophilic group 4 metal chlorides,  $\alpha$ -keto ylides in THF, led to the formation of titanium, zirconium and hafnium edge-shared  $[M_2Cl_{10}]^{2-}$  complexes (**1a-3d**). With adding dimethyl sulfoxide as a ligand to these complexes at room temperature crystalline solid  $[M(DMSO)_8] \cdot 4Cl \cdot mH_2O \cdot DMSO$  ( $M = Ti$  (**1g**),  $Zr$  (**2g**) and  $Hf$  (**3g**);  $m = 0-3$ ) together with phosphonium salts in mother liquid were formed. Its metal complexes have been characterized by elemental analysis, IR and  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectroscopy. The dominating coordination structures of **1g-3g** are seven-coordinated complexes.

**Key Words:**  $\alpha$ -Keto ylides, Edge-shared complexes, Seven-coordinated complexes, Oxophilic group 4 metal, Titanium (IV), Zirconium (IV) and Hafnium (IV) complexes.

### INTRODUCTION

The utility of metalated phosphorus ylides in synthetic chemistry has been well documented<sup>1,2</sup>. Phosphorus ylides are remarkable ligands, which have attracted much attention in synthetic, catalytic and theoretical fields of transition metal chemistry<sup>3</sup>. The complexes of  $\alpha$ -keto-stabilized phosphorus ylides with late transition-metal ions are thoroughly investigated;<sup>4</sup> there are few examples of such complexes with early transition metals<sup>5-7</sup>.

The oxophilic group 4 metals, Ti, Zr and Hf can be classified as a hard metals. 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<sup>7,8</sup>. 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  $[Ph_3C]_2[M_2Cl_{10}]^-$ <sup>9</sup> 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<sup>10a</sup>. The bonding parameters of the  $[Hf_2Cl_{10}]^{2-}$  anion and the crystal structure of

$[Me_2SCH_2Cl]_2[Zr_2Cl_{10}]$ , have been reported<sup>10b,11</sup>. 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  $(Ar_3PCH_2COR)_2[M_2Cl_{10}]$  ( $R = OCH_2C_6H_5$ ,  $C_4H_5S$ ,  $C_6H_4NO_2$  and  $C_6H_4Cl$ ,  $Ar = Ph$ ;  $R = C_6H_4NO_2$ ,  $C_6H_4Cl$ ,  $Ar = PhMe$ ). But the most interesting point of present 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<sup>12</sup>. The nature of DMSO as a monodentate ligand is explored in this set of experiments<sup>13,14</sup>. 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<sup>15</sup>, but to a number of soft electron-pair acceptors, it is also coordinating *via* the sulfur atom<sup>16</sup>. The dominating coordination figures of zirconium(IV) and hafnium(IV) complexes are the square antiprism<sup>17</sup>, very often distorted octahedron and distorted seven-coordinated complexes are fairly common<sup>18,19</sup>. 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  $Ar_3PCH_2COR$  ( $R = OCH_2C_6H_5$ ,  $C_4H_5S$ ,  $C_6H_4NO_2$  and  $C_6H_4Cl$ ,  $Ar = Ph$ ;  $R = C_6H_4NO_2$ ,  $C_6H_4Cl$ ,  $Ar = PhMe$ ) in mother liquid were formed.

## EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone just before use. All other solvents were reagent grade and used without further purifications. Metal halide salts were purchased and used as received from Aldrich Chemical Co. The phosphorous ylides  $\text{Ph}_3\text{P}=\text{CHCOOCH}_2\text{C}_6\text{H}_5$  ( $\text{Y}^1$ )<sup>4a</sup>,  $\text{Ph}_3\text{P}=\text{CHCOC}_4\text{H}_3\text{S}$  ( $\text{Y}^2$ )<sup>4b</sup>,  $\text{Ph}_3\text{P}=\text{CHCOC}_6\text{H}_4\text{NO}_2$  ( $\text{Y}^3$ )<sup>5</sup>,  $\text{Ph}_3\text{P}=\text{CHCOC}_6\text{H}_4\text{Cl}$  ( $\text{Y}^4$ )<sup>6</sup> were synthesized according to the published procedures.

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  $\text{cm}^{-1}$  and the measurements were made by the KBr disk method. Melting points were measured on a SMP<sub>3</sub> apparatus. Solution-state <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra at ambient temperature were obtained in DMSO-*d*<sub>6</sub> or CDCl<sub>3</sub> 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 Bis[benzoylacetatetriphenylphosphonium] di- $\mu$ -chloro-bis[tetrachlorotitanate(IV)] (1a):** A 100-mL Schlenk tube was charged with (0.53 mL, 0.53 mmol of TiCl<sub>4</sub> (1 M solution in CH<sub>2</sub>Cl<sub>2</sub>) and 20 mL of THF. To this yellow solution was added  $\text{Y}^1$  (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. Yield (0.21 g, 70%); m.p. 69-70 °C; IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1731 (C=O), 921 (P-C); <sup>1</sup>H NMR (DMSO)  $\delta$ : 5.5 (d,  $J$  = 13.35 Hz, 2H, CH), 5.0 (s, 2H, CH<sub>2</sub>), 7.01-7.95 (m, 20H, Ph); <sup>31</sup>P NMR (DMSO)  $\delta$ : 20.77 (s), 26.37 (s, triphenylphosphoxide); <sup>13</sup>C NMR (DMSO)  $\delta$ : 31.0 (d,  $J$  = 56.0 Hz, CH<sub>2</sub>), 67.9 (s, 1C, CH<sub>2</sub>), 126.4 [s, 1C, C(Ph(i))], 131.4 [s, 2C, C(Ph(o))], 129.3 [s, 2C, C(Ph(m))], 131.8 [s, 1C, C(Ph(p))], 118.3 [d,  $J$  = 88.5 Hz, 3C, PPh<sub>3</sub>(i)], 133.8 [d,  $J$  = 10.58 Hz, 6C, PPh<sub>3</sub>(o)], 130.3 [d,  $J$  = 12.70 Hz, 6C, PPh<sub>3</sub>(m)], 135.2 [s, 3C, PPh<sub>3</sub>(p)], 164.8 (s, CO). Anal. calcd. for C<sub>54</sub>H<sub>48</sub>Cl<sub>10</sub>O<sub>4</sub>P<sub>2</sub>Ti<sub>2</sub>: C 50.94, H 3.80; Found C 50.90, H 3.32.

**Data for Bis[(4-thionylmethyl)triphenylphosphonium] di- $\mu$ -chloro-bis[tetrachlorotitanate(IV)] (1b):** pale brown solid. Yield (0.21 g, 70 %); m.p. 225-228 °C (decomp); IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1654 (C=O) 938 (P-C); <sup>1</sup>H NMR (DMSO)  $\delta$ : 6.34 (d,  $J$  = 13.3 Hz, 2H, CH<sub>2</sub>); 7.32-8.37 (m, 18H, arom.). <sup>31</sup>P NMR (DMSO): 21.51 (s). <sup>13</sup>C NMR (DMSO)  $\delta$ : 35.39 (d,  $J$  = 58.7, CH<sub>2</sub>); 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, PPh<sub>3</sub>(i)]; 133.66 [d,  $J$  = 10.2 Hz, 6C, PPh<sub>3</sub>(o)]; 129.82 [d,  $J$  = 13.0 Hz, 6C, PPh<sub>3</sub>(m)]; 129.09 [s, 3C, PPh<sub>3</sub>(p)]; 184.73 (d,  $J$  = 4.5, CO). Anal. calcd. for C<sub>48</sub>H<sub>40</sub>Cl<sub>10</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>Ti<sub>2</sub>: C 47.06, H, 3.29; Found C 47.22, H 3.20.

**Data for Bis[(*p*-nitrophenylmethylene)triphenylphosphonium] di- $\mu$ -chloro-bis[tetrachlorotitanate(IV)] (1c):** Orange solid. 0.27 g (94 %). m.p. 153-155 °C decomp. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1685 (C=O), 995 (P-C). <sup>1</sup>H NMR (DMSO)  $\delta$ : 6.43 (d,  $J$  = 13.7, 2H, CH<sub>2</sub>); 7.76-8.34 (m, 19H, arom.). <sup>31</sup>P NMR (DMSO)  $\delta$ : 21.32 (s). <sup>13</sup>C NMR (DMSO)  $\delta$ : 36.65 (d,  $J$  = 58.5 Hz, CH<sub>2</sub>); 140.07 [s, C(Ph(i))]; 135.24 [s, C(Ph(o))];

124.35 [s, C(Ph(m))]; 151.15 [s, C(Ph(p))]; 119.39 [d,  $J$  = 89.8 Hz, PPh<sub>3</sub>(i)]; 134.21 [d,  $J$  = 8.7, PPh<sub>3</sub>(o)]; 130.49 [d,  $J$  = 11.5, PPh<sub>3</sub>(m)]; 131.19 [s, PPh<sub>3</sub>(p)]; 192.39 (s, CO). Anal. calcd. for C<sub>52</sub>H<sub>42</sub>Cl<sub>10</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Ti<sub>2</sub>: 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- $\mu$ -chloro-bis[tetrachlorotitanate(IV)] (1d):** Cream solid. 0.14 g (72 %). m.p. 98-100 °C. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1674 (C=O), 990 (P-C). <sup>1</sup>H NMR (DMSO)  $\delta$ : 6.47 (d,  $J$  = 13.62 Hz, 2H, CH<sub>2</sub>); 7.21-8.33 (m, 19H, arom.). <sup>31</sup>P NMR (DMSO)  $\delta$ : 21.50 (s). <sup>13</sup>C NMR (DMSO)  $\delta$ : 36.20 (d,  $J$  = 61.4 Hz, CH<sub>2</sub>); 140.26 [s, C(Ph(i))]; 135.11 [s, C(Ph(o))]; 129.47 [s, C(Ph(m))]; 119.59 [d,  $J$  = 88.6 Hz, PPh<sub>3</sub>(i)]; 134.17 [d,  $J$  = 10.3 Hz, PPh<sub>3</sub>(o)]; 130.42 [d,  $J$  = 12.68 Hz, PPh<sub>3</sub>(m)]; 131.64 [s, PPh<sub>3</sub>(p)]; 192.27 (s, CO). Anal. calcd. for C<sub>52</sub>H<sub>42</sub>Cl<sub>12</sub>O<sub>2</sub>P<sub>2</sub>Ti<sub>2</sub>: C 48.72, H 3.30. Found C 48.56, H 3.25.

**Preparation of Bis[benzoylacetatetriphenylphosphonium] di- $\mu$ -chloro-bis[tetrachlorozirconate(IV)] (2a):** A 100-mL Schlenk tube was charged with (0.12 g, 0.53 mmol) of ZrCl<sub>4</sub> and 20 mL of THF. To this colourless solution was added  $\text{Y}^1$  (0.20 g, 0.53 mmol) in 8 mL of THF. The solution, which remained colourless, was stirred for 2 h. The colourless solution was concentrated to 2 mL and diethyl ether (15 mL) added to precipitate the moisture-sensitive pale yellow complex. Yield (0.19 g, 58 %); m.p. 82-84 °C; IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1732 (C=O), 996 (P-C); <sup>1</sup>H NMR (DMSO)  $\delta$ : 5.5 (d,  $J$  = 13.75 Hz, 2H, CH), 5.1 (s, 2H, CH<sub>2</sub>), 6.97-8.12 (m, 20H, Ph); <sup>31</sup>P NMR (DMSO)  $\delta$ : 20.85 (s), 26.35 (s, triphenylphosphoxide); <sup>13</sup>C NMR (DMSO)  $\delta$ : 29.7 (d,  $J$  = 55.1 Hz, CH<sub>2</sub>), 67.6 (s, 1C, CH<sub>2</sub>), 126.3 [s, 1C, C(Ph(i))], 131.2 [s, 2C, C(Ph(o))], 129.0 [s, 2C, C(Ph(m))], 131.6 [s, 1C, C(Ph(p))], 118.1 [d,  $J$  = 88.9 Hz, 3C, PPh<sub>3</sub>(i)], 133.6 [d,  $J$  = 10.80 Hz, 6C, PPh<sub>3</sub>(o)], 130.0 [d,  $J$  = 12.83 Hz, 6C, PPh<sub>3</sub>(m)], 134.9 [s, 3C, PPh<sub>3</sub>(p)], 164.6 (s, CO). Anal. calcd. for C<sub>54</sub>H<sub>48</sub>Cl<sub>10</sub>O<sub>4</sub>P<sub>2</sub>Zr<sub>2</sub>: C 47.69, H 3.56; Found C 47.50, H 3.50.

**Data for Bis[(4-thionylmethyl)triphenylphosphonium] di- $\mu$ -chloro-bis[tetrachlorozirconate(IV)] (2b):** Pale yellow solid. Yield (0.19 g, 58 %); m.p. 286-288 °C decomp. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1654 (C=O), 937 (P-C). <sup>1</sup>H NMR (DMSO)  $\delta$ : 6.35 (d,  $J$  = 12.5 Hz, 2H, CH<sub>2</sub>); 7.33-8.35 (m, 18H, arom.). <sup>31</sup>P NMR (DMSO)  $\delta$ : 21.49 (s). <sup>13</sup>C NMR (DMSO)  $\delta$ : 35.60 (d,  $J$  = 51.4 Hz, CH<sub>2</sub>); 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, PPh<sub>3</sub>(i)]; 133.98 [d,  $J$  = 10.6 Hz, PPh<sub>3</sub>(o)]; 130.19 [d,  $J$  = 12.6 Hz, PPh<sub>3</sub>(m)]; 129.09 [s, PPh<sub>3</sub>(p)]; 185.14 (d,  $J$  = 5.8, CO). Anal. calcd. for C<sub>48</sub>H<sub>40</sub>Cl<sub>10</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>Zr<sub>2</sub>: C 43.95, H 3.07; Found C 44.15, H 3.22.

**Data for Bis[(*p*-nitrophenylmethylene)triphenylphosphonium] di- $\mu$ -chloro-bis[tetrachlorozirconate(IV)] (2c):** Orange solid. 0.11 g (35 %). m.p. 140-143 °C decomp. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 1686 (C=O), 994 (P-C). <sup>1</sup>H NMR (DMSO)  $\delta$ : 6.56 (d,  $J$  = 11.6, 2H, CH<sub>2</sub>); 7.75-8.38 (m, 19H, arom.). <sup>31</sup>P NMR (DMSO)  $\delta$ : 21.02 (s). <sup>13</sup>C NMR (DMSO)  $\delta$ : 36.6 (d,  $J$  = 55.7, CH<sub>2</sub>); 140.06 [s, C(Ph(i))]; 135.23 [s, C(Ph(o))]; 124.36 [s, C(Ph(m))]; 151.18 [s, C(Ph(p))]; 119.38 [d,  $J$  = 88.1, PPh<sub>3</sub>(i)]; 134.20 [d,  $J$  = 8.5, PPh<sub>3</sub>(o)]; 130.47 [d,  $J$  = 10.1, PPh<sub>3</sub>(m)]; 131.17 [s, PPh<sub>3</sub>(p)]; 192.44 (s, CO). Anal. calcd. for C<sub>52</sub>H<sub>42</sub>Cl<sub>10</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Zr<sub>2</sub>: 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- $\mu$ -chloro-bis[tetrachlorozirconate(IV)] (2d):** White solid. 0.24 g (77 %). m.p. 103-105 °C. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1674 (C=O), 989 (P-C).  $^1H$  NMR (DMSO)  $\delta$ : 6.41 (d,  $J$  = 13.8 Hz, 2H,  $CH_2$ ); 7.21-8.26 (m, 19H, arom.).  $^{31}P$  NMR (DMSO)  $\delta$ : 21.52 (s).  $^{13}C$  NMR (DMSO)  $\delta$ : 36.29 (d,  $J$  = 61.8,  $CH_2$ ); 140.27 [s, C(Ph(i))]; 135.11 [s, C(Ph(o))]; 129.46 [s, C(Ph(m))]; 119.64 [d,  $J$  = 88.9 Hz, PPh<sub>3</sub>(i)]; 134.20 [d,  $J$  = 10.5 Hz, PPh<sub>3</sub>(o)]; 130.42 [d,  $J$  = 12.7 Hz, PPh<sub>3</sub>(m)]; 131.66 [s, PPh<sub>3</sub>(p)]; 192.30 (s, CO). Anal. calcd. for C<sub>52</sub>H<sub>42</sub>Cl<sub>12</sub>O<sub>2</sub>P<sub>2</sub>Zr<sub>2</sub>: C 45.63, H 3.09; Found C 45.37, H 3.20.

**Data for Bis[benzoylacetatetriphenylphosphonium]di- $\mu$ -chloro-bis[tetrachlorohafnate(IV)] (3a):** Pale brown solid. Yielded (0.20 g, 61 %); m.p. 90-92 °C; IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1732 (C=O), 1625, 1601, 1587, 1486, 1438, 1379, 1263, 1127, 1072, 968 (P-C), 906, 805, 746, 728, 695;  $^1H$  NMR (DMSO)  $\delta$ : 5.6 (d,  $J$  = 14.51 Hz, 2H, CH), 5.1 (s, 2H,  $CH_2$ ), 6.93-7.92 (m, 20H, Ph);  $^{31}P$  NMR (DMSO)  $\delta$ : 20.83 (s), 26.20 (s, triphenylphosphoxide);  $^{13}C$  NMR (DMSO)  $\delta$ : 67.6 (s, 1C,  $CH_2$ ), 128.4 [s, 1C, C(Ph(i))], 131.2 [s, 2C, C(Ph(o))], 129.0 [s, 2C, C(Ph(m))], 131.7 [s, 1C, C(Ph(p))], 118.2 [d,  $J$  = 88.9 Hz, 3C, PPh<sub>3</sub>(i)], 133.7 [d,  $J$  = 10.56 Hz, 6C, PPh<sub>3</sub>(o)], 130.0 [d,  $J$  = 12.84 Hz, 6C, PPh<sub>3</sub>(m)], 135.0 [s, 3C, PPh<sub>3</sub>(p)], 164.6 (s, CO). Anal. calcd. for C<sub>54</sub>H<sub>48</sub>Cl<sub>10</sub>O<sub>4</sub>P<sub>2</sub>Hf<sub>2</sub>: C 42.27, H 3.15; Found C 42.18, H 3.10.

**Data for Bis[(4-thionylmethyl)triphenylphosphonium]di- $\mu$ -chloro-bis[tetrachlorohafnate(IV)](3b):** Pale brown solid. 0.22 g (59 %). m.p. 297-299 °C decomp. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1655 (C=O), 939 (P-C).  $^1H$  NMR (DMSO)  $\delta$ : 6.15 (d,  $J$  = 13.8 Hz, 2H,  $CH_2$ ); 7.08-8.15 (m, 18H, arom.).  $^{31}P$  NMR (DMSO)  $\delta$ : 21.38 (s).  $^{13}C$  NMR (DMSO)  $\delta$ : 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, PPh<sub>3</sub>(i)]; 133.68 [d,  $J$  = 10.5 Hz, PPh<sub>3</sub>(o)]; 129.96 [d,  $J$  = 12.9 Hz, PPh<sub>3</sub>(m)]; 129.23 [s, PPh<sub>3</sub>(p)]; 184.50 (s, CO). Anal. calcd. for C<sub>48</sub>H<sub>40</sub>Cl<sub>10</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>Hf<sub>2</sub>: C 38.79, H 2.71; Found C 38.65, H 2.84.

**Data for Bis[(p-nitrophenylmethylene)triphenylphosphonium]di- $\mu$ -chloro-bis[tetrachlorohafnate(IV)] (3c):** Orange solid. 0.12 g (45 %). m.p. 136-138 °C decomp. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1683 (C=O), 994 (P-C).  $^1H$  NMR (DMSO)  $\delta$ : 6.56 (d,  $J$  = 13.7 Hz, 2H,  $CH_2$ ); 7.77-8.35 (m, 19H, arom.).  $^{31}P$  NMR (DMSO)  $\delta$ : 21.26 (s).  $^{13}C$  NMR (DMSO)  $\delta$ : 36.71 (d,  $J$  = 62.0 Hz,  $CH_2$ ); 140.08 [s, C(Ph(i))]; 135.25 [s, C(Ph(o))]; 124.34 [s, C(Ph(m))]; 151.10 [s, C(Ph(p))]; 119.40 [d,  $J$  = 89.3 Hz, PPh<sub>3</sub>(i)]; 134.22 [d,  $J$  = 9.1 Hz, PPh<sub>3</sub>(o)]; 130.50 [d,  $J$  = 12.1 Hz, PPh<sub>3</sub>(m)]; 131.12 [s, PPh<sub>3</sub>(p)]; 192.36 (s, CO). Anal. calcd. for C<sub>52</sub>H<sub>42</sub>Cl<sub>10</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Hf<sub>2</sub>: 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- $\mu$ -chloro-bis[tetrachlorohafnate(IV)] (3d):** White solid. 0.26 g (75 %). m.p. 107-109 °C. IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1673 (C=O), 990 (P-C).  $^1H$  NMR (DMSO)  $\delta$ : 6.42 (d,  $J$  = 13.6 Hz, 2H,  $CH_2$ ); 7.38-8.41 (m, 19H, arom.).  $^{31}P$  NMR (DMSO)  $\delta$ : 21.53 (s).  $^{13}C$  NMR (DMSO)  $\delta$ : 36.20 (d,  $J$  = 60.4 Hz,  $CH_2$ ); 140.28 [s, C(Ph(i))]; 135.12 [s, C(Ph(o))]; 129.48 [s, C(Ph(m))]; 119.59 [d,  $J$  = 89.0 Hz, PPh<sub>3</sub>(i)]; 134.18 [d,  $J$  = 10.7 Hz, PPh<sub>3</sub>(o)]; 130.43 [d,  $J$  = 12.9 Hz, PPh<sub>3</sub>(m)]; 131.63 [s, PPh<sub>3</sub>(p)]; 192.24 (s, CO). Anal. calcd. for C<sub>52</sub>H<sub>42</sub>Cl<sub>12</sub>O<sub>2</sub>P<sub>2</sub>Hf<sub>2</sub>: C 40.47, H 2.74; Found C 40.35, H 2.50.

**Preparation of octakis(dimethyl sulfoxide)titanium (IV) (1g):** With 0.1 g of (RCOCH<sub>2</sub>PAR<sub>3</sub>)<sub>2</sub>[Ti<sub>2</sub>Cl<sub>10</sub>] (R = OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>3</sub>S, C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> and C<sub>6</sub>H<sub>4</sub>Cl; Ar = Ph and (R = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> and C<sub>6</sub>H<sub>4</sub>Cl; Ar = PhMe) was added DMSO in room temperature. The solution, which remained colourless, so 5 day crystalline solid was formed. The colourless solution contain two product, one of the product [Ti(DMSO)<sub>8</sub>] in crystalline solid and another product, phosphonium salt in mother liquid. m.p. 140-142 °C, IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1020 (S=O, symmetric stretch), 950 (S=O, asymmetric stretch), 488 (Ti-O, symmetric stretch), 448 (Ti-O, asymmetric stretch). Anal. calcd. for C<sub>16</sub>H<sub>48</sub>O<sub>8</sub>S<sub>8</sub>Ti: C 28.56, H 7.19; Found C 28.02, H 6.88.

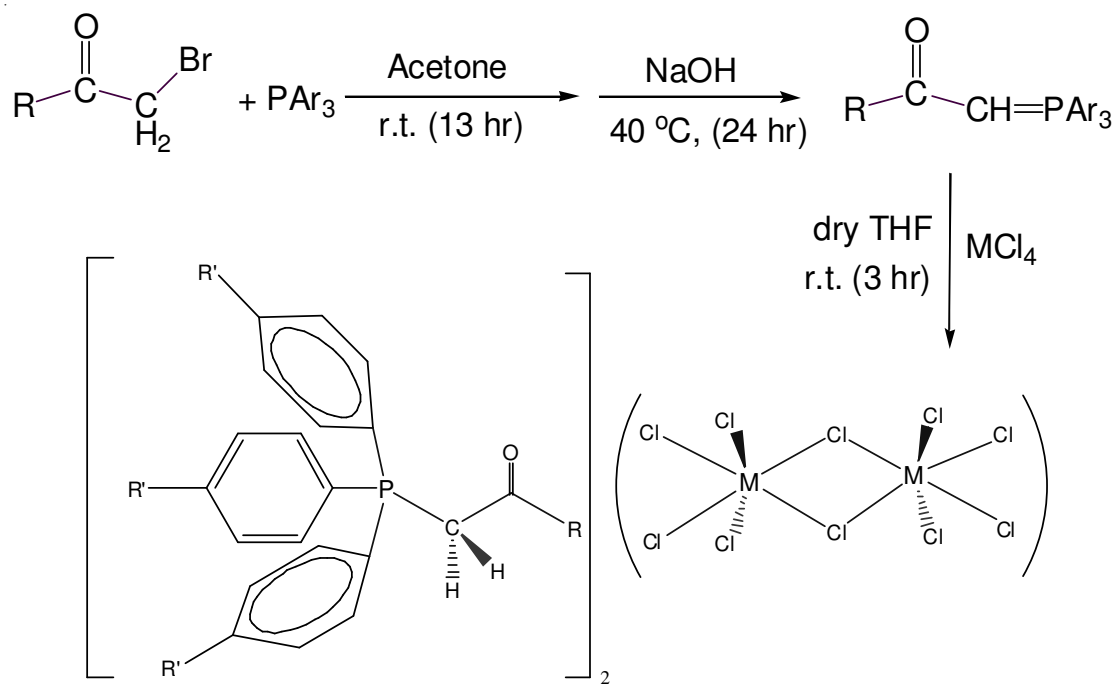
**Data for octakis(dimethyl sulfoxide)zirconium (IV) (2g):** m.p. 153-155 °C, IR (KBr,  $\nu_{max}$ ,  $cm^{-1}$ ): 1030 (S=O, symmetric stretch), 953 (S=O, asymmetric stretch), 484 (Ti-O, symmetric stretch), 436 (Ti-O, asymmetric stretch). Anal. calcd. for C<sub>16</sub>H<sub>48</sub>O<sub>8</sub>S<sub>8</sub>Zr: C 26.83, H 6.75; Found C 26.51, H 6.63.

**Data for octakis(dimethyl sulfoxide)hafnium (IV) (3g):** m.p. 168-170 °C, IR,  $\nu_{max}$ ,  $cm^{-1}$ ; 1024 (S=O, symmetric stretch), 952 (S=O, asymmetric stretch), 483 (Ti-O, symmetric stretch), 441 (Ti-O, asymmetric stretch). Anal. Calc. for C<sub>16</sub>H<sub>48</sub>O<sub>8</sub>S<sub>8</sub>Hf: C 23.92, H 6.02; Found C 23.12, H 5.78.

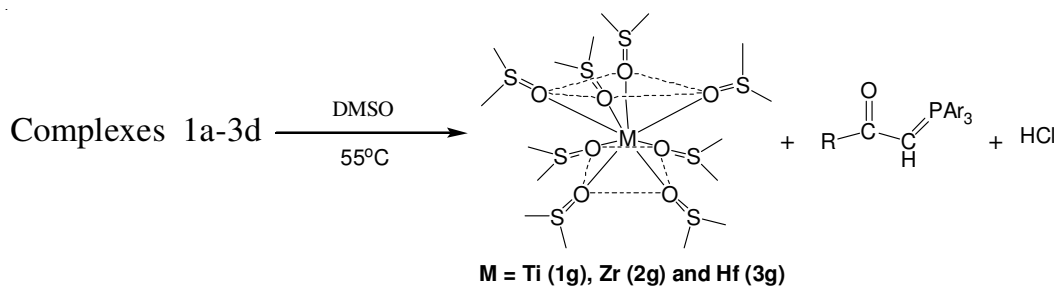
## RESULTS AND DISCUSSION

The reaction between the group 4 metal halide salts and the  $\alpha$ -keto ylides  $Y^1$ ,  $Y^2$ ,  $Y^3$  and  $Y^4$  in THF led to the formation of complexes of the type (Ar<sub>3</sub>PCH<sub>2</sub>COR)<sub>2</sub>[M<sub>2</sub>Cl<sub>10</sub>] (**1a-3f**) (Fig. 1). The anionic  $[M_2Cl_{10}]^{2-}$  and the cationic (RCOCH<sub>2</sub>PAR<sub>3</sub>)<sup>+</sup> units are held together by electrostatic forces. The M<sub>1</sub> and M<sub>2</sub> atoms in the  $[M_2Cl_{10}]^{2-}$  dimer environment are six-coordinate with a distorted octahedral configuration. In this work, the reaction of MCl<sub>4</sub> with  $\alpha$ -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 5 day in room temperature, crystalline solid **1g-3g** together with phosphonium salts in mother liquid were formed (Fig. 2).

Proton decoupled  $^{31}P$  NMR spectra in room temperature showed only one sharp singlet around 21 ppm for **1a-3d**. The  $^{31}P$  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<sup>20</sup> suggest the existence of the  $[Zr_2X_{10}]^{2-}$  anion in the reaction between ZrCl<sub>4</sub> and Ph<sub>3</sub>CCl 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<sup>17</sup> and octakis(dimethyl sulfoxide) hafnium(IV) chloride dimethyl sulfoxide dehydrate<sup>16</sup> 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 DMSO molecules in a fairly regular square antiprism<sup>17</sup>.

Fig. 1. Synthesis scheme for the preparation of ligand and its complexes **1a-3d**

	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>
R	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>3</sub> S	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> Cl	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>3</sub> S	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> Cl	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>3</sub> S	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> Cl
R'	H	H	H	H	H	H	H	H	H	H	H	H
M	Ti	Ti	Ti	Ti	Zr	Zr	Zr	Zr	Hf	Hf	Hf	Hf

M = Ti (**1g**), Zr (**2g**) and Hf (**3g**)Fig. 2. Synthesis scheme for the preparation of **1g-3g**

The  $\nu(\text{CO})$  and  $\nu(\text{P}^+ - \text{C}^-)$  in **1a-3d** are compared in Table-1.

Complexes ylides	$\nu(\text{C}=\text{O})$	$\nu(\text{P}^+ - \text{C}^-)$	Ref.
APPY <sup>a</sup>	1530	–	24
BPPY <sup>b</sup>	1525	–	25
<b>Y<sup>1</sup></b>	1610	887	4a
<b>Y<sup>2</sup></b>	1527	879	4b
<b>Y<sup>3</sup></b>	1529	884	5
<b>Y<sup>4</sup></b>	1579	882	6
<b>1a</b>	1731	923	Present work
<b>2a</b>	1732	996	Present work
<b>3a</b>	1732	968	Present work
<b>1b</b>	1654	938	Present work
<b>2b</b>	1654	937	Present work
<b>3b</b>	1655	939	Present work
<b>1c</b>	1685	995	Present work
<b>2c</b>	1686	994	Present work
<b>3c</b>	1683	994	Present work
<b>1d</b>	1674	990	Present work
<b>2d</b>	1674	989	Present work
<b>3d</b>	1673	990	Present work

<sup>a</sup> acetylmethylenetriphenylphosphorane;

<sup>b</sup> benzoylmethylenetriphenylphosphorane

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  $\nu_{\text{SO}}$ , lying in the near infrared range. Among other possible methods of determining the coordination centers of DMSO, this method occupies essentially a monopoly position. It is not applicable, however, in these cases where the range in which  $\nu_{\text{SO}}$  appears is overlapped by the bands due to other vibrations<sup>12</sup>. 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,  $\nu_{\text{M-S}} = 500-260$ ,  $\nu_{\text{M-O}} = 530-380 \text{ cm}^{-1}$ )<sup>12,21,22</sup>, 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  $\text{cm}^{-1}$ .<sup>23</sup> The MO and SO stretching vibration frequencies **1g-3g** are listed in Table-2.

The <sup>1</sup>H 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 that involving a phosphonium cation and a  $\mu$ -dichloro  $M_2Cl_{10}$  dianion.

TABLE-2  
(M-O) AND (S=O) SYMMETRIC AND ASYMMETRIC  
STRETCHING VIBRATION FREQUENCIES IN **1g-3g**

Complexes	(S=O) Symmetric stretch	(S=O) Asymmetric stretch	(M-O) Symmetric stretch	(M-O) Asymmetric stretch
DMSO	1054	954	-	-
Ti(DMSO) <sub>8</sub>	1020	950	488	448
Zr(DMSO) <sub>8</sub>	1030	953	484	436
Hf(DMSO) <sub>8</sub>	1024	952	483	441

The  $^{13}C$  NMR spectra of **1a-3d** in room temperature are the up field shift of the signals due to ylidic carbon. High solubility of ylides in  $CDCl_3$  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  $^{13}C$  NMR spectrum revealed resonances only in the range of 127-130 ppm, associated with the phenyl groups.

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