

## Novel Metal–Carbon Multiply Bonded Twelve-Electron Complexes of Ti and Zr Supported by a Bis(Phosphoranimine) Chelate

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Metal-carbon multiply bonded complexes (e.g., carbenes) have widespread importance in catalysis and organic transformations.<sup>1–8</sup> Such species are often invoked or implicated as important intermediates in olefin metathesis reactions,<sup>9–12</sup> Fischer–Tropsch processes,<sup>13</sup> and metal-catalyzed carbene transfers with diazo compounds.<sup>14</sup> The nature and reactivity of the prototypical carbene complexes,  $M=CR_2$  depends greatly on the electronic and steric nature of the substituent, R. Those containing electronegative heteroatom substituents, such as O, N, or S, are designated as Fischer carbenes whereas those with only hydrogen- or carbon-atom substituents are designated as Schrock carbenes (alkylidenes). Chemically, the former are generally electrophilic whereas the latter are nucleophilic.<sup>1–5,15</sup> A few systems contain a multiple metal–carbon bond in which the carbon carries a phosphorus substituent. The uranium phosphoylides,<sup>16</sup>  $Cp_3UC(H)PR_3$ , provide an example of such substitution and have been termed a third form of carbene because of the difference in the reactivity pattern which accompanies such substitution.<sup>17</sup> Herein we describe the preparation of novel, electron-deficient (i.e., 12 valence electron) group 4 metal complexes with a carbon center clearly multiply bound to the metal and to two phosphorus substituents. Resonance structures (vide infra) of these complexes suggest that they may also display a substantial ylide character<sup>18</sup> contributed by the phosphorus atom centers. In either case, the carbon center is

expected to show a nucleophilic reactivity similar to the Schrock carbenes. Our complexes are the first examples of stable carbene complexes of group 4 metals in ligand environments which do not involve Cp. They relate to previous examples of group 4 metal carbene complexes of titanium<sup>19</sup> and zirconium<sup>20</sup> which are cyclopentadienyl supported.<sup>21</sup> Related bridging alkylidene or carbene complexes of the group 4 metals are known.<sup>22</sup>

These new complexes were accessed through a novel but simple route: metathetical reaction of the dilithiated salt<sup>23</sup> with the metal tetrahalides. Thus, titanium or zirconium tetrachlorides (as their THF adducts)<sup>24</sup> reacted with dilithio bis(trimethylsilyliminodi-(phenyl)phosphorano)methanide **1**<sup>23</sup> to give good yields of the  $[MCl_2\{C(Ph)_2P=NSiMe_3\}_2-k^3C,N,N']]$  ( $M = Ti$  (**2**) or  $Zr$  (**3**))<sup>25,26</sup> complexes (Scheme 1) via clean elimination of LiCl. The resultant complexes are pale yellow (**2**) or colorless (**3**) crystalline solids. The complexes are highly soluble in relatively polar and aromatic solvents such as diethyl ether, benzene, and toluene and are thermally stable; toluene solutions of either complex heated under an argon atmosphere in a closed container at 140 °C for 7 d did not show any appreciable decomposition.

The <sup>31</sup>P NMR spectra of the complexes consist of only one sharp singlet, due to two equivalent phosphorus centers, with a chemical shift close to that of the previously reported dilithium salt.<sup>23</sup> The <sup>13</sup>C{<sup>1</sup>H} APT spectrum gave a positive triplet signal (<sup>1</sup>J<sub>PC</sub> ≈ 145 Hz) for the carbene which collapsed to a positive singlet upon phosphorus decoupling. The carbene NMR resonance of the titanium complex **2** (191.0 ppm) is shifted further downfield than the resonances displayed by titanium ylide complexes,<sup>18</sup> but is shifted upfield relative to the carbene complexes of titanium (260–300 ppm).<sup>19</sup> However, the same resonance of **3** (101.7 ppm)

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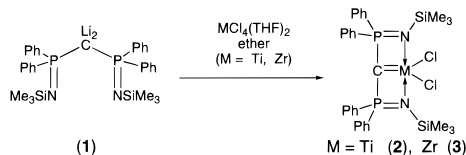
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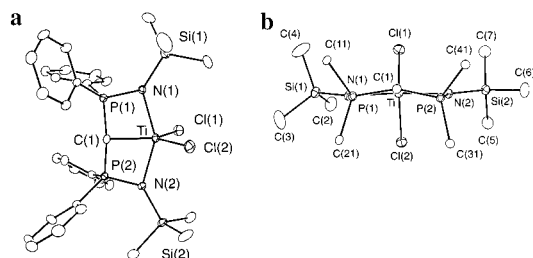
(25) Preparations of **2** and **3**: The dilithium salt **1**<sup>23</sup> (0.20 g, 0.35 mmol) was added to a stirred suspension of  $TiCl_4(THF)_2$ <sup>24</sup> (0.12 g, 0.35 mmol) in diethyl ether (10 mL) at room temperature. The mixture was stirred at room temperature for 2 days. The diethyl ether was then evaporated, and the resultant yellow solid product was extracted with 8 mL of toluene and filtered to remove LiCl. The toluene solution was then reduced to one-half volume, and 5 mL of hexane was added. The yellow crystalline product, **2**, formed at room temperature over a period of 1 day, was filtered and dried under vacuum. (Yield: 0.13 g, 54.1%).<sup>26</sup> The Zr analogue was prepared in a similar fashion except that the concentrated solution was cooled to –15 °C for 2 days whereupon colorless crystals of **3** formed. (Yield: 0.16 g, 63.5%).<sup>26</sup>

(26) Satisfactory analyses (given in Supporting Information) were obtained.

## Scheme 1



lies in the region observed for the ylide complexes of zirconium<sup>18</sup> and is therefore more shielded than that of typical zirconium carbene complexes (230–300 ppm).<sup>20,21</sup> In addition, the M=C distance for the titanium complex is relatively short, vide infra, which suggests that the Ti=C bond possesses more double-bond character and is hence more carbenelike than the Zr=C bond. It may therefore be appropriate to assign significant zwitterionic Zr<sup>δ+</sup>–C<sup>δ-</sup> character to the zirconium–carbon bond in the latter complex.



**Figure 1.** (a) A full ORTEP<sup>29</sup> view of  $[\text{TiCl}_2\{\text{C}(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^3\text{C},\text{N},\text{N}'\}]$  **2** showing the atom-labeling scheme. The hydrogen atoms have been removed for clarity, and the remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances (Å) and angles (°) are: Ti–C(1) = 2.008(4), Ti–N(1) = 2.061(4), Ti–N(2) = 2.088(4), P(1)–N(1) = 1.621(3), P(2)–N(2) = 1.621(4), P(1)–C(1) = 1.678(4), P(2)–C(1) = 1.679(4), Ti–Cl(1) = 2.276(2), Ti–Cl(2) = 2.283(2) Å, P(1)–C(1)–P(2) = 157.3(3)°, N(1)–Ti–N(2) = 148.9(1)°, N(1)–P(1)–C(1) = 97.3(2)°, N(2)–P(2)–C(1) = 97.4(2)°.<sup>30</sup> (b) A side view of the central plane of **2**, shown in the same format. The C(1) atom is 0.297(4) Å out of the plane defined by Ti–N(1)–P(1)–P(2)–N(2), which deviate,  $\leq 0.04$  Å from this plane.

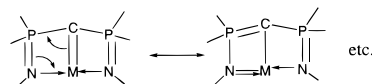
The molecular structures of  $[\text{MCl}_2\{\text{C}(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^3\text{C},\text{N},\text{N}'\}]$  (M = Ti **2**,<sup>27</sup> Zr **3**<sup>28</sup>) determined by X-ray crystallography were virtually identical. Two views of **2**<sup>29</sup> (representative of both molecules) are given in Figure 1, and selected metrical details are given in the caption.<sup>30</sup> Several points are worthy of note. The basic frame consists of two nearly planar, fused, four-membered rings {M, N(1), P(1), C(1)} and {M, N(2), P(2), C(1)} (where M = Ti (**2**), Zr (**3**)) subtended from the shared edge defined by the M=C(1) bond. In both the cases, the C(1) atom is displaced significantly {0.297 (4) Å for **2** and 0.458 (7) Å for **3**} from the plane defined by the atoms M, P(1), N(1), P(2), and N(2) as a result of the bend in the P–C–P angle {157.3 (3)° (**2**), 148.3 (5)° (**3**)}. The two four-membered rings are not coplanar; there is a dihedral angle of 11.1 (2)° in the case of **2** (and 22.2 (4)° in the case of **3**) between these two planar four-membered rings forming a distorted “open book” conformation. The M=C(1) bond distance, 2.008(4) Å for **2** (and 2.190(8) Å for **3**), is short compared to related alkyl complexes which is consistent with multiple-bond character expected for a metal carbene. The bond distances within the bicyclic framework are also considerably

(27) Crystal Data for  $[\text{TiCl}_2\{\text{C}(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^3\text{C},\text{N},\text{N}'\}]$  **2**: Monoclinic,  $P2_1/c$  (No. 14),  $a = 16.5364$  (12),  $b = 12.1208$  (9),  $c = 17.8033$  (11) Å,  $\beta = 103.357$  (5)°,  $V = 3471.9$  (4) Å<sup>3</sup>,  $Z = 4$ . The structure was solved by direct methods and refined by full matrix least squares procedures:  $R_1 = 0.0580$  and  $0.1094$ , ( $wR_2 = 0.1048$  and  $0.1270$ ) for 6122 reflections with  $F_o^2 > 2\sigma(F_o^2)$  and all data, respectively.

(28) Crystal Data for  $[\text{ZrCl}_2\{\text{C}(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^3\text{C},\text{N},\text{N}'\}]$  **3**: Tetragonal,  $P4$  (No. 81),  $a = 18.6534$  (4),  $c = 11.6746$  (4) Å,  $V = 4062.2$  (2) Å<sup>3</sup>,  $Z = 4$ . The structure was solved by direct methods and refined by full matrix least squares procedures:  $R_1 = 0.0671$  and  $0.0684$ , ( $wR_2 = 0.1841$  and  $0.1862$ ) for 5382 reflections with  $F_o^2 > 2\sigma(F_o^2)$  and all data, respectively.

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## Scheme 2



altered in comparison with the related values in bis(iminophosphorano)methanes;<sup>31,32</sup> the P=N bond distances are elongated and the endocyclic P–C bond distances are shortened, but exocyclic P–C bond distances are not affected. These factors suggest that there is a strong delocalization of  $\pi$ -electron density within each of the four-membered rings arising from the effective conjugation of the M=C bond and the P=N bonds which results in the development of resonance forms with ylidic character (Scheme 2).

The moderate acidity of the methylene protons in ligands containing the P–C–P backbone has been previously exploited for the synthesis of singly deprotonated derivatives through monolithiation.<sup>33,34</sup> A few doubly deprotonated methanide ligands have been suggested<sup>35,36</sup> but without crystal structure evidence. A few structurally characterized group 10 and group 13 metal complexes exist<sup>34,37–40</sup> in which double deprotonation of the methylene center of the ligand has been demonstrated, but none of these products came from rationally designed synthetic routes. Furthermore, all of these structurally characterized examples have a bimetallic bridge structure in contrast to the present group 4 complexes.

Preliminary reactivity studies of **2** and **3** show susceptibility to electrophilic attack characteristic of high oxidation state group 5 alkylidene complexes. A 1,2-addition across the polar  $\text{M}^{\delta+}=\text{C}_\alpha^{\delta-}(\text{PP}')$  yields the  $\text{C}_\alpha$  protonated product illustrated by the reaction of adamantanol with **3** to form  $[\text{ZrCl}_2\{\text{CH}(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^3\text{C},\text{N},\text{N}'\}(\text{OAd})]$ .<sup>41</sup> Unsaturated electrophilic molecules react via a [2 + 2] cycloaddition path as illustrated by the reaction of **3** with adamantylisocyanate to form the metallacycle  $[\text{ZrCl}_2\{\text{C}(\text{C}(\text{O})\text{N}(\text{Ad}))(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^4\text{C},\text{N},\text{N}',\text{N}''\}]$ .<sup>41</sup> Reactivity studies will be described in forthcoming reports.

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**Supporting Information Available:** This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(30) Selected interatomic distance (Å) and angle (°) parameters for  $[\text{ZrCl}_2\{\text{C}(\text{Ph})_2\text{P}(\text{=NSiMe}_3)_2\text{-}\kappa^3\text{C},\text{N},\text{N}'\}]$  **3** are: Zr–C(1) = 2.190(8), Zr–N(ave) = 2.164(7), P(1)–N(ave) = 1.630(6), P(1)–C(1) = 1.658(7), P(2)–C(1) = 1.674(6), P(1)–C(1)–P(2) = 148.3(5)°, N(1)–Zr–N(2) = 137.8(3)°, N(1)–P(1)–C(1) = 100.3(4)°, N(2)–P(2)–C(1) = 99.7(4)°.

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