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Titanocene and zirconocene complexes of a phosphorus analog of an Arduengo's carbene: Application in the synthesis of 1,3-diphosphafulvenes†

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Titanocene and zirconocene carbene complexes of a phosphorus equivalent of an Arduengo's carbene have been synthesized in the coordination sphere of titanocene and zirconocene and exhibit a nucleophilic character which has been exploited in the synthesis of 1,3-diphosphafulvenes.

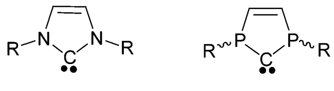
Over the last decade, the chemistry of carbenes has undergone an impressive renewal due to the discovery of stable heteroatom-C substituted species.[1] Among these, N-heterocyclic carbenes such as imidazol-2-ylidenes ("Arduengo's carbenes") proved to be the most versatile and have found numerous applications, essentially as powerful σ-donor ligands in many transition metal-based catalysts.[2]

Though phosphanyl-substituted carbenes ("Bertrand's carbenes") have already been isolated as free species and used in the synthesis of complexes[3,4] and several bis(iminophosphoranyl)carbene complexes ("Cavell's carbene complexes") have been characterized,[5] phosphorus analogs of imidazol-2-ylidenes have eluded isolation so far either as free ligands or as complexes.[6,7] Recent theoretical calculations by Schoeller and Nyulaszi clearly suggest that, though these analogs exhibit a substantial cyclic delocalization, the important inversion barrier at phosphorus that prevents planarization of the ring makes them unstable against dimerization.[8]

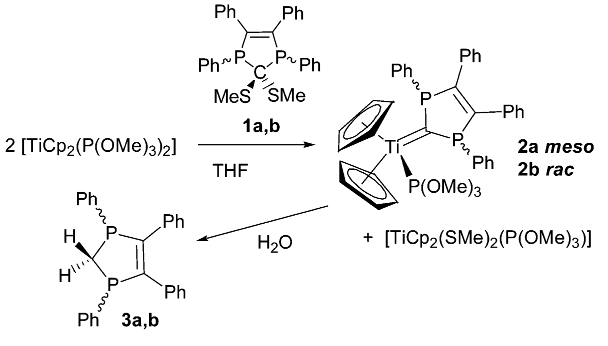
We recently explored various synthetic pathways leading to transition metal complexes of these phosphorus equivalents of imidazol-2-ylidenes. Herein we report on results obtained during the study of metallocene group 4 complexes (Ti, Zr). The starting point of our study was inspired by the synthesis of transient titanium carbene complexes through the titanocene-mediated desulfurization of thioacetals.[9] Having in hand the 2,2-dimethyl thioacetal of the 1,3,4,5-tetraphenyl-1,3-diphospholene[10] **1a** (*meso*) and **1b** (*rac*) (ratio *meso* : *rac* = 4 : 1) , we logically attempted its desulfurization with 2 equivalents of the [$TiCp_2(P(OMe)_3)_2$] complex. The reaction, which takes place at room temperature in THF, cleanly yields complexes **2a,b** in a 4 : 1 ratio (Scheme 1). Unfortunately, **2a,b** exhibit a short life-time and decomposition rapidly occurs in THF at room temperature (no ^{31}P NMR signal remained after 12 hours standing at 25 °C). However, indirect evidence of their formation was given by a trapping reaction of a freshly prepared solution with water at 25 °C. The tetraphenyl-1,3-diphospholenes **3a,b** (ratio: 1 : 1) were isolated as a mixture in quantitative yield (Scheme 2).[11]

Assuming that the replacement of titanium by zirconium would yield a stronger metal–carbon bond, we reproduced these experiments with zirconocene. Reaction of [$ZrCp_2$] with compound **1** in THF at room temperature cleanly yielded complexes **4a,b** in a 4 : 1 ratio according to ^{31}P NMR spectroscopy. Contrary to their titanium counterparts, **4a,b** proved to be stable in solution for at least a week in THF at room temperature but were found to be unstable in the absence of solvent. Unfortunately, despite many attempts, no suitable single crystal could be obtained from the crude mixture, each crystallization yielding microcrystals of the [$ZrCp_2(SMe)_2$] complex whose structure has already been recorded.[12] Further evidence that supports the formulation proposed for **4a,b** was given by coordination of PMe_3 to zirconium. Addition of PMe_3 resulted in the formation of two new complexes **2a,b** that were characterized in ^{31}P NMR as AX_2 (*meso* **5a**) and as broad ABX (*rac* **5b**) spin systems. Both complexes were characterized by ^{13}C NMR spectroscopy in the crude mixture. The most significant piece of data is given by the chemical shift of the carbenic carbon atom in **5a** which appears as a very characteristic AX_2 spin system with a large ^1J(P–C) coupling constant of 87.3 Hz as often encountered in phosphanyl carbenes.[3d] However, complexes **5a,b** also proved to be reluctant towards crystallization (Scheme 3).‡

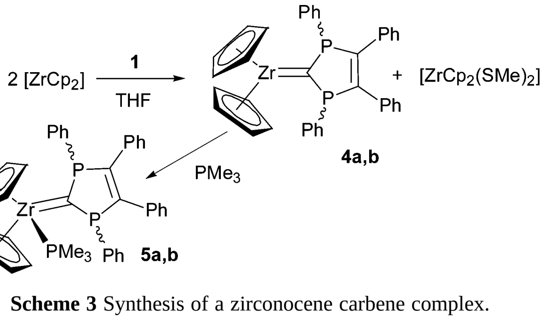
The reactivity of **4a,b** towards ketones and aldehydes was investigated. Reactions with poorly substituted aliphatic ketones and aldehydes in THF at room temperature did not yield satisfactory results and many unidentified compounds were formed. However, when sterically encumbered compounds such 2-adamantanone or aromatic derivatives are employed, a clean reaction takes place yielding the expected 1,3-diphosphafulvenes (Scheme 4). All trapping compounds **6–10** were obtained, after chromatographic separation, as a mixture of *meso* **(a)** and *rac* **(b)** derivatives in a 4 : 1 ratio, respectively. Some of these derivatives



Scheme 1 N-Heterocyclic carbenes and their phosphorus analogs.



Scheme 2 Synthesis of a titanocene carbene complex.



Scheme 3 Synthesis of a zirconocene carbene complex.

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† Electronic supplementary information (ESI) available: Characterizations of all compounds described in this paper, X-ray crystal structures of compounds **6a**, **8b**, **9a** and theoretical data of the *meso*-[$ZrCp_2(C_3H_4P_2)$] complex. See http://www.rsc.org/suppdata/cc/b4/b403436h/

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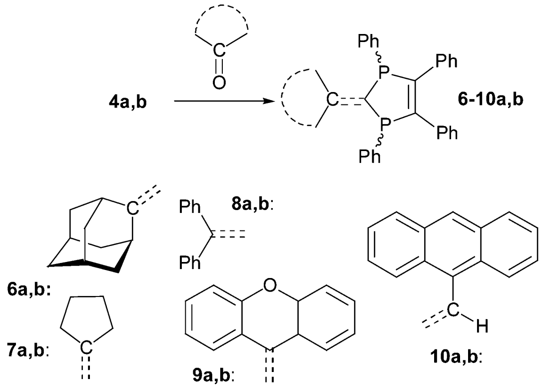

Scheme 4 Reaction of **4a,b** toward some aldehydes and ketones.

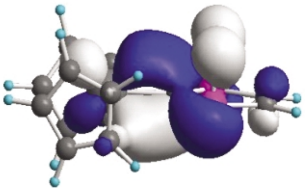

Fig. 1 HOMO of [ZrCp$_2$(C$_3$H$_4$P$_2$)] as given by DFT calculations.

(**6a**, **8b** and **9a**) could be crystallized and their stereochemistries were ascertained by X-ray crystal structure analyses.§

The nucleophilic character of these new carbene complexes was confirmed by preliminary DFT calculations. The parent *meso* and *rac* [ZrCp$_2$(C$_3$H$_4$P$_2$)] complexes were chosen as models. Geometry optimizations were carried out using the 6-31G* (C, H, P) and LANL2DZ (Zr) basis sets. As expected, an NBO analysis reveals that the carbenic carbon atom bears a substantial negative charge ($q_C = -1.26$, $q_{Zr} = +1.59$). An examination of MOs clearly shows that the 2pz orbital at the carbenic carbon atom strongly contributes to the HOMO of the complex as expected for a Schrock-type complex (HOMO of the *meso* complex represented) (Fig. 1).

Further studies will now focus on a complete theoretical study of these new group 4 complexes as well as on their reactivity. Experiments aimed at expanding these syntheses to other metallic centers are also under active investigation in our laboratories.

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Notes and references

‡ General procedure for the synthesis of complexes **4a,b** and their trapping reactions with ketones and aldehydes: BuLi (2.1 mL, 1.5 M in hexanes, 3.2 mmol) was added to a a solution of Cp$_2$ZrCl$_2$ (460 mg, 1.6 mmol) in THF (30 mL) at −78 °C. The mixture was stirred at −78 °C for one hour and warmed to 0 °C. This mixture was then transferred by cannula to a Schlenk flask containing **1** (340 mg, 0.8 mmol). The resulting burgundy red mixture was warmed to room temperature then stirred for 3 hours. Complexes **4a,b** are highly water sensitive and decompose when taken to dryness. NMR data were recorded on the crude mixture by evaporating the most part of the solution (2 mL remaining) and by adding d$_6$-benzene (1 mL) as internal reference. Trapping reactions were achieved as follows: ketone or aldehyde (1.6 mmol, 2 equiv.) were added to the crude solution of **4a,b**. An immediate discoloration of the mixture was observed and ^{31}P NMR spectroscopy showed the complete formation of the corresponding fulvene derivatives **a** (*meso)* and **b** (*rac*). After evaporation of the solvent, the compounds were purified by column chromatography using toluene/hexane (3 : 7) as mixture and recovered as a solid for **6a/6b** (70%), **7a/7b** (70%), **8a/8b** (95%), **9a/9b** (80%), **10a/10b** (60%). Selected data: **4a** (*meso*): ^{31}P NMR (C$_6$D$_6$, 25 °C): δ 87.1 (s); ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 142.4 (t, $^1J_{\mathrm{CP}}$ 12.7 Hz, PCP). **5a**: ^{31}P NMR (C$_6$D$_6$, 25 °C): δ −9.9 (t, $^3J_{\mathrm{PP}}$ 7.3 Hz, PMe$_3$), 75.3 (d, $^3J_{\mathrm{PP}}$ 7.3 Hz, PCP); ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 220.2 ppm (dt, $^1J_{\mathrm{CP}}$ 87.3 Hz, $^2J_{\mathrm{CP}}$ 11.5 Hz; PCP). **5b**: ^{31}P NMR (C$_6$D$_6$, 25 °C): δ −11.2 (t, $^3J_{\mathrm{PP}}$ 6.1 Hz, PMe$_3$), 114.4 (broad, PCP), 119.3 (broad, PCP); ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 212.3 (m; PCP).

§ *Crystal data* for **6a**: C$_{38}$H$_{36}$Cl$_2$P$_2$, M = 625.51, triclinic, space group $P\bar{1}$, a = 10.067(1), b = 12.325(1), c = 13.669(1) Å, α = 72.220(1), β = 77.590(1), γ = 80.800(1)°, V = 1569.1(2) Å^3, Z = 2, D = 1.324 g cm^{-3}, μ = 0.336 cm^{-1} (MoKα, λ = 0.71069 Å), T = 150.0(1) K, R_1 = 0.0385, $^wR_2$ = 0.1104, GoF = 1.061, unique data = 9134 (14286 measured, R_{int} = 0.0152, KappaCCD diffractometer), 380 refined parameters. *Crystal data* for **8b**: C$_{40}$H$_{30}$P$_2$, M = 572.58, monoclinic, space group $P2_1/c$, a = 11.734(1), b = 6.327(1), c = 40.956(2) Å, β = 91.354(1), V = 3039.8(6) Å^3, Z = 4, D = 1.251 g cm^{-3}, μ = 0.171 cm^{-1}(MoKα, λ = 0.71069 Å), T = 150.0(1) K, R_1 = 0.0552, $^wR_2$ = 0.1561, GoF = 1.006, unique data = 4288 (7293 measured, R_{int} = 0.0363, KappaCCD diffractometer), 379 refined parameters. *Crystal data for* **9a**: C$_{40}$H$_{28}$OP$_2$, M = 586.56, triclinic, space group $P\bar{1}$, a = 9.324(1), b = 17.429(1), c = 19.246(1) Å, α = 101.240(1), β = 96.960(1), γ = 98.770(1)°, V = 2994.8(4) Å^3, Z = 4, D = 1.301 g cm^{-3}, μ = 0.178 cm^{-1}(MoKα, λ = 0.71069 Å), T = 150.0(1) K, R_1 = 0.0430, $^wR_2$ = 0.1065, GoF = 0.997, unique data = 10913 (16597 measured, R_{int} = 0.0265, KappaCCD diffractometer), 775 refined parameters. CCDC 235099, 227151 and 235100 respectively. See http://www.rsc.org/suppdata/cc/b4/b403436h/ for crystallographic data in .cif or other electronic format.

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