Novel vanadium and titanium phosphorus ylide complexes

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The reactions of [{(Me$_3$Si)$_2$N}$_2$MCl(thf)] (M = V 1a, Ti 2a) and of [{(C$_6$H$_{11}$)$_2$N}$_2$M(μ-Cl)$_2$LiL$_2$] (M = V 1b, Ti 2b; L = thf, tmeda) with CH$_2$PPh$_3$ proceeded in toluene and at room temperature to form the corresponding zwitterionic complexes [(R$_2$N)$_2$MCl(CH$_2$PPh$_3$)] (M = V 3a,b, Ti 4a), while the analogous reaction of 2b gave the diamagnetic [{(C$_6$H$_{11}$)$_2$N}$_2$TiCl(CHPPh$_3$)] 4b.

Since the initial discovery by Wittig of the enormous synthetic potential offered by phosphorus ylides,[1] there has been a steady growth of interest for studying and understanding the chemistry of these species with transition metals.[2] The employment of the Wittig reagents in transition-metal chemistry was mainly stimulated by their ability to work as a source of methylene which was deemed as promising for the preparation of reactive metal alkylidene species. However, in only relatively few cases, have phosphorus ylides been successfully used as precursors for the formation of transition-metal carbenes[3] and carbynes.[4] By contrast, Wittig reagents have been proven versatile ligands for the stabilization of several transition[5] and non-transition metals[6] with which they can form exceedingly stable complexes using a variety of bonding modes.[7] While acting as a ligand, phosphorus ylides adopt a zwitterionic electronic structure which plays a pivotal role in metal-promoted organic synthesis[8] and in the reactivity with coordinated ligands.[9]

In the chemistry of high- and medium-valent Ti and V, phosphorus ylides have been used to form mono-[10] and dinuclear metallacyclic structures.[11] In the sole case of a monocyclopentadienyl titanium derivative was the intact coordination of a phosphorus ylide in a zwitterionic structure claimed.[12] Following our interest in the chemistry of these metals stabilized by bulky organic amides, we became interested in studying the reactivity of d^1 and d^2 Ti^{III} and V^{III} metal centres with phosphorus ylides. In this preliminary paper we describe our findings.

The reactions of [{(Me$_3$Si)$_2$N}$_2$MCl(thf)] (M = V **1a**,[13] Ti **2a**[14]) and of [{(C$_6$H$_{11}$)$_2$N}$_2$M(μ-Cl)$_2$LiL$_2$] (M = V, L = thf **1b**; M = Ti, L = tmeda **2b**) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with CH$_2$PPh$_3$ proceeded in toluene and at room temperature to form the corresponding zwitterionic [(R$_2$N)$_2$MCl(CH$_2$PPh$_3$)] (M = V **3a,b**, Ti **4a**) (Scheme 1). The complexes were obtained in good yield as very air-sensitive crystals after solvent evaporation *in vacuo* and crystallization from pentane.†

Complexes **3a,b** and **4a** are paramagnetic with magnetic moments as expected for the d^2 and d^1 electronic configurations of V^{III} and Ti^{III} respectively. The IR spectra of these complexes and the combustion analysis data were in agreement with the proposed formulation.

For complexes **3a,b** and **4a** it was possible to grow crystals of suitable size to undertake X-ray crystal structure determinations.‡

Complexes **3a**, **3b** and **4a** all possess similar structures in which the coordination geometry of the metal centre is distorted tetrahedral and is defined by two nitrogen atoms from two amide groups, one chlorine and the CH$_2$ group of the coordinated ylide (Fig. 1).

The reaction took a significantly different pathway for complex **2b**. The reaction with phosphorus ylide yielded a dark reddish-brown solid **4b**, whose diamagnetism indicated that oxidation of the metal centre to the tetravalent oxidation state occurred during the reaction while attempts to obtain a crystal structure were hampered by unfavourable crystal shape. Combustion analysis data indicated that the compound was formed by the addition of one phosphorus ylide to one

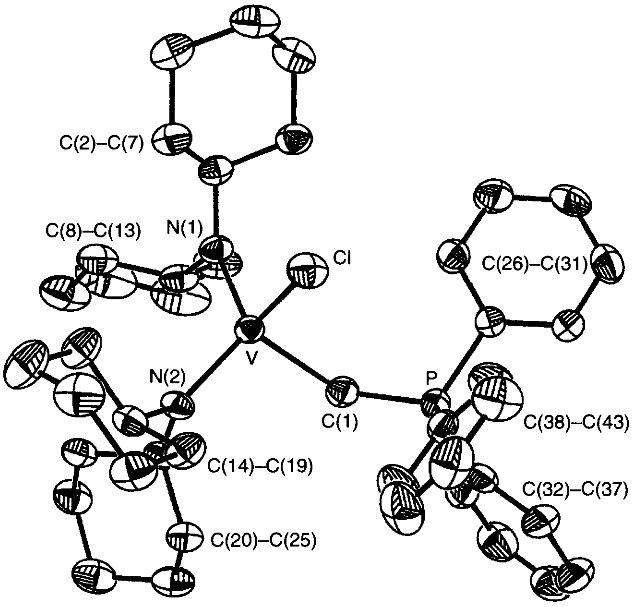
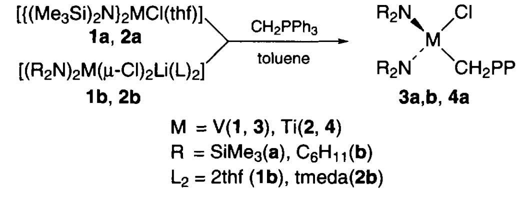
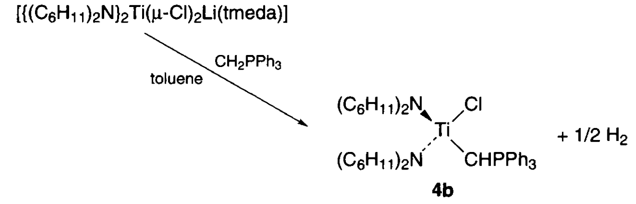


Fig. 1 Thermal ellipsoid plot of **3a**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): V–Cl 2.295(1), V–C(1) 2.165(4), V–N(1) 1.935(4), V–N(2) 1.953(4), C(1)–P 1.767(4), Cl–V–N(1) 100.4(1), Cl–V–N(2) 120.0(1), Cl–V–C(1) 98.2(1), V–C(1)–P 128.6(2), N(1)–V–C(1) 124.1(2), N(2)–V–C(1) 99.3(2), N(1)–V–N(2) 115.2(2) V···P 3.547(1).



Scheme 1



Scheme 2

$[\{(C_6H_{11})_2N\}_2TiCl]$ moiety. The presence of chlorine in 1 : 1 molar ratio with titanium was confirmed by X-ray fluorescence. The mean feature of the ^{1}H NMR spectrum is the presence of a doublet centred at δ 7.51 (J_{P-H} 5.7 Hz); DEPT experiments identify the signal as a methyne which corresponds to a doublet at δ 135.4 (J_{P-C} 41 Hz) of the ^{13}C NMR spectrum (HQMS).[15] No resonance could be conclusively assigned to the phenyl quaternary carbon atom. The presence of the PPh_3 moiety was clearly demonstrated by the ^{31}P NMR spectrum which showed a singlet at δ 7.55 in the fully decoupled spectrum, while the coupling with proton gave a rather complicated feature. The characteristic resonances of the aromatic and cyclohexyl groups were observed at the expected positions in both the ^{1}H and the ^{13}C NMR spectra. These features, in addition to the signal integration, demonstrated that the phosphorus ylide lost one hydrogen atom during the oxidation of the metal centre. The yield of the reaction was well above 50% and the formation of hydrogen gas was clearly detected during Toepler pump experiments (0.46 equiv. of H_2 per mole of **2b**).

Further work to study the reactivity of these zwitterionic species is currently underway.

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Footnotes

† **3a**: dark green crystals (78% yield). IR (Nujol) ν/cm^{-1}: 3052w, 3022w, 3006w, 2952vs, 2895vs, 1587m, 1485m, 1437vs, 1253vs, 1245sh, 1236s, 1183s, 1116s, 996m, 986vs, 971vs, 922vs, 883vs, 845vs, 843sh, 811vs, 793sp, 782s, 746s, 730s, 718m, 692vs, 664vs, 634s, 614m, 544m, 523sp, 512m, 510sh, 504m, 489w, 486w. Anal: Calc. (found) for $C_{31}H_{53}ClN_2PSi_4V\cdot 1/2C_7H_8$: C 56.80(56.44), H 7.88(7.69), N 3.84(3.77)%. μ_{eff} = 2.73 μ_B at room temp. **4a**: orange crystals (40% yield). IR (Nujol) ν/cm^{-1} 3060m, 3020s, 2890m, 1592sp, 1494m, 1441s, 1259s, 1127s, 930vs, 872s, 844vs br, 770s, 747vs, 719s, 701vs, 689s, 640m, 513m, 500sp, 497sp. Anal: Calc. (found) for $C_{31}H_{53}ClN_2PSi_4Ti\cdot 0.5C_7H_8$: C 57.04(56.94), H 7.91(7.89), N 3.86(3.71)%. μ_{eff} = 1.83 μ_B at room temp. **3b**: dark crystals (70% yield). IR (Nujol) ν/cm^{-1} 3052m, 2665m, 1589w, 1247m, 1160s, 1120s, 1099s, 1035s, 952s, 889s, 823s, 738m br, 690s br, 528s. Anal: Calc. (found) for $C_{43}H_{61}ClN_2PV\cdot C_5H_{12}$: C 72.47(72.41), H 9.25(9.19), N 3.52(3.37)%. μ_{eff} = 2.77 μ_B at room temp. **4b**: orange diamagnetic crystals (75% yield). Anal: Calc. (found) for $C_{43}H_{60}ClN_2PTi$: C 71.80(71.71), H 8.41(8.29), N 3.89(3.67)%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 8.73(m, Ph, 6H), 7.52(d, J_{P-H} 5.7 Hz, CH_{ylide}, 1H), 7.05(m, Ph, 9H), 3.72(m, $CH_{cyclohexyl}$, 4H), 2.19(m, C_6H_{11}, 4H), 1.90(m, C_6H_{11}, 20H), 1.62(m, C_6H_{11}, 4H), 1.50(m, C_6H_{11}, 4H), 1.39(m, C_6H_{11}, 4 H), 1.08(m, C_6H_{11}, 4H). ^{13}C NMR (125 MHz, C_6D_6, 27 °C): δ 135.4(d J_{P-C} 41 Hz, CH_{ylide}), 133.2(d J_{P-C} 10.3 Hz, CH_{phenyl}), 131.1 (d J_{P-C} 3.6 Hz, CH_{phenyl}), 128.0 (d J_{P-C} 48.6 Hz, CH_{phenyl}; one CH_{phenyl} signal under solvent), 59.0, 36.5, 36.1, 27.2 (double intensity), 26.3 (each s, $CH_{2\,cyclohexyl}$). ^{31}P NMR (202 MHz, C_6D_6 25 °C): δ 7.55.

‡ *Crystal data* for **3a**: $C_{31}H_{53}ClN_2PSi_4V\cdot C_7H_8$, M = 729.54, triclinic, space group $P\bar{1}$, a = 9.901(2), b = 12.089(2), c = 18.319(3) Å, α = 78.09(1), β = 76.02(2), γ = 80.24(1)°, U = 2065.3(6) Å^3, Z = 2, D_c = 1.173 g cm^{-3}, $F(000)$ = 778, μ = 4.8 cm^{-1}, T = −50 °C, R = 0.069, wR_2 = 0.176, GOF = 0.964 for 425 parameters and 4439 reflections out of 7257 unique. For **3b**: $C_{43}H_{61}ClN_2PV\cdot C_5H_{12}$, M = 795.44, monoclinic, space group $P2_1/n$, a = 16.729(1), b = 12.709(1), c = 23.207(2) Å, β = 1109.46(1)°, U = 4622.8(6) Å^3, Z = 4, D_c = 1.143 g cm^{-3}, $F(000)$ = 1720, μ = 3.4 cm^{-1}, T = −50 °C, R = 0.050, wR_2 = 0.117, GOF = 0.947 for 480 parameters and 4264 observed reflections out of 8128 unique. For **4a**: $C_{31}H_{53}ClN_2PSi_4Ti$, triclinic, space group $P\bar{1}$, a = 9.937(2), b = 12.085(4), c = 18.373(7) Å, α = 78.55(3), β = 75.55(2), γ = 80.35(2)°, U = 2078(1) Å^3.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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