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# Facile formation of a titanium–carbon bond from $TiCl_4$ by HCl elimination: the synthesis and structure of $TiCl_3[Me_3SiNP(Ph)_2CHCH_2P(Ph)_2NSiMe_3]$†

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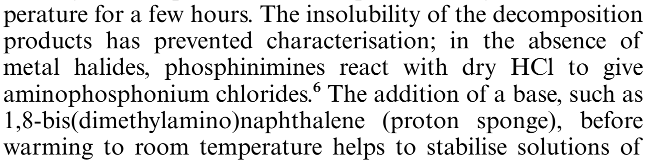
**The reaction of $TiCl_4$ with the bis-phosphinimine $Me_3SiN{=}P(Ph)_2CH_2CH_2P(Ph)_2{=}NSiMe_3$ 1 proceeds with evolution of HCl and metallation of one $CH_2$ group to give $TiCl_3\{Me_3SiNP(Ph)_2CHCH_2P(Ph)_2NSiMe_3\}$ 2. The crystal structure of 2 is solved and shows a comparatively long Ti–C bond.**

There are numerous reports that the reaction of trimethylsilylphosphinimines $R_3P{=}NSiMe_3$ with early[1] and late[2] transition metal halides results in dehalosilylation and formation of phosphiniminato complexes $R_3P{=}N{-}MX_n$. The phosphiniminato ligand may be $\eta^1$-bonded, or form a chelate ring.[2] The reaction of the dilithiated methylene-bridged ligand $Li_2C\{Ph_2P{=}NSiMe_3\}$ with $MCl_4$ (M = Ti, Zr) to give the carbene complex $MCl_2[\eta^3\text{-}C(Ph_2P{=}NSiMe_3)_2]$ has also been described.[3] There are, however, to our knowledge no reports of the facile metallation of these ligands by a metal chloride *via* HCl evolution, in preference to $Me_3SiCl$ elimination. We report here an unusual reaction between $TiCl_4$ and the bis-phosphinimine ligand $Me_3SiN{=}P(Ph)_2CH_2CH_2P(Ph)_2{=}NSiMe_3$ **1**.

Compound **1** is easily prepared in high yield by the Staudinger reaction[4] from bis(diphenylphosphino)ethane with trimethylsilylazide in refluxing toluene.[5] Treatment of **1** with $TiCl_4$ in $CH_2Cl_2$ at −78 °C results in the formation of deep red $TiCl_3[Me_3SiNP(Ph)_2CHCH_2P(Ph)_2NSiMe_3]$ **2**, evidently by metallation of one $CH_2$ moiety and formation of HCl (Scheme 1). The $^{31}P$ NMR of the reaction, in the absence of a base at −78 °C, shows only two doublets at $\delta$ 24.8 and 41.8 ($J_{PP}$ = 79.6 Hz) for **2** and suggests a clean and quantitative conversion, although decomposition occurs upon standing at room temperature for a few hours. The insolubility of the decomposition products has prevented characterisation; in the absence of metal halides, phosphinimines react with dry HCl to give aminophosphonium chlorides.[6] The addition of a base, such as 1,8-bis(dimethylamino)naphthalene (proton sponge), before warming to room temperature helps to stabilise solutions of **2** against decomposition, and the product is isolated as deep red crystals in 70% yield. If the base is added prior to $TiCl_4$, the reaction remains incomplete, and some unreacted **1** is recovered.



**Scheme 1**

The bis(trimethylsilylphosphinimino) ligand in **2** acts as a $[NCN]^-$ tridentate monoanion. The low symmetry of **2** is reflected in the $^1H$, $^{13}C$ and $^{31}P$ NMR spectra. There are two inequivalent $SiMe_3$ groups. Each of the three protons on the $-C_2H_3-$ bridge are magnetically inequivalent; they are coupled to two inequivalent phosphorus nuclei and are part of an ABCMX spin system which was assigned with the aid of a simulated spectrum (Fig. 1). Of the four phenyl rings, two on one phosphorus are inequivalent, while the other two on the second phosphorus atom are equivalent, consequently the phenyl region of the $^{13}C$ NMR spectrum is complex with three sets of *ipso*, *ortho*, *meta* and *para* signals.

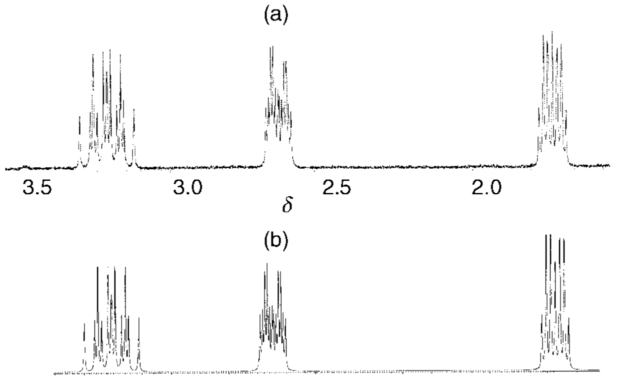
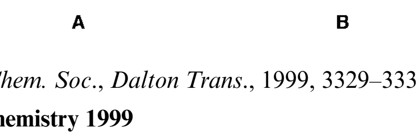


**Fig. 1** Observed (a) and simulated (b) $^1H$ NMR spectra of the three protons of the $-C_2H_3-$ bridge in **2**.

Recrystallisation of **2** from dichloromethane gives deep red crystals of $\mathbf{2}\cdot2CH_2Cl_2$, the structure of which was confirmed by X-ray diffraction (Fig. 2).‡ The compound forms a distorted octahedron, with a σ-bond between Ti and one of the carbons on the ethane bridge, and dative bonds between Ti and the two nitrogen atoms. The Cl atoms occupy the remaining meridional coordination sites. The P(1)–C(1) bond of 1.775(4) Å is shorter than P(2)–C(2) [1.836(4) Å], which is typical for a P–C single bond,[6,7] but significantly longer than the P=C double bond in $Ph_3P{=}CH_2$ [1.661(8) Å].[8] The Ti–C(1) bond [2.275(5) Å] is long compared to the Ti–$CH_3$ bonds in $CH_3TiCl_3$ (2.047(6) Å)[9] or in the octahedral chelate complexes $TiMeCl_3(Me_2PC_2H_4PMe_2)$ [2.149(5) Å][10] and $TiMe_2$(salen) [2.15(1) Å].[11] The titanium-bound carbon atom C(1) is intermediate between trigonal-planar and tetrahedral (angle sum 346°). The distances Ti–N(1) and Ti–N(2) [2.080(4) and 2.111(4) Å, respectively] are considerably longer than the Ti–N σ-bond in $CpTiCl_2(NPPh_3)$ [1.78(1) Å][1b] but do not reach the values of purely dative Ti–N bonds, *e.g.* in $TiMe_2$(salen) (average 2.145 Å).[11] The P–N bonds differ only slightly, *cf.* N(1)–P(1) [1.604(4) Å] and N(2)–P(2) [1.614(4) Å]. This bond length distribution suggests that the bonding in **2** is best described by structure **A**, with a minor contribution of a phosphorus ylide resonance structure **B**.

The scope of $[NCN]^-$ ligands in early transition metal chemistry and the reactivity of **2** are currently under investigation.



**A** **B**

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3329/

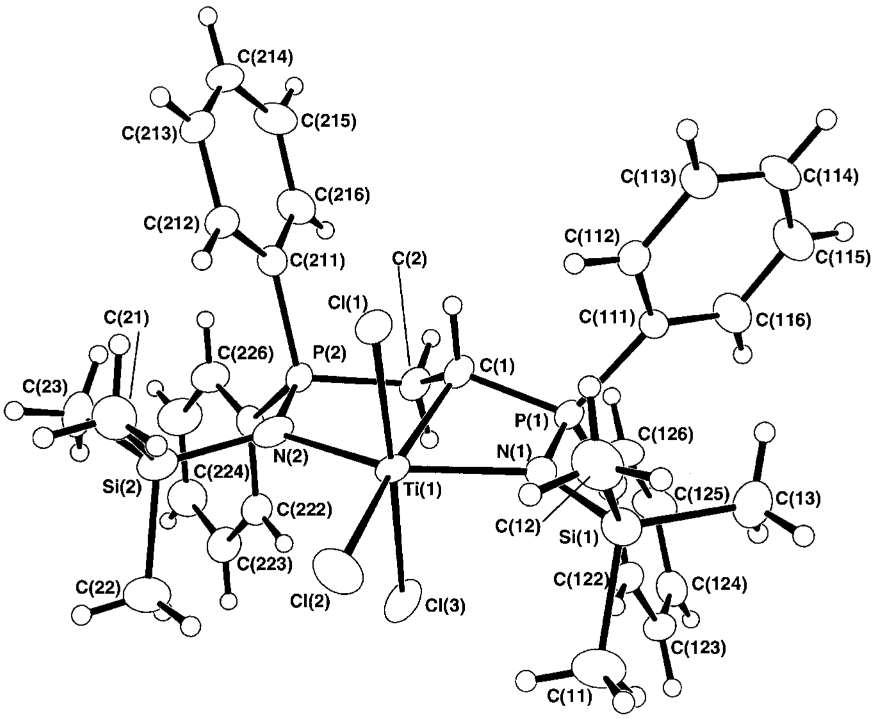

**Fig. 2** The molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ti–N(1) 2.080(4), Ti–N(2) 2.111(4), Ti–C(1) 2.275(5), Ti–Cl(1) 2.370(2), Ti–Cl(2) 2.3517(10), Ti–Cl(3) 2.360(2), P(1)–C(1) 1.775(4), P(2)–C(2) 1.836(4), P(1)–C(111) 1.807(4), P(1)–C(121) 1.831(4); N(1)–Ti–N(2) 151.47(13), N(1)–Ti–C(1) 69.3(2), N(2)–Ti–C(1) 82.8(2), N(1)–Ti–Cl(2) 102.30(12), N(2)–Ti–Cl(2) 106.11(13), C(1)–Ti–Cl(2) 169.08(12), C(1)–Ti–Cl(1) 85.88(11), Cl(1)–Ti–Cl(3) 177.17(6), Ti–N(1)–Si(1) 128.4(2), Ti–N(1)–P(1) 103.3(2), Ti–C(1)–P(1) 90.8(2), Ti–C(1)–H(1) 107(2), C(2)–C(1)–H(1) 113(2), C(2)–C(1)–P(1) 123.8(3), H(1)–C(1)–P(1) 109(2). Ellipsoids are drawn at 40% probability.

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## Notes and references

‡ Synthesis of **2**·2$CH_2Cl_2$: a Schlenk tube charged with $SiMe_3$-$NP(Ph)_2CH_2CH_2P(Ph)_2NSiMe_3$ **1** (1.94 g, 3.39 mmol) was dissolved in $CH_2Cl_2$ (50 $cm^3$) and cooled to −78 °C. Adding a toluene solution of $TiCl_4$ (0.67 g, 3.39 mmol) resulted in a colour change from clear to deep red over 1 h while warming to 0 °C. The solution was re-cooled to −78 °C and treated with a $CH_2Cl_2$ (10 $cm^3$) solution of 1,8-bis(dimethylamino)naphthalene (0.73 g, 3.39 mmol). The reaction mixture was allowed to warm slowly up to ambient temperature, filtered, reduced to *ca.* 30 $cm^3$ and placed in the freezer at −20 °C overnight, providing **2**·2$CH_2Cl_2$ as deep red crystals; (1.90 g, 62%). X-Ray quality crystals were grown from the filtrate at −20 °C over 3 days and provided an additional 0.23 g (total yield 70%). Found (calc.): C, 48.6 (48.87); H, 5.3 (5.34); N, 3.4 (3.45)%. $^1H$ NMR ($CD_2Cl_2$, 20 °C, 300.13 MHz): $\delta$ 0.22 (s, 9H, $SiMe_3$), 0.25 (s, 9H, $SiMe_3$), 1.78 (dddd, 1H, CH, $J_{HH} = 13.9$ and 4.8, $J_{HP} = 4.8$ and 4.3), 2.75 (dddd, 1H, $CH_2$, $J_{HH} = 13.9$ and 4.8, $J_{HP} = 5.1$ and 2.6), 3.31 (dddd, 1H, $CH_2$, $J_{HH} = 13.9$ and 13.9, $J_{HP} = 17.9$ and 10.6 Hz), 8.1–7.4 (m, 20H, Ph); $^{13}C$-{$^1H$} NMR ($CD_2Cl_2$, 20 °C, 75.46 MHz): $\delta$ 3.1 (d, $SiMe_3$, $J_{CP} = 3.3$), 4.6 (d, $SiMe_3$, $J_{CP} = 3.2$), 38.4 (dd, CH, $J_{CP} = 76.3$ and 6.1, $J_{CH} = 142.0$), 40.5 (d, $CH_2$, $J_{CP} = 75.4$, $J_{CH} = 137.0$), 124.4 (dd, *ipso*-C of Ph, $J_{CP} = 174.1$ and 89.1), 128.9 (d, *m*-C of Ph, $J_{CP} = 12.8$), 129.1 (d, *m*-C of Ph, $J_{CP} = 10.6$), 129.2 (d, *m*-C of Ph, $J_{CP} = 12.1$), 130.2 (dd, *ipso*-C of Ph, $J_{CP} = 82.9$, 1.9), 132.0 (d, *o*-C of Ph, $J_{CP} = 11.3$), 132.4 (d, *p*-C of Ph, $J_{CP} = 3.0$), 132.9 (d, *p*-C of Ph, $J_{CP} = 3.0$), 133.2 (d, *p*-C of Ph, $J_{CP} = 2.3$), 133.6 (dd, *o*-C of Ph, $J_{CP} = 10.2$ and 8.3), 134.2 (dd, *o*-C of Ph, $J_{CP} = 9.8$), 135.1 (dd, *ipso*-C of Ph, $J_{CP} = 80.2$ and 2.2 Hz). $^{31}P$ NMR ($CD_2Cl_2$, 20 °C, 121.49 MHz): $\delta$ 24.8 (d, $J_{PP} = 79.6$), 41.8 (d, $J_{PP} = 79.6$ Hz).

*Crystal data:* compound **1**: $C_{32}H_{41}Cl_3N_2P_2Si_2Ti{\cdot}2CH_2Cl_2$, $M = 895.89$, monoclinic, *Cc*, $a = 22.4593(7)$, $b = 9.4978(3)$, $c = 21.4978(6)$ Å, $\beta = 113.0940(14)°$, $V = 4218.3(2)$ Å$^3$, $Z = 4$, $D_c = 1.411$ g $cm^{-3}$. 8233 independent reflections were collected $\mu$ (Nonius KappaCCD diffractometer, Mo-K$\alpha$, 180 K) = 0.806 $mm^{-1}$, $R_{int} = 0.0608$. Solved by direct methods (SHELXS-97)[12] and refined by full-matrix least squares (SHELXL-97)[13] on $F^2$ of all unique data to $R_1 = 0.0476$ (observed data), $wR = 0.1201$ (all data), $S = 1.041$. CCDC reference number 186/1626. See http://www.rsc.org/suppdata/dt/1999/3329/ for crystallographic files in .cif format.

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