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# Reactivity of an *N*-mesityl bis(phosphinimino)methane with group 10 metals

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## Abstract

In an attempt to form a group 10 'carbenoid' derivative by double deprotonation of the *N*-mesityl substituted bis(phosphinimino)methane  $[CH_2(Ph_2P=N-2,4,6-Me_3C_6H_2)_2]$ , reaction with  $[PdCl_2(MeCN)_2]$  yielded a singly metallated dichloropalladate(II) complex as the only product. This was completely characterised specroscopically and by single crystal crystal X-ray diffraction. In contrast, reaction of  $[CH_2(Ph_2P=N-2,4,6-Me_3C_6H_2)_2]$  with  $[PtMe_2(COD)]$  produced a bis(phosphinimino)methanide complex, which had also undergone *ortho*-metallation of two *P*-phenyl groups to effect a triple C–H activation reaction. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Platinum; Palladium; Phosphiniminomethanide

## 1. Introduction

Great attention has recently been directed toward the coordination chemistry of a variety of N,N-bidentate monoanions such as those illustrated in Chart 1. Although the  $\beta$ -diketiminato ligand structure, I [1] has been especially prominent, a number of topologically related ligand systems have also attracted attention. We, and others, have employed the *N*-mesityl bis(phosphinimino)methanide, II (and its N-SiMe<sub>3</sub> substituted analogue) as a supporting environment for explorations of low-coordinate main group and mid (groups 7–9) transition metal reactivity [2–4].

While the use of I has enabled notable advances in understanding of the discrete molecular steps involved in alkane activation chemistry by Pt(II) and Pt(IV) centres [5], the researches of Cavell and co-workers have realised a fascinating variety of unusual reactivities and structures derived from the platinum-coordinated 'carbenoid' ligand complex, II [6]. Compound II is derived by reaction of [PtCl<sub>2</sub>(COD)] with the dilithio bis(phosphinimino)methanediide,  $[Li_2C-(Ph_2P=NSiMe_3)_2]_2$  IV. As the *N*-mesityl analogue of the unusual dianion IV is not yet available, we report here our attempts to develop alternative routes to similar 'carbenoid' compounds of the heavier group 10 metals, palladium and platinum. Although this has not yet been successful, we have uncovered some notable contrasts in the outcome of reactions of M(II) centres toward the protonated version of II, the bis(phosphinimino)methane,  $[CH_2(Ph_2P=N-2,4,6-Me_3C_6H_2)_2]$ , V resulting in the formation and characterisation of the palladium(II) and platinum(II) organometallics, compounds 1 and 2 (Chart 1).

## 2. Results and discussion

Reaction of V with a single molecular equivalent of  $[PdCl_2(NCMe)_2]$  in  $CH_2Cl_2$  produced an immediate colour change to dark orange at room temperature. Work up and crystallisation from hexane produced dark red crystals of an air stable compound, 1, which was characterised by solution <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopies and (FAB) mass spectrometry. This latter technique revealed a highest mass fragment of 792 consistent with loss of HCl and

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Chart 1.

formation of the singly metallated complex [Pd(II)Cl]. The solution spectroscopic data were not however consistent with this, likely, square planar and symmetrical configuration. The <sup>1</sup>H NMR spectrum revealed two singlet resonances for each of the *ortho*- and *para*-methyls as well as the *meta*-methine centres of two inequivalent *N*-mesityl substituents. The *P*-phenyl region of the spectrum was also considerably more complex than anticipated. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicated an unsymmetrical disposition of the bis(phosphinimino)methanide ligand and appeared as an AX pair of doublet signals centred at 39.9 and 27.6 ppm [<sup>2</sup>J<sub>PP</sub> = 15.4 Hz].

This inference was confirmed by a single crystal X-ray diffraction analysis, which revealed that, although deproto-

nation of the ligand precursor had occurred under these mild conditions, compound **1** also contained the HCl liberated during the deprotonation process and may be best described as a dichloropalladate(II). The molecular structure of **1** is illustrated in Fig. 1. Details of the X-ray analysis are provided in Table 1, while selected bond lengths and angles are provided in Tables 2 and 3, respectively. Coordination around the palladium centre is approximately square planar. Two of the coordination sites about Pd are occupied by the three-membered chelate provided by the methanide carbon (C1) centre and one of the phosphinimino substituents of the  $\kappa$ -C, $\kappa$ -N bis(phosphinimo)methanide ligand. The chlorides occupy the two remaining sites. Despite the restricted bite angle of the three-membered N(1)–P(1)–C(1) chelate [N(1)–Pd–C(1),

Table 1							
Selected	data	collection	parameters	for	compounds	1	and 2

	1	2
Chemical formula	$C_{43}H_{44}Cl_2N_2P_2Pd$	$C_{45}H_{42}D_3N_3P_2Pt(C_2D_3N)$
Formula weight	828.06	931.9
T (K)	173(2)	173(2)
Crystal size (mm <sup>3</sup> )	$0.30 \times 0.25 \times 0.20$	$0.25 \times 0.20 \times 0.10$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	22.0530(3)	10.6441(1)
b (Å)	11.2115(1)	17.3375(2)
<i>c</i> (Å)	16.7783(2)	22.4742(3)
α (°)	90	90
β (°)	106.964(1)	97.576(1)
γ (°)	90	90
Ζ	4	4
$V(\text{\AA}^3)$	3967.88(8)	4111.23(8)
$d_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.38	1.51
$\mu (mm^{-1})$	0.72	3.53
$\theta$ Range (°)	3.72-27.49	3.75-25.70
$R_1$ ; $wR_2 [I \ge 2\sigma(I)]$	0.036, 0.068	0.032, 0.072
$R1$ ; $wR_2$ all data	0.053, 0.073	0.035, 0.073
Measured/independent reflections/ $R_{int}$	49405/9050/0.055	65986/7674/0.053
Reflections with $I > 2\sigma(I)$	7456	7092



Fig. 1. ORTEP drawing (30% ellipsoids) of compound 1. Hydrogen atoms except those attached to C1 and N2 removed for clarity.

Table 2 Selected bond lengths  $(\text{\AA})$  for compounds 1 and 2

	1	2
Pd-N(1)	2.043(2)	
Pt-N(3)		2.003(4)
M-C(1)	2.103(2)	2.051(4)
Pd–Cl(2)	2.3177(6)	
Pd–Cl(1)	2.3257(6)	
Pt-C(15)		2.051(4)
Pt-C(3)		2.074(4)
P(1)-N(1)	1.594(2)	1.643(4)
P(1)-C(1)	1.784(2)	1.789(4)
P(1)-C(2)	1.803(2)	1.771(4)
P(1)-C(8)	1.807(2)	1.805(5)
P(2)-N(2)	1.639(2)	1.572(4)
P(2)-C(1)	1.768(2)	1.804(4)
P(2)-C(14)	1.797(3)	1.801(4)
P(2)-C(20)	1.801(2)	1.829(5)
N(1)-C(26)	1.425(3)	1.437(6)
N(2)-C(35)	1.441(3)	1.407(6)

Table 3 Selected bond angles (°) for compounds 1 and 2

	1	2
N(1)–Pd–C(1)	75.74(8)	
N(3)-Pt-C(1)		178.84(16)
N(3)-Pt-C(15)		93.19(16)
N(1)-Pd-Cl(2)	172.33(6)	
C(1)– $Pd$ – $Cl(2)$	96.62(6)	
N(1)-Pd-Cl(1)	94.91(6)	
C(1)– $Pd$ – $Cl(1)$	169.38(7)	
Cl(2)-Pd-Cl(1)	92.63(2)	
C(1) - Pt - C(15)		85.83(16)
N(3)-Pt-C(3)		92.37(17)
C(1)– $Pt$ – $C(3)$		88.59(17)
C(15)-Pt-C(3)		174.29(17)
N(1)-P(1)-C(1)	97.62(10)	111.5(2)
N(1)-P(1)-C(2)	114.29(10)	110.9(2)
C(1)-P(1)-C(2)	118.32(11)	104.9(2)
N(1)-P(1)-C(8)	117.54(11)	110.6(2)
C(1)–P(1)–C(8)	106.27(11)	107.7(2)
C(2)–P(1)–C(8)	103.27(11)	111.1(2)
N(2)-P(2)-C(1)	107.42(11)	108.1(2)
N(2)-P(2)-C(14)	104.24(11)	121.1(2)
C(1)-P(2)-C(14)	112.19(12)	99.3(2)
N(2)-P(2)-C(20)	110.44(12)	112.9(2)
C(1)-P(2)-C(20)	111.31(11)	109.7(2)
C(14)-P(2)-C(20)	110.95(12)	104.7(2)
C(26)–N(1)–P(1)	136.76(17)	119.9(3)
C(26)-N(1)-Pd	126.16(15)	
P(1)-N(1)-Pd	94.14(9)	
C(35)–N(2)–P(2)	124.22(18)	134.2(3)
P(2)-C(1)-P(1)	125.87(13)	119.4(2)
P(2)-C(1)-M	115.63(12)	109.1(2)
P(1)-C(1)-M	86.78(10)	108.3(2)

75.74(8)°], the remaining angles provided by the *cis*-disposed ligands are close to 90°. The Pd–Cl bond distances [Pd–Cl(1) 2.3257(6), Pd–Cl(2) 2.3177(6) Å] are similar despite the increased coordination number of the Cl(2) centre which displays an additional hydrogen bonded interaction to the N(2) proton of the 'free' P(2)–N(2) arm of the

chelated ligand. Any effect is probably offset by the relative *trans* influences of the C(1) and N(1) donors.

It did not prove possible to enforce any further deprotonation of the C(1) centre within compound 1, to produce palladium carbenoid species analogous to III, either by heating (100 °C) or by addition of an external base (DBU, Et<sub>3</sub>N). Monitoring of these reactions by <sup>31</sup>P{<sup>1</sup>H} NMRin  $d_8$ -toluene indicated either decomposition to complex mixtures of products or no apparent reaction respectively.

Although the directly analogous reaction of V and [PtCl<sub>2</sub>(NCMe)<sub>2</sub>] has not yet yielded identifiable products, reaction of  $[Pt(PPh_2Me)Cl(\mu-Cl)]_2$  and a closely related N-tolyl-substituted bis(phosphinimino)methane has been reported by Elsevier and co-workers to produce the similarly N,C-coordinated complex [PtCl(PPh<sub>2</sub>Me){CH- $(Ph_2PNC_6H_4-4-Me)(Ph_2P=N(H)C_6H_4-4-Me)\}^+Cl$ [7]. This cation was also formed irrespective of added base and, for this reason, we attempted the alternative methane-elimination route to the platinum carbenoid species illustrated in Scheme 1. Extended heating and NMR (<sup>1</sup>H,  ${}^{31}P{}^{1}H{}$  monitoring of an NMR-scale reaction of [PtMe<sub>2</sub>-(COD)] and V in  $C_6D_6$  indicated that no reaction had occurred. In contrast, a similar reaction performed in  $d_3$ -MeCN resulted in the complete disappearance of Pt-Me resonance at 0.63 ppm in the <sup>1</sup>H NMR spectrum after 18 h at 100 °C. These conditions also resulted in the loss of the characteristic methylene triplet of V centred at 4.01 ppm and the appearance of a series of resonances consistent with the formation of unligated COD. Attempted <sup>31</sup>P NMR monitoring of this reaction at regular intervals over a 7 day period was not informative and revealed only the resonances due to the starting material and several unidentifiable resonances, which, once apparent, did not alter in relative intensity. Upon slow cooling, however, colourless crystals of compound 2 deposited within the NMR tube, and we assume that plausible intermediates (vide infra) are either short-lived or present in too low concentration as to be observable, while the ultimate product, compound 2, deposits and is depleted from solution as the reaction proceeds and is thus not observed. The crystalline material would not redissolve in  $d_3$ -MeCN, but proved to be highly soluble in CDCl<sub>3</sub> enabling the full spectroscopic characterisation of compound 2. Although the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consisted of a single resonance at 46.0 ppm, indicative of symmetrical coordination of the deprotonated ligand, it was apparent that the desired



synthesis of a carbenoid species had again been unsuccessful. Compound **2** did not contain coordinated COD and it was clear that the PCH<sub>2</sub>P methylene of **V** had not been doubly deprotonated as evidenced by a triplet resonance (1H by integration) at 3.26 ppm ( ${}^{2}J_{PP} = 9.2$  Hz) in the  ${}^{1}$ H NMR spectrum. Attempts to acquire  ${}^{195}$ Pt NMR data were unsuccessful, most likely due to the anisotropic magnetic environment of the metal centre.

The origin of these solution data was made clear by a single crystal X-ray analysis performed on crystals of compound 2. The results of this study, illustrated in Fig. 2, were consistent with the solution data and revealed that V had undergone a triple C–H activation reaction. Details of



Fig. 2. ORTEP drawing (30% ellipsoids) of compound **2**. Hydrogen atoms except those attached to C1 and N1 removed for clarity.

the X-ray analysis are provided in Table 1, while selected bond lengths and angles are provided in Tables 2 and 3 respectively. Three coordination sites about the square planar platinum centre are provided by the deprotonated C(1)methanide carbon and two bonds to  $sp^2$  carbon atoms which have been formed by ortho-metallation of two of the P-bound phenyl rings. A coordinated molecule of acetonitrile, trans to the methanide carbon centre, occupies the remaining coordination site. Charge balance is maintained by protonation of one of the non-coordinated phosphinimine (N1) nitrogen atoms. The resulting chemical inequivalence of the phosphorus nuclei was not, however, apparent in the NMR spectra most likely due to rapid exchange of the proton between the two phosphinimino nitrogen centres and the development of apparent  $C_2$  symmetry. Although the bond lengths and angles within the structure itself are entirely normal and consistent with previously reported Pt(II) alkyl and aryl derivatives [8], and such intramolecular aromatic substitution by late transition metal complexes has been known to occur for over 40 years [9], a transformation of a neutral bis(phosphinimino)methane into a formally trianionic chelate is unique. It is interesting to note that Cavell has reported that III underwent thermally initiated *ortho*-metallation of a single P-phenyl with concomitant protononation of the carbenoid C=Pt bond [6a]. This latter process occurred diastereoselectively to generate P and C stereocentres with fixed relative absolute configurations and it was speculated that metallation involved the intermediacy of an undetectable platinum(IV) hydride intermediate. The formation of compound 2 occurred with similar diastereoselectivity and, although we have not yet definitively identified any intermediates and a number of viable alternative pathways may be envisaged, it is plausible that 2 results from a similar mechanism (Scheme 2) and the intermediacy of a carbenoid species similar to that depicted in Scheme 1.



Scheme 2. Proposed 'carbenoid' pathway to compound 2.

We are continuing to investigate this hypothesis and will report the outcome of these studies in a future publication.

## 3. Experimental section

All manipulations were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of either nitrogen or argon. All solvents were distilled under nitrogen and dried with conventional drying agents. NMR spectra were recorded at 270 or 500 (<sup>1</sup>H), 125.8 (<sup>13</sup>C) and 202.5 (<sup>31</sup>P) MHz from samples in either C<sub>6</sub>D<sub>6</sub> or  $d_8$ -toluene or CDCl<sub>3</sub>; chemical shifts are given relative to SiMe<sub>4</sub>. Mass spectra were recorded under fast atom bombardment (FAB) on samples in a matrix of nitrobenzyl alcohol. In spectral assignments Mes = 2,4,6-trimethylphenyl. The ligand precursor V was synthesised by a literature procedure [4g].

#### 3.1. Preparation of compound 1

A solution of V (0.25 g, 3.8 mmol), in  $CH_2Cl_2$  (10 cm<sup>3</sup>) was added at room temperature to a  $CH_2Cl_2$  (10 cm<sup>3</sup>) solution of [PdCl<sub>2</sub>(NCMe)<sub>2</sub>] (0.1 g, 3.8 mmol), resulting in an immediate colour change from yellow to orange/red. This solution was stirred for 14 h before complete removal of volatiles. The red solid was crystallised from hexane at room temperature to yield 1 as dark red crystals (0.25 g, 79%). Anal. Calc. for C43H44Cl2N2P2Pd: C, 62.38; H, 5.31; N, 3.38. Found: C, 62.55; H, 5.50; N, 3.23%. <sup>1</sup>H NMR (CDCl<sub>3</sub>); δ 1.39 (s, 3H, *p-Me*, mesN), 1.54 (s, 3H, p-Me, mesN=P), 1.96 (s, 6H, o-Me, mesN), 1.99 (s, 6H, *p-Me*, mesN=P), 2.78 (dd, 1H,  ${}^{2}J_{PH} = 14.8$ , 1.6 Hz, PCHP), 5.25 (s, 1H, NH), 6.39 (s, 2H, *m*-CH, mesN), 6.39 (s, 2H, m-CH, mesN=P), 6.80-8.20 (m, 20H, Ph-P). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -15.5 (dd, <sup>1</sup>J<sub>PP</sub> = 79.2, 75.5 Hz, PCP), 20.4 (o-Me), 20.7 (o-Me), 20.8 (p-Me), 122.1 (d,  ${}^{1}J_{PP} = 93.1 \text{ Hz}, i-CP$ , 125.2 (Ar), 125.4 (d,  ${}^{1}J_{PP} =$ 106.9 Hz, *i*-CP), 127.9 (d,  $J_{PP} = 12.5$  Hz, PhP), 128.1 (Ar), 128.4 (d,  $J_{PP} = 11.3$  Hz, PhP), 128.4, 128,7, 128.8 (Ar), 129.5 (d,  $J_{PP} = 11.3$  Hz, PhP), 131.8 (d,  $J_{PP} =$ 23.9 Hz, PhP), 131.8 (Ar), 132.6 (Ar), 132.9 (d,  $J_{\rm PP} = 12.0$  Hz, PhP), 133.4 (d,  $J_{\rm PP} = 16.3$  Hz), 133.8 (Ar), 134.4 (d,  $J_{PP} = 11.0$  Hz, PhP), 135.9 (Ar), 136.3, 136.4 (Ar), 136.7 (d,  $J_{PP} = 8.9$  Hz, PhP), 137.8 (Ar). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  27.6 (d,  ${}^{2}J_{PP} = 15.4$  Hz), 39.9 (d,  $^{2}J_{\text{PP}} = 15.4 \text{ Hz}$ ). MS (FAB: m/z): 792 [2, M<sup>+</sup>-HCl], 756 [5, M<sup>+</sup>-HCl-Cl], 651 [5], 440 [100], 330 [40], 183 [35], 147 [55].

## 4. Preparation of compound 2

A mixture and [PtMe<sub>2</sub>(COD)] (0.035 g, 0.11 mmol) and V (0.070 g, 0.11 mmol) were dissolved in  $d_3$ -MeCN and transferred to an NMR tube equipped with a Youngs tap. Initial NMR analysis of the pale yellow solution indicated that no reaction had occurred. The NMR tube was then heated to 100 °C for 18 hours, after which time the

Pt-Me signal (0.62 ppm) in the <sup>1</sup>H spectrum and the  $^{31}P$ NMR (-17 ppm) signal for V had completely disappeared. Upon standing at room temperature overnight colourless crystals of compound 2 deposited and were isolated by filtration (0.07 g, 70%). A sample for analysis was prepared by grinding and exposure to a dynamic vacuum. Anal. Calc. for C<sub>43</sub>H<sub>43</sub>D<sub>3</sub>N<sub>3</sub>P<sub>2</sub>Pt: C 60.86, H 4.78, N 4.73. Found: C 60.65, H 4.65, N 4.80. <sup>1</sup>H NMR (CDCl<sub>3</sub>);  $\delta$ 2.11 (s, 6H, p-Me), 2.14 (s, 12H, o-Me), 3.26 (t, 1H,  ${}^{2}J_{HP} = 9.2 \text{ Hz}, {}^{2}J_{HPt} = 54 \text{ Hz}, \text{ PCHP}), 6.60 (s, 4H, m-$ CH,mes), 6.82 (4, 6H, o-CH,PhP), 7.16-7.51 (m, 18H, *Ph*–P). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  19.9 (*p*-Me), 20.9 (*o*-Me), 30.9 (CHP) 122.3 (Ar), 127.9 (Ar), 128.4 (Ar), 130.8 (Ar), 131.8 (Ar), 136.5.  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  46.0. MS (FAB: m/z): 888 [30, M<sup>+</sup>], 844 [10, M<sup>+</sup>- $d_3$ -MeCN], 650 [5], 277 [100], 57 [70].

## 5. Crystal structure determinations

Data for 1 and 2 were collected at 173 K on a Nonius KappaCCD diffractomer,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å. An absorption correction (MULTISCAN) was applied. The structures were solved by direct methods (SHELXS-97) [10] and refined by full matrix least squares (SHELXL-97) [11] with non-H atoms anisotropic and H atoms included in riding mode except for the H atoms on C1 and N1 of compound 1, and C1 and N1 of compound 2 which were refined.

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### Appendix A. Supplementary material

CCDC 285813 and 285814 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts.retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2006.10.020.

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