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Orthometalation of Functionalized Phosphinoamines with Late Transition Metal Complexes

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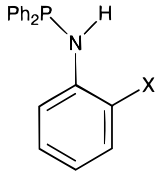
Summary: The neutral metal complexes cis-$[Pt(CH_3)_2\{o\text{-}Ph_2PN(H)C_6H_4C(O)CH_3\text{-}P\}_2]$ *and* $[RhCl_2(Cp^*)\{o\text{-}Ph_2PN(H)C_6H_4C(O)Ph\text{-}P\}]$ *are excellent precursors for new five-membered M−P−N−C−C metallacycles via* $\sigma(C_{sp^2}-H)$ *bond activation. The synthesis and characterization including the molecular structures of cis-*$[Pt\{o\text{-}Ph_2PN(H)C_6H_3C(O)CH_3\text{-}P,C\}_2]\cdot OEt_2$ *and* $[RhCl(Cp^*)\{o\text{-}Ph_2PN(H)C_6H_3C(O)Ph\text{-}P,C\}]\cdot 0.5CHCl_3$ *are reported.*

Orthometalation reactions constitute an important class of reaction that have been widely employed in the synthesis of numerous organometallic compounds.[1] Whereas the predominance of these cyclometalated compounds are mononuclear, several recent examples of bi- and tetranuclear complexes have been described.[2] In large, such interest derives from the use of these compounds in disparate areas including catalysis,[3] organic synthesis,[4] in material science,[5] and resolution procedures[6] and as antitumor agents.[7]

The chemical literature contains a plethora of reports describing orthometalated triarylphosphine or phosphite complexes.[1a,3,6,8] Furthermore the first example of a cyclometalated compound with a water-soluble triarylphosphine, TPPTS [tris(3-sodium sulfonatophenyl)phosphine], was recently described by Pruchnik and coworkers.[9] Although cleavage of aromatic C−H bonds in tertiary phosphines and phosphites is well-known, to the best of our knowledge, examples with phosphinoamines bearing one (or more) combinations of P−N/P−C bonds have not been investigated. This is rather surprising given the recent interest displayed in this unique class of ligand.[10] Here we describe the synthesis of two new functionalized phosphinoamine ligands and report our preliminary orthometalation studies of these coordinated ligands at platinum(II) and rhodium(III) metal centers.

The new ligands $o\text{-}Ph_2PN(H)C_6H_4X$ [X = C(O)CH$_3$, **1**; X = C(O)Ph, **2**], closely related to $Ph_2PN(H)C_6H_5$,[11] were successfully synthesized from cheap, commercially available Ph_2PCl and $o\text{-}H_2NC_6H_4X$ in respectable yields (ca. 70%). Moreover this general procedure has allowed us to routinely prepare these ligands in batches up to ca. 10 g. Both **1** and **2** were characterized by the usual spectroscopic and analytical techniques.[12] The $^{31}P\{^1H\}$ NMR spectra (36.2 MHz) of **1** (and **2**) show single P resonances at δ(P) 25.6 (for **1**) and 26.5 ppm (for **2**), which is typical for this class of ligand.[10c] Furthermore we formulate **1** and **2** as monosubstituted compounds since in the ^1H NMR spectra a small $^2J(PH)$ coupling of ca. 7.5 Hz was observed. Oxidation of **1** with 30% aqueous hydrogen peroxide gave the phosphorus(V) compound $o\text{-}Ph_2P(O)N(H)C_6H_4C(O)CH_3$, **3**, whose molecular structure has been determined (Figure 1). The X-ray crystal structure[13] is broadly as anticipated, with a P(1)−O(1) bond length of 1.472(2) (molecule 1) and 1.470(2) Å (molecule 2), shorter than that observed in $Ph_2PN(H)P(O)Ph_2$ [1.508(2) Å], which exists in the solid state as a hydrogen-bonded dimer pair.[10c] Furthermore there is also a strong intramolecular N−H···O hydrogen bond [N(1)···O(19) 2.62 Å, H(1)···O(19) 1.78 Å; N(1)−H(1)···O(19) 143° (molecule 1); N(21)···O(21) 2.64 Å, H(21)···O(21) 1.82 Å; N(21)−H(21)···O(21) 141° (molecule 2)].



X = C(O)CH$_3$ **1**
X = C(O)Ph **2**

Ligand displacement of cod (cod = cycloocta-1,5-diene) from $[Pt(CH_3)_2(cod)]$ with 2 equiv of **1** in dichloromethane gave *cis*-$[Pt(CH_3)_2(\mathbf{1})_2]$, **4** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **4** showed a single resonance

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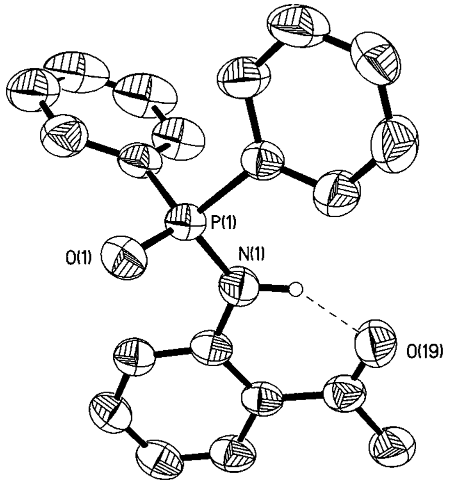
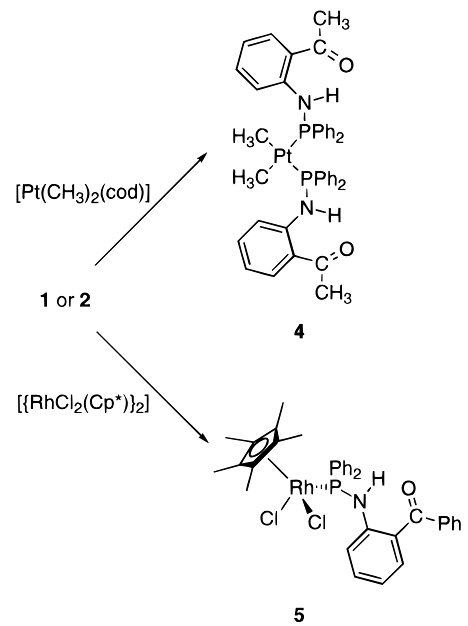
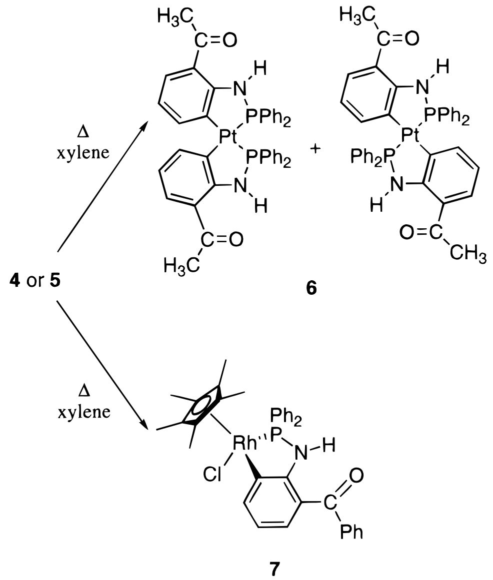


Figure 1. Molecular structure of **3**, shown with 50% thermal ellipsoids. Only one of the two independent molecules is depicted. All C−H hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) (equivalent values for the second molecule are given in square brackets): P(1)−O(1) 1.472(2) [1.470(2)], P(1)−N(1) 1.654(2) [1.660(2)], C(19)−O(19) 1.226(3) [1.228(2)]; O(1)−P(1)−N(1) 115.84(8) [117.04(9)].

Scheme 1



Scheme 2



at δ(P) 51.3 ppm flanked by ^{195}Pt satellites [^1J(PtP) 2028 Hz]. Bridge cleavage of the dimer [{RhCl$_2$(Cp*)}$_2$] with 2 equiv of **2** in dichloromethane gave the mononuclear compound [RhCl$_2$(Cp*)**2**], **5**, in good yield. The ^{31}P{^{1}H} NMR spectrum of **5** showed a doublet centered at δ(P) 55.5 ppm with a ^1J(RhP) of 154 Hz.[12]

Thermal activation of a C−H bond is a common procedure for synthesizing orthometalated complexes. Accordingly when **4** (or **5**) was refluxed in xylene for between 24−48 h under a nitrogen atmosphere (Scheme 2), the orthometalated compounds [Pt{*o*-Ph$_2$PN(H)-C$_6$H$_3$C(O)CH$_3$-*P*,*C*}$_2$], **6**, and [RhCl(Cp*){*o*-Ph$_2$PN(H)-C$_6$H$_3$C(O)Ph-*P*,*C*}], **7**, were obtained in reasonable yields (64% for **6**, 53% for **7**).[14] When the thermolysis of **5** was performed in the presence of excess NEt$_3$, several phosphorus-containing species, in addition to **7**, were identified. The ^{31}P{^{1}H} NMR spectra of **6** (and **7**) were

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(12) Selected spectroscopic data for compounds **1**−**7**. For **1**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 25.6. ^{1}H δ 9.71 (NH) [^2J(PH) 7.5 Hz], 7.76−6.68 (aromatic H), 2.57 (CH$_3$). IR (KBr): ν(NH) 3212, 3198, 3190 and ν(CO) 1633 cm^{-1}. FAB MS: *m*/*z* 319 (M$^+$). (Found: C, 74.57; H, 5.91; N, 4.32. C$_{20}$H$_{18}$NOP·0.25H$_2$O requires C, 74.17; H, 5.76; N, 4.32). For **2**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 26.5. ^{1}H δ 9.23 (NH) [^2J(PH) 7.8 Hz], 7.66−6.67 (aromatic H). IR (KBr): ν(NH) 3314, 3237 and ν(CO) 1619, 1612 cm^{-1}. FAB MS: *m*/*z* 381 (M$^+$). (Found: C, 77.26; H, 5.24; N, 3.21. C$_{25}$H$_{20}$NOP·0.25H$_2$O requires C, 77.80; H, 5.31; N, 3.63). For **3**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 18.5. ^{1}H δ 10.70 (NH) [^2J(PH) 8.3 Hz], 7.94−6.90 (aromatic H), 2.66 (CH$_3$). IR (KBr): ν(NH) 3097, 3072, ν(CO) 1640 and ν(PO) 1208 cm^{-1}. (Found: C, 71.44; H, 5.39; N, 4.07. C$_{20}$H$_{18}$NO$_2$P requires C, 71.63; H, 5.42; N, 4.18). For **4**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 51.3 [^1J(PtP) 2028 Hz]. ^{195}Pt{^{1}H}: δ −4502. ^{1}H δ 10.01 (NH) [^3J(PtH) 21.5 Hz], 7.95−6.71 (aromatic H), 2.56 (CH$_3$), 0.54 (Pt−CH$_3$), [^2J(PtH) 69.2, ^3J(PH) 6.5 Hz]. IR (KBr): ν(NH) 3163, 3129 and ν(CO) 1643 cm^{-1}. (Found: C, 57.95; H, 4.57; N, 3.21. C$_{42}$H$_{42}$N$_2$O$_2$P$_2$Pt requires C, 58.39; H, 4.91; N, 3.24%). For **5**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 55.5 [^1J(RhP) 154 Hz]. ^{1}H δ 9.75 (NH) [^2J(PH) 11.5 Hz], 8.14−7.03 (aromatic H), 1.42 (C$_5$(CH$_3$)$_5$) [^4J(PH) 3.8 Hz]. IR (KBr): ν(NH) 3175 and ν(CO) 1628 cm^{-1}. (Found: C, 59.48; H, 5.18; N, 1.69. C$_{35}$H$_{35}$NOPRhCl$_2$·0.25CH$_2$Cl$_2$ requires C, 59.48; H, 4.99; N, 1.97). For **6**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 88.9 [^1J(PtP) 2191 Hz], 88.0 [^1J(PtP) 3238 Hz]. ^{195}Pt{^{1}H}: δ −4510, −4636. ^{1}H δ 10.5 [^3J(PtH) 57.6 Hz], 10.1 [^3J(PtH) 40.3 Hz] (NH), 7.86−6.28 (aromatic H), 2.53, 2.49 (CH$_3$). IR (KBr) ν(NH) 3191 and ν(CO) 1634 cm^{-1}. FAB MS: *m*/*z* 832 (M$^+$) (Found: C, 57.38; H, 4.39; N, 3.21. C$_{40}$H$_{34}$N$_2$O$_2$P$_2$Pt requires C, 57.76; H, 4.13; N, 3.37). For **7**: NMR (CDCl$_3$) ^{31}P{^{1}H}: δ 105.4 [^1J(RhP) 172 Hz]. ^{1}H δ 9.75 (NH), 7.75−6.55 (aromatic H), 1.48 (C$_5$(CH$_3$)$_5$) [^4J(PH) 3.4 Hz]. IR (KBr): ν(NH) 3231 and ν(CO) 1608 cm^{-1}. FAB MS: *m*/*z* 655 (M$^+$) (Found: C, 61.18; H, 5.01; N, 1.79. C$_{35}$H$_{34}$NOClPRh·0.5CH$_2$Cl$_2$ requires C, 61.21; H, 5.08; N, 2.01). All ^{1}H NMR spectra were recorded at 250 MHz and referenced to external TMS, whereas ^{31}P{^{1}H} NMR spectra were recorded at 36.2 MHz and referenced to external phosphoric acid.

(13) Structural data were collected using a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation. Crystal data for **3**: C$_{20}$H$_{18}$NO$_2$P, 335.32, monoclinic, space group $P2_1/c$, a = 12.343(1) Å, b = 11.2683(1) Å, c = 25.1886(2) Å, β = 103.54(1)°, V = 3406.07(4) Å^3, Z = 8, D_c = 1.308 g/cm^3, μ = 0.173 mm^{-1}, R (R_w) 0.045 (0.096) for 4873 observed reflections. **6**: C$_{40}$H$_{34}$N$_2$OP$_2$Pt·OEt$_2$ 905.84, monoclinic, space group $C2/c$, a = 25.1102(4) Å, b = 10.2756(1) Å, c = 15.8647(2) Å, β = 99.298(1)°, V = 4039.66(9) Å^3, Z = 4, D_c = 1.489 g/cm^3, μ = 3.593 mm^{-1}, R (R_w) 0.045 (0.109) for 4635 observed reflections. **7**: C$_{35}$H$_{34}$ClNOPRh·0.5CHCl$_3$, 713.65, monoclinic, space group $P2_1/a$, a = 14.1667(6) Å, b = 31.3669(14) Å, c = 15.2768(7) Å, β = 106.843(1)°, V = 6497.3(5) Å^3, Z = 8, D_c = 1.459 g/cm^3, μ = 0.810 mm^{-1}, R (R_w) 0.047 (0.087) for 9291 observed reflections.

(14) A typical procedure is illustrated here for the synthesis of compound **6**. Under a nitrogen atmosphere, a suspension of **4** (80 mg, 0.093 mmol) in xylene (20 mL) was heated to reflux for ca. 48 h. The solvent was reduced in vacuo, the solid residue extracted with CH$_2$Cl$_2$ (5 mL), and this extract filtered through Celite. The solvent volume was reduced and diethyl ether (20 mL) added to afford **6**, with a further crop isolated from the filtrate (49 mg, 64%).

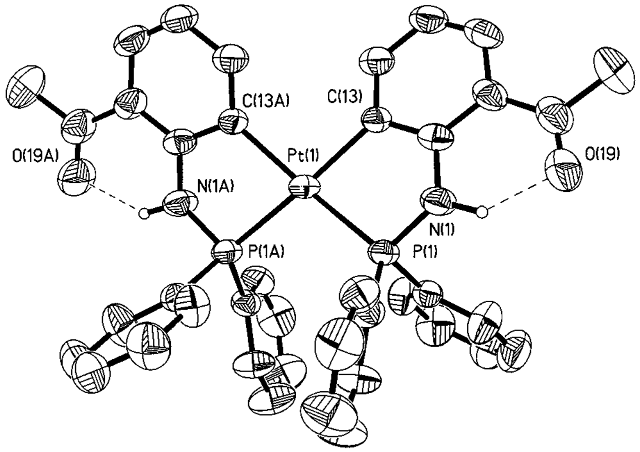

Figure 2. Molecular structure of **6**, shown with 50% thermal ellipsoids. All C−H hydrogen atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt(1)−C(13) 2.090(5), Pt(1)−P(1) 2.2726(12), P(1)−N(1) 1.692(5), C(19)−O(19) 1.221(8); C(13)−Pt(1)−C(13*) 95.9(2), C(13)−Pt(1)−P(1*) 170.63(13), C(13)−Pt(1)−P(1) 80.59(13), P(1)−Pt(1)−P(1*) 104.20(6), Pt(1)−P(1)−N(1) 101.9(2).

particularly informative, with large (ca. 40−50 ppm) downfield shifts in δ(P) consistent with the coordinated P^{III} center being part of a five-membered M−P−N−C−C metallacycle.[12] In the case of platinacycle **6** two closely spaced singlets at δ(P) 88.9 [^{1}J(PtP) 2191 Hz] and 88.0 ppm [^{1}J(PtP) 3238 Hz], in an approximate ratio of ca. 1:1 ($CDCl_3$ solution), are assigned to a mixture of cis and trans isomers, respectively. This is further corroborated by the observation of two well-separated NH resonances, centered at ca. 10 ppm and with ^{195}Pt satellites, in the ^{1}H NMR spectrum of **6**. In the IR spectrum of **6** the similarity of $\nu_{C=O}$ with that of **1** supports the absence of any carbonyl interaction with the platinum center. Monitoring the thermolysis of **4** by ^{31}P{^{1}H} NMR revealed the formation of an intermediate species, tentatively assigned as [Pt(CH_3){*o*-$Ph_2PN(H)C_6H_3C(O)CH_3$-*P,C*}(**1**)] [δ(P) 52.2, ^{1}J(PtP) 2287 Hz (**1** trans to orthometalated σ bonded C); 86.4 ppm, ^{1}J(PtP) 2067 Hz].[15] No attempts to separate the isomers of **6** nor test for methane formation were pursued.

The X-ray structures of **6** and **7** are depicted in Figures 2 and 3, respectively.[13] Suitable crystals of **6** were grown from slow diffusion of Et_2O into a $CDCl_3$/CH_2Cl_2 solution (cis:trans ratio of ca. 5:1, established first by ^{31}P{^{1}H} NMR). In **6** the molecule is disposed about a crystallographic 2-fold axis on which the platinum lies. The platinum(II) center is approximately square-planar [C(13)−Pt(1)−C(13*) 95.9(2), C(13)−Pt(1)−P(1*) 170.63(13), C(13)−Pt(1)−P(1) 80.59(13), P(1)−Pt(1)−P(1*) 104.20(6)°] with two chelating orthometalated [*o*-$Ph_2PN(H)C_6H_3C(O)CH_3$-*P,C*]$^{-}$ ligands arranged in a cis geometry. Furthermore the unique $PtPNC_2$ five-membered ring is slightly puckered [Pt(1)−P(1)−N(1)−C(14)−C(13) mean plane, with maximum deviation of N(1) 0.18 Å out of this plane]. The Pt(1)−C(13) distance [2.090(5) Å] is longer than that in [Pt(dppe)Ph_2] [dppe = 1,2-(diphenylphosphino)ethane] [2.05(1) Å][16] presumably as a consequence of the different π-acceptor properties of the two phosphorus-containing ligands. The structure of **7** reveals a classic three-legged piano stool geometry with the rhodium(III) center coordinated by

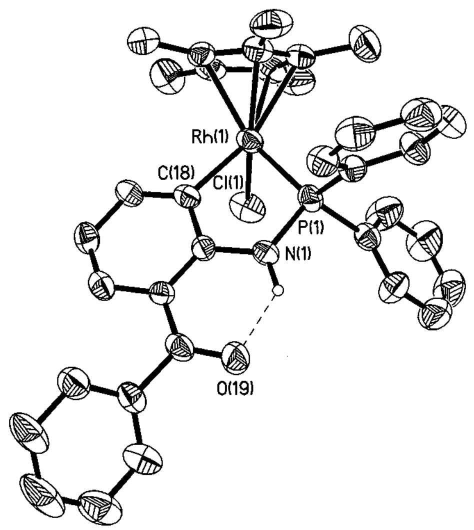

Figure 3. Molecular structure of **7**, shown with 50% thermal ellipsoids. Only one of the two independent molecules is depicted. All C−H hydrogen atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg) (equivalent values for the second molecule are given in square brackets): Rh(1)−P(1) 2.244(2) [2.240(2)], Rh(1)−Cl(1) 2.394(2) [2.385(2)], Rh(1)−C(18) 2.063(6), [2.055(6)], P(1)−N(1) 1.680(5) [1.684(5)], C(19)−O(19) 1.244(7) [1.239(7)]; P(1)−Rh(1)−Cl(1) 92.76(7) [91.46(6)], P(1)−Rh(1)−C(18) 81.2(2) [80.9(2)], Cl(1)−Rh(1)−C(18) 82.9(2) [84.3(2)], Rh(1)−P(1)−N(1) 104.9(2) [104.6(2)].

a η^5 Cp*, one chloride, and an η^2 [*o*-$Ph_2PN(H)C_6H_3C(O)Ph$-*P,C*]$^{-}$ orthometalated ligand. The Rh−P distance [2.244(2) (molecule 1); 2.240(2) Å (molecule 2)] is broadly as expected. The carbonyl moieties in compounds **6** and **7** are both involved in strong intramolecular hydrogen bonding to the N−H proton [for **6**, N(1)···O(19) 2.60 Å, H(1)···O(19) 1.80 Å; N(1)−H(1)···O(19) 138°; for **7**, N(1)···O(19) 2.63 Å, H(1)···O(19) 1.85 Å; N(1)−H(1)···O(19) 135° (molecule 1) and N(41)···O(59) 2.66 Å, H(41)···O(59) 1.91 Å; N(41)−H(41)···O(59) 131° (molecule 2)]. The structures of **6** and **7** represent extremely rare examples of crystallographically characterized compounds containing a M−P−N−C−C chelate ring.[17]

The utility of phosphinoamine ligands, $R_2PN(H)R$ (R = aryl substituent), has allowed for the first time new examples of cyclometalated M−P−N−C−C compounds to be prepared. This genre of complex could prove beneficial in a number of applications and is currently an area under further investigation in our laboratory.

Acknowledgment. We should like to thank the EPSRC for a studentship (K.G.G.), Infineum UK Ltd for financial support, and Johnson Matthey plc for loans of precious metals. Fast atom bombardment (FAB) mass spectra were run by the EPSRC mass spectrometry service at Swansea.

Supporting Information Available: Tables of complete crystallographic data for **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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