A total loss of innocence: double *ortho*-metallation of bis(triphenylphosphano)iminium cation, $[N(PPh_3)_2]^+$, by tris(η-naphthalene)tantalate(1−)†‡

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For the first time $[N(PPh_3)_2]^+$, or $[PPN]^+$, has been shown to undergo an irreversible reaction with a transition metal complex under ambient conditions and affords a product containing a unique structural motif in which two phenyl groups on *one* PPh_3 substituent of $[PPN]^+$ are *ortho*-metallated, while the third phenyl ring is hydrogenated to provide a tantalum bound 1,3-cyclohexadiene group.

Bis(triphenylphosphano)iminium, or PPN cation ($[N(PPh_3)_2]^+$), has been employed for over 40 years as an extremely useful, weakly perturbing, and generally unreactive counterion for the isolation and crystallization of numerous salts of inorganic and organometallic anions.[1–3] Although $[PPN]^+$ reacts with hydroxide/methoxide,[4] undergoes reversible charge-transfer interactions with several carbonylmetallates,[5] and decomposes as the $[PPN][Rh(CO)_4]$ salt at 200 °C under CO pressure in acetone–water,[6,7] no irreversible reactions with transition metal compounds, under ambient conditions, have been previously noted, even with anions that are good reducing agents, such as $[Ta(CO)_6]^{-}$[8] or $[Ta(\eta\text{-}C_4H_6)_3]^{-}$.[9] We now report on a remarkable reaction of $[PPN]^+$ at 20 °C with the highly reactive and strongly reducing metallate ion, $[Ta(\eta\text{-}C_{10}H_8)_3]^{-}$, **1** ($C_{10}H_8$ = naphthalene).[10]

Addition of a solution/slurry of bright yellow $[Na(thf)_2]$[**1**], thf = tetrahydrofuran, to one equivalent of [PPN]Cl in thf showed no observable change at 0 °C, perhaps owing to the poor solubility of [PPN]Cl. However, on warming to 20 °C over a period of about 26 h, the reaction mixture had turned a deep green color. From this reaction, olive-green microcrystals of **2** were isolated in good yield (75% based on **1**).¶ The ^1H NMR spectrum of **2** exhibited a large number of overlapping resonances such that definitive assignments were difficult; however, its $^{31}P\{^1H\}$ NMR spectrum showed only two resonances of equal intensity, one of which had a chemical shift only slightly upfield of that observed for [PPN]Cl.[4] Single-crystal X-ray crystallography was necessary to reveal the structural complexity of **2**.‖ In this reaction, $[PPN]^+$ has coordinated to the tantalate, resulting in the loss of two naphthalene ligands, and formation of a neutral 16-electron product of composition $Ta(C_{10}H_8)(PPN)$. Fig. 1 depicts the molecular structure of **2**, in which two phenyl rings on one PPh_3 group of $[PPN]^+$ have undergone *ortho*-metallation. This process was accompanied by formal transfer of two hydrogen atoms to the third phenyl ring, changing it into an otherwise normal η^4-1,3-cyclohexadiene ligand. *In toto*, the reaction appears to be without precedent.[11] Other structural features of **2** are unexceptional, including the average Ta–C(phenyl) distance, 2.28(1) Å, a value similar to that observed in $[Ta(C_6H_5)_6]^-$, 2.25(2) Å,[12] the $Ta(\eta^4\text{-}C_{10}H_8)$ unit, which is nearly identical to those present in **1**,[10] the uncoordinated $NPPh_3$ group and the P–N–P angle, both of which have metrical parameters well within the range of those observed for $[PPN]^+$ salts.[4,13] A schematic of the unusual coordination environment about tantalum for **2** is shown in Fig. 2.

One equivalent of trimethyl phosphite readily combined with green **2** to afford dark orange **3**, which was isolated in 69% yield. As in the case of **2**, the ^1H NMR spectrum of **3** was complex; however, its $^{31}P\{^1H\}$ NMR spectrum showed three equally intense resonances, two of which were in positions similar to those of **2**, and the other corresponded to coordinated $P(OMe)_3$.[4] A single-crystal X-ray structure confirmed that its composition corresponded to an 18-electron complex,

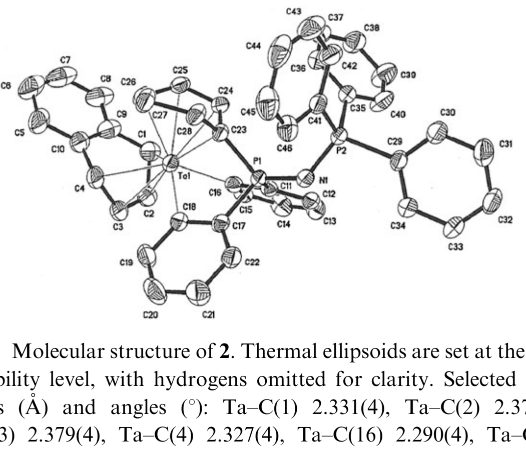

Fig. 1 Molecular structure of **2**. Thermal ellipsoids are set at the 50% probability level, with hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Ta–C(1) 2.331(4), Ta–C(2) 2.376(4), Ta–C(3) 2.379(4), Ta–C(4) 2.327(4), Ta–C(16) 2.290(4), Ta–C(18) 2.275(4), Ta–C(23) 2.288(4), Ta–C(24) 2.347(4), Ta–C(25) 2.405(4), Ta–C(26) 2.336(4), N(1)–P(1) 1.609(3), N(1)–P(2) 1.578(3), C(1)–C(2) 1.460(6), C(2)–C(3) 1.388(6), C(3)–C(4) 1.443(6), C(23)–C(24) 1.450(5), C(24)–C(25) 1.395(5), C(25)–C(26) 1.414(6), C(26)–C(27) 1.520(6), C(27)–C(28) 1.537(5), C(28)–C(23) 1.533(5) P(1)–N(1)–P(2) 131.4(2).

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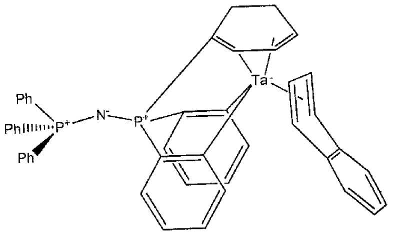

Fig. 2 Line drawing of **2** showing the coordination environment about tantalum.

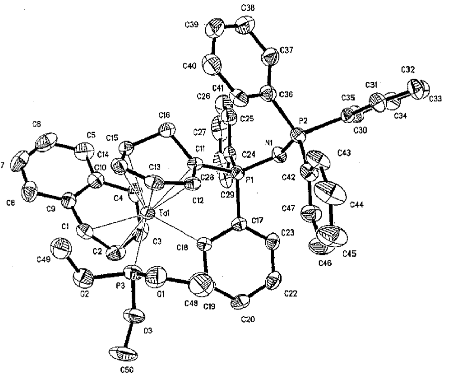

Fig. 3 Molecular structure of **3**. Thermal ellipsoids are set at the 50% probability level, with hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Ta–C(1) 2.348(3), Ta–C(2) 2.310(3), Ta–C(3) 2.370(3), Ta–C(4) 2.433(3), Ta–C(18) 2.292(3), Ta–C(11) 2.309(3), Ta–C(12) 2.334(3), Ta–C(13) 2.433(3), Ta–C(14) 2.375(3), Ta–C(15) 2.322(3), Ta–P(3) 2.5641(8), N(1)–P(1) 1.618(3), N(1)–P(2) 1.575(3), C(1)–C(2) 1.468(5), C(2)–C(3) 1.381(5), C(3)–C(4) 1.417(5), C(11)–C(12) 1.455(4), C(12)–C(13) 1.405(4), C(13)–C(14) 1.409(5), C(14)–C(15) 1.415(4), C(15)–C(16) 1.521(4), C(11)–C(16) 1.523(4), P(1)–N(1)–P(2) 134.7(2).

$Ta(C_{10}H_8)(PPN)(P(OMe)_3)$; however, the coordinated PPN unit had undergone yet another unexpected transformation.|| Fig. 3 shows the molecular structure of **3** and reveals that the conversion of **2** to **3** resulted in the hydrogenation of one of the *ortho*-phenylene units to afford a normal phenyl group, bound only to phosphorus, and dehydrogenation of the η^4-cyclohexadiene to provide an unexceptional η^5-cyclohexadienyl ligand.[14] Also present are largely unmodified $Ta(\eta^4\text{-}C_{10}H_8)$, *ortho*-phenylene and uncoordinated $NPPh_3$ groups, along with a normal $Ta–P(OMe)_3$ unit, which has a Ta–P distance within the range of those previously observed in niobium and tantalum–PX_3 species, (X = alkyl, aryl, OR).[9,15] Coordination of $P(OMe)_3$ to the 16-electron complex **2** likely introduced sufficient steric crowding about the tantalum center to promote hydrogen transfer from the η^4-cyclohexadiene ligand to an *ortho*-phenylene group, perhaps *via* a short-lived tantalum hydride intermediate. However, additional studies will be necessary to shed light on the mechanistic details of this interesting reaction.

Although the transformation of **2** to **3** entails no fundamentally new chemistry, particularly in the case of the well-known conversion of a coordinated η^4-diene to an η^5-dienyl ligand,[16] the change of **1** to **2** involving a double *ortho*-metallation of two phenyl groups attached to the same atom, *i.e.*, a single PPh_3 group on $[PPN]^+$, appears to be previously unknown. Perhaps the closest related reactions are those of the isoelectronic carbodiphosphorane, $C(PPh_3)_2$, with electrophilic late transition metal complexes, studied extensively by Cavell and coworkers.[17] Although these interactions often result in double *ortho*-metallations, the modified $C(PPh_3)_2$ groups in these products are much different in character from the transformed $[N(PPh_3)_2]^+$ units in **2** or **3**. Thus, only one phenyl group on each PPh_3 substituent undergoes *ortho*-metallation in $C(PPh_3)_2$, thereby providing a structurally distinct class of pincer complexes.[17]

In conclusion, we have established the first facile and irreversible reaction of the commonly used and generally unreactive counterion $[PPN]^+$ with a d-block complex, tris(naphthalene)tantalate(1−). This interaction provided a previously unknown example of a double *ortho*-metallation reaction in which two phenyl groups on the same triphenylphosphane substituent were metallated by a transition metal. Doubtlessly many other strongly-reducing anions will be found to irreversibly react with $[PPN]^+$ under mild conditions; however, it is surprising that no other well-defined reaction of this type has been documented since the initial synthesis of PPN salts by Appel and Hauss in 1961.[18]

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Notes and references

¶ Reactions and isolations of air sensitive products were conducted under strictly anaerobic conditions, as described previously.[10] **2**: $[Na(thf)_2][\mathbf{1}]$ (2.018 g, 2.74 mmol) and [PPN]Cl (1.706 g, 2.97 mmol) were mixed in thf (50 mL, −30 °C) and the components were stirred while warming to 20 °C over a period of 18 h and then further stirred for 8 h at this temperature. Filtration of the resulting dark green solution, followed by removal of all but about 10 mL of solvent *in vacuo* and addition of pentane (100 mL), afforded a green-brown solid. This was collected on a frit, washed thoroughly with pentane (3 × 15 mL) and dried *in vacuo* to afford satisfactorily pure olive-green **2** (1.664 g, 75%). Anal. Calc. for $C_{46}H_{38}NP_2Ta$ (%): C 65.18; H 4.52; N 1.65; found: C 65.04; H 4.95; N 1.52. $^{31}P\{^1H\}$ NMR (121 MHz, $[^2H_8]$thf, 20 °C, ref. H_3PO_4) δ 15.8 (d, 1P, J = 6.7 Hz), 2.32 (d, 1P, J = 6.7 Hz) ppm (*cf.* [PPN]Cl: $^{31}P\{^1H\}$NMR (121 MHz, $[^2H_6]$ dmso, 20 °C, ref. H_3PO_4) δ 21.7 (s) ppm). Dark green plates of **2**(thf) for the X-ray crystal study were grown from a pentane-layered thf solution at 20 °C over a two day period. **3**: Addition of 3.00 mL of a 0.212 M solution of $P(OMe)_3$ in thf (0.636 mmol) to an intense green solution of **2** (0.494 g, 0.583 mmol) in thf (30 mL) at 20 °C rapidly gave a dark orange mixture. After being stirred for 20 h at 20 °C, the solution was filtered and concentrated to 10 mL *in vacuo*. Addition of pentane (100 mL) provided a slurry, which was filtered, washed with pentane (3 x 5 mL), in which it was slightly soluble, and dried *in vacuo*. By this procedure satisfactorily pure orange **3** (0.392 g, 69%) was obtained. Anal. Calc. for $C_{49}H_{47}NO_3P_3Ta$ (%): C 60.56; H 4.87; N 1.44; found: C 60.49; H 5.03; N 1.38. $^{31}P\{^1H\}$ NMR (121 MHz, $[^2H_8]$thf, 20 °C, ref. H_3PO_4) δ 151.9 (s, 1P, $P(OMe)_3$), 38.5 (apparent s, 1P), 9.9 (apparent s, 1P) ppm. Red polyhedra of $\mathbf{3}(thf)_{0.5}$ for the X-ray study were grown from a pentane-layered thf solution at 20 °C over a one week period.

‖ **Crystal data for 2(thf)**: $C_{50}H_{46}NOP_2Ta$, M = 919.77, monoclinic, space group $P2_1/n$; a = 10.624(1), b = 26.941(3), c = 14.399(1) Å, β = 104.132(2)°, V = 3996.6(7) Å^3, T = 173(2) K, Z = 4, μ(Mo-Kα) = 2.870 mm^{-1}, 46 849 reflections collected, 9182 unique (R_{int} = 0.0433). Refinement on F^2, final $R1$ = 0.0362 (for 7806 reflections with $I > 2\sigma(I)$). w$R2$ = 0.0745 (for all data). CCDC 695311.

Crystal data for 3(thf)$_{0.5}$: $C_{51}H_{51}NO_{3.5}P_3Ta$, M = 1007.79, monoclinic, space group $C2/c$, a = 14.526(1), b = 20.685(2), c = 29.699(2) Å, β = 93.490(2)°, V = 8907(1) Å^3, T = 173(2) K, Z = 8, μ(Mo-Kα) = 2.621 mm^{-1}, 52 222 reflections collected, 10191 unique (R_{int} = 0.0430). Refinement on F^2, final $R1$ = 0.0264 (for 8282 reflections with $I > 2\sigma(I)$). w$R2$ = 0.0626 (for all data).

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