

Zero-valent ML₂ complexes of group 10 metals supported by terphenyl phosphanes†

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Bulky terphenyl phosphane ligands PMe₂Ar' (Ar' = terphenyl group) facilitate the isolation of zero-valent bis-phosphane complexes of nickel, palladium and platinum. The former show coordination numbers greater than two in the solid state due to the existence of Ni–C_{arene} interactions with the terphenyl fragment.

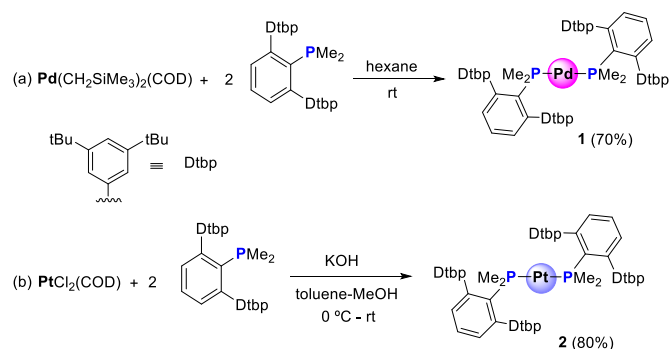
Low-coordinate, zero-valent transition metal complexes of group 10 metal (Ni, Pd and Pt) have long attracted the attention of chemists, as witnessed by the pioneering work of Malatesta¹ on three-coordinate Pd(0) and Pt(0) phosphane complexes in the late 1950s. Besides being instrumental for understanding the activation of small molecules,² these species play a central role in a variety of useful catalytic transformations.³

Among many examples of M(0) complexes of the nickel triad in low coordination numbers, those of two-coordinate ML₂ complexes are limited.⁴ This is because the isolation of such coordinatively unsaturated species relies on the use of sterically demanding ligands, which prevent more favorable higher coordination geometries. Examples of zero-valent ML₂ complexes of Pd and Pt bearing bulky phosphanes,^{5–6} N-heterocyclic carbenes (NHCs)⁷ and isocyanide⁸ ligands have been known. However, two-coordinate Ni(0) analogues are rare and instances known are largely restricted to compounds supported by large NHCs ligands.^{7a,9} As for the phosphane derivatives, the low-coordinate dinuclear complex [Ni(PCy₃)₂]₂(μ-N₂) was structurally characterized by Jonas¹⁰ in the 70s. Recently, few Ni(0) species stabilized solely by pincer

ligands with arene¹¹ or alkene¹² backbones have been described. However, in the latter the metal center displays strong π-interactions with the backbone of the pincer ligand, both in solution and in the solid state, accordingly they are better described as three-coordinate species. To date, two-coordinate bis-phosphane nickel(0) complexes remain unknown.

During the last few years, we have developed a broad family of sterically crowded dialkylterphenyl phosphane ligands, PR₂Ar' (Ar' = terphenyl group),¹³ which stabilize low-coordinate late transition metal complexes by adopting hemilabile κ¹-P,ηⁿ-C_{arene} binding modes.^{13a,14} In this study, we report the ability of terphenyl phosphanes to support zero-valent bis-phosphane complexes for all group 10 metals.

The reaction of Pd(CH₂SiMe₃)₂(COD)¹⁵ (COD = 1,5-cyclooctadiene) with two equivalents of the phosphane PMe₂Ar^{Dtbp2} (Dtbp = 3,5-di-tert-butylphenyl) in hexane at room temperature afforded the formation of the palladium(0) bis-phosphane complex Pd(PMe₂Ar^{Dtbp2})₂, **1**. (Scheme 1a). The product was isolated as a yellow crystalline solid in a yield of 70% by cooling hexane solutions (-20 °C) overnight.



Scheme 1. Synthesis of complexes **1** and **2**.

Then, we targeted the synthesis of the platinum counterpart Pt(PMe₂Ar^{Dtbp2})₂, **2**. Several synthetic routes were explored using different Pt(II) precursors (i.e. K₂PtCl₄ or

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PtCl₂(PMe₂Ar^{Dtbp2})₂) and a variety of reductants. However, none of these methods yielded satisfactory results. We were pleased to find **2** could be prepared in high yield following the procedure developed by Colacot and co-workers^{5e} for the synthesis of bis-phosphane Pd(0) complexes (Scheme 1b). We observed that the reaction only proceeded when KOH was used as the base. Complex **2** was isolated in 80% yield as a pure yellowish solid by precipitation from methanol.

Complexes **1** and **2** were sensitive to air and moisture in solution and in the solid state. The ³¹P{¹H} NMR spectra of **1** and **2** consist of a singlet resonance at -12.8 ppm and 14.2 ppm (¹J_{Pt} = 3794 Hz), respectively, the latter being significantly shifted to higher frequency (Δδ of 50 ppm) with respect to the free phosphane ligand. In these complexes, the four *t*-butyl substituents on the Dtbp rings become equivalent and give rise to a singlet at *ca.* 1.4 ppm in their ¹H NMR spectra. The equivalency of these groups are consistent with κ¹-P monodentate coordination of the phosphane along with fast rotation on the NMR timescale around the P-C_{ipso} bonds.^{13a} In addition, the ¹H and ¹³C NMR resonances arising from the methyl groups bound to phosphorus appear as virtual-coupled triplets. This, along with the observation of virtual triplets for the *ipso* and *ortho* ¹³C nuclei of the central aryl ring of the terphenyl moiety in the ¹³C{¹H} NMR spectra of **1** and **2** support a *trans* arrangement of the phosphane ligands in these adducts, as expected bearing in mind the steric properties of the PMe₂Ar^{Dtbp2} ligands.¹³

The molecular structures of **1** and **2** in the solid-state were confirmed by X-ray crystallographic analysis (Fig. 1 and S3). As anticipated, complexes **1** and **2** adopt an almost linear geometry (P-M-P angle of *ca.* 172 °). The two phosphane ligands are coordinated in a κ¹-P fashion, adopting a pseudo-staggered conformation (dihedral angle *ca.* 91 °). The M-P bond lengths (2.2701(7) Å for **1** and 2.2378(5) Å for **2**) falls in the range previously reported for analogous structures in which Pd(0)⁵ and Pt(0)^{6a-c} are supported by electron-rich phosphane donors. Compared to palladium, the number of platinum(0) bis-phosphane complexes structurally characterized by X-ray crystallography is very scant.^{6,16}

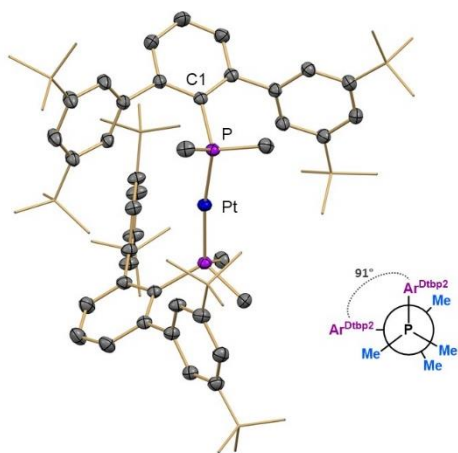
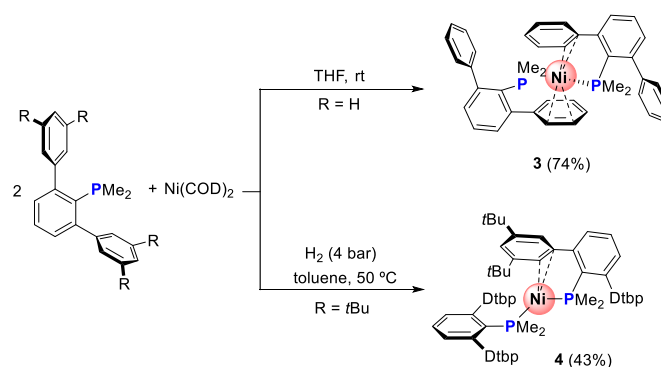


Figure 1. Solid-state structures of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pt-P 2.2378(5), P-Pt-P 172.26(3).

With the aim of completing the series of zero-valent M(PMe₂Ar^{Dtbp2})₂ complexes of the nickel triad, the synthesis of the Ni(0) adduct was then undertaken. No reaction was observed upon treatment of Ni(COD)₂ with 2 equivalents of the phosphane ligand PMe₂Ar^{Dtbp2} in toluene, either at room temperature or by heating up to 100 °C. However, with the less bulky terphenyl phosphane PMe₂Ar^{Ph2},^{13a,17} which contains an unsubstituted *m*-terphenyl group, the displacement of COD ligands by the phosphane occurred almost instantaneously in THF at room temperature (Scheme 2). Addition of pentane induced the precipitation of the complex Ni(PMe₂Ar^{Ph2})₂ **3**, as a red solid in quantitative yield. Analytically pure material was obtained by recrystallization from diethyl ether:pentane (2:1) mixtures (74% isolated yield).

Encouraged by this result, our attention turned back to the preparation of the elusive Ni(PMe₂Ar^{Dtbp2})₂. Recently, Ogoshi and co-workers have reported the hydrogenation of COD to cyclooctane in the presence of a Ni(0)-NHC complex.¹⁸ We were pleased to find that mixtures of Ni(COD)₂ and the phosphane PMe₂Ar^{Dtbp2} (in 1:2 ratio) reacted at 50 °C under hydrogenation conditions (4 bar of H₂) to afford the desired product Ni(PMe₂Ar^{Dtbp2})₂, **4** (Scheme 2). This compound was isolated in 43% as a reddish-brown crystalline solid by recrystallization from a saturated pentane solution at low temperature.



Scheme 2. Synthesis of complexes **3** and **4**.

The bis-phosphane Ni(0) adducts **3** and **4** are extremely oxygen-sensitive in solution and as solids. As shown in Fig. 2, the geometries adopted by the nickel adducts **3** and **4** in the solid state clearly differ from the linear arrangement displayed by their heavier counterparts. In the structure of **3**, both phosphane donors exhibit a bidentate κ¹-P,η²-C_{arene} binding mode, resulting in a formally four-coordinate Ni(0) center. The complex has a distorted trigonal pyramidal structure (τ₄ = 0.91)¹⁹ in which the apex is occupied by one of the C_{ipso}-C_{ortho} bonds of a closer flanking phenyl ring. Both Ni-η²-C_{arene} interactions are non-symmetrical and of different magnitude, as reflected in their Ni-C_{arene} separations. Thus, that of the apex presents the largest Ni-C_{arene} bond distances, *i.e.* Ni-C_{ipso} (C33 in Fig. 2) of 2.322(3) Å and Ni-C_{ortho} (C34 in Fig. 2) of 2.403(3) Å,

both well above the 1.97 Å value of the sum of the covalent radii of C_{sp^2} (0.73 Å) and Ni (1.24 Å).²⁰ The second Ni–C_{arene} interaction, which involved the C_{ortho}(C18) and the C_{meta}(C17) of a side phenyl ring of the second phosphane ligand, features shorter Ni–C bond distances, *i.e.* Ni–C_{ortho} of 2.058(2) Å and Ni–C_{meta} of 2.186(3), comparable to those found in Ni(0) complexes supported by diphosphane pincer ligands with arene and olefinic backbones (*ca.* 1.97–2.13 Å).^{11a,11c,12} Localization of the double bond character within arene ring, which features the stronger interaction with the Ni center, is clear from the alternating shorter (C18–C17, C16–C15, C14–C13) and longer (C17–C16, C15–C15, C13–C18) C–C bond distances. In complex **4** (Fig. 2) the Ni(0) center lies in a distorted trigonal coordination environment formed by the two phosphorous atoms and a non-symmetric η^2 -C_{ipso}–C_{ortho} weak interaction with the proximal Dtbp ring of one the phosphane ligand. The Ni–C_{ipso} (C8) bond distance of 2.142(5) Å is shorter than that of the Ni–C_{ortho} (C7) of 2.294(6) Å. There is not a clear disruption of aromaticity in the interacting Dtbp ring. The bulkiness of the *t*-butyl substituents on the terphenyl moiety precludes the formation of a second Ni–C_{arene} bonds with a Dtbp ring of the other phosphane ligand. To the best of our knowledge, complexes **3** and **4** are the first examples of structurally characterized nickel(0) adducts supported solely by two phosphane ligands.

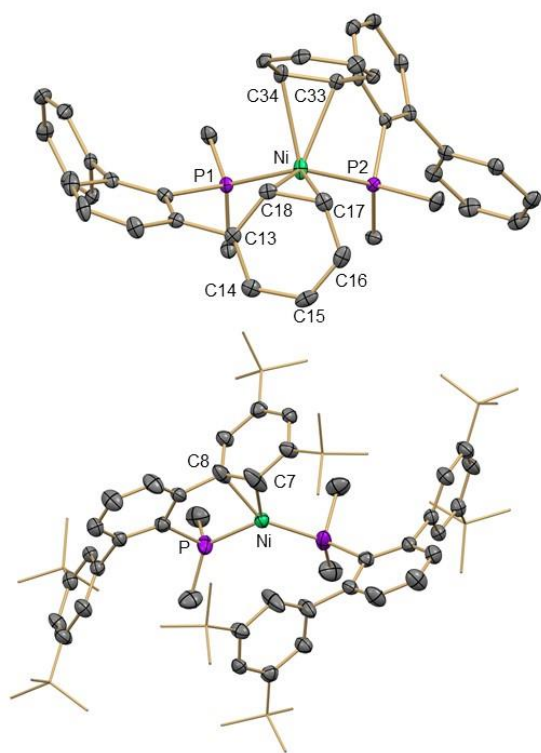


Figure 2. Solid-state structures of **3** (top) and **4** (bottom). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°] for **3**: Ni–P1 2.1978(7), Ni–P2 2.1700(7), Ni–C33 2.322(3), Ni–C34 2.403(3), Ni–C17 2.186(3), Ni–C18 2.058(2), C18–C17 1.413(3), C17–C16, 1.422(4), C16–C15 1.363(4), C15–C14 1.417(4), C14–C13 1.371(4), C13–C18, 1.429(3), C33–C34 1.411(3), P1–Ni–P2 112.55(3); for **4**: Ni–P 2.137(2), Ni–C7 2.142(5), Ni–C8 2.292(7), C7–C8 1.413(7), P–Ni–P 115.37(7)

Solid-state structures of **3** and **4** were not retained in solution. Room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** and **4** show equivalent phosphorus atoms, as indicated by the presence of sharp singlets at 2.2 and –4.3 ppm, respectively. The difference in ^{31}P chemical shift relative to the uncoordinated ligands ($\Delta\delta$ *ca.* 32 ppm for **3** and 38 ppm for **4**) supports a monodentate coordination mode of the phosphanes in these complexes.^{13a} Moreover, in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of adduct **3** virtual triplets for the methyl groups bound to phosphorus nuclei are clearly discernible. However, the ^1H NMR spectrum of **4** exhibits a substantial broadening of most signals, which become sharpened at 60 °C with the concomitant observation of the expected virtual-coupled triplet for the P–Me groups. Attempts to gain information about the dynamic processes taking place in solution by carrying out low-temperature ^1H NMR experiments with both complexes **3** and **4** were unsuccessful (see ESI for details).

When optimizing the hydrogenation conditions to prepare the nickel complex **4**, another phosphorus-containing species **5** with a ^{31}P chemical shift of –8.0 ppm was detected. $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the reaction disclosed that **5** was generated before complex **4** started to develop and was consumed at the same time that the concentration of **4** increased, suggesting that **5** could be a reaction intermediate. Although purification of complex **5** by recrystallization proved difficult, X-ray quality crystals were obtained by cooling at –20 °C a pentane solution where **5** was the major component (Fig. 3). The solid-state structure shows that **5** displays a distorted trigonal geometry around the metal center, where the phosphane is coordinated in bidentate κ^1 -P, η^2 -C_{arene} fashion and the third coordination site is occupied by a double bond of a cyclooctene molecule, formed upon the partial hydrogenation of COD. The interacting C_{ortho} of the proximal Dtbp ring is bent out the arene plane and towards the nickel atom by 0.16 Å. Consequently, in complex **5** both Ni–C_{arene} bond distances, *i.e.* Ni–C_{ipso} (C7 in Fig. 3) of 2.017(3) Å and Ni–C_{ortho} (C8) of 2.121(3) Å are shorter than those found in **4**, and comparable to those of the Ni– η^2 -COE linkage (Ni–C37 and Ni–C38), characterized by Ni–C bonds lengths of about 2.01 Å. Partial localization of the double bonds within the interacting Dtbp ring is also observed.

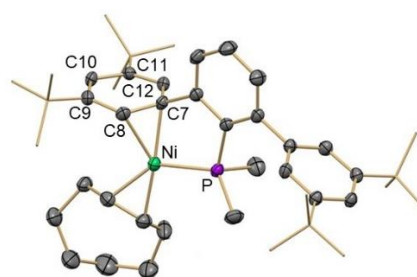


Figure 3. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å]: Ni–P 2.1635(7), Ni–C7 2.017(2), Ni–C8 2.121(3), Ni–C37 2.021(3), Ni–C38 2.000(3), C7–C8 1.428(4), C8–C9 1.431(4), C9–C10 1.371(4), C10–C11 1.425, C11–C12 1.370(3), C37–C38 1.399(4)

Examples of homogeneous hydrogenation catalysts based on nickel are scarce.²¹ Work aimed at identifying the nature of the nickel complex that mediates the hydrogenation of COD is in progress.

To sum up, zero-valent M(PMe₂Ar')₂ (Ar' = terphenyl fragment) complexes of Ni, Pd and Pt have been synthesized and structurally characterized. Whereas the latter are truly 14e-two-coordinate species, the Ni(0) species exhibit coordination numbers greater than two in the solid state. The facility of bulky terphenyl phosphanes to adopt bidentate $\kappa^1\text{-P}, \eta^2\text{-C}_{\text{arene}}$ coordination mode has proven to be key in stabilizing the bis-phosphane Ni(0) adducts.

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Conflicts of interest

There are no conflicts to declare.

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