

Formation and structures of palladium-cyanomethyl complexes generated under unexpectedly mild conditions: quantifying the acidification of acetonitrile coordinated to a palladium center

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Synopsis Palladium-cyanomethyl complexes were formed from the deprotonation of acetonitrile using unprecedentedly mild bases, demonstrating an acidification of this solvent by at least 8 p*K_a* units in the presence of the Pd(II) phosphine complexes. The structures of these complexes demonstrate a strong *trans* influence of the cyanomethyl ligand.

Abstract The reaction of the palladium-triphosphine complex [Pd(triphos)(PPh₃)]²⁺ with guanidine or phosphazene bases in acetonitrile forms the cyanomethyl complex [Pd(triphos)(CH₂CN)]⁺, where triphos is the triphosphine ligand PhP(CH₂CH₂PPh₂)₂. A cyanomethyl complex with a tridentate PN^{HP} ligand, HN(CH₂CH₂PPh₂)₂, was also formed in a similar reaction with solvent, demonstrating that this reaction is relatively general to square-planar Pd(II) phosphine complexes. The crystal structures of these cyanomethyl complexes possess distorted square planar geometries with the cyanomethyl group *trans* to the central P and N atoms, demonstrating a *trans* influence that is significantly greater than observed in analogous halide complexes but weaker than complexes with monodentate phosphines. The bases used to form the triphosphine complex are too weak to deprotonate free acetonitrile, and the observed reaction demonstrates a dramatic acidification of the solvent in the presence of the palladium ion. The p*K_a* of the coordinated acetonitrile is estimated to be approximately 25 from these results, which represents a decrease of at least 8 p*K_a* units relative to the free solvent; through a thermodynamic cycle, the heterolytic M–C bond energy can also be estimated to be as low as 11 kcal/mol using the H–C bond energies as a reference.

Keywords: Palladium; cyanomethyl; acidity; *trans*-influence.

1. Introduction

Metal-cyanomethyl complexes are the simplest examples of α-cyanoalkyl ligands and are therefore a fundamental category of organometallic species. They can be formally viewed as deprotonated acetonitrile complexes, and they have been shown to react as nucleophiles in carbon-carbon bond-forming reactions to form nitrile compounds, but these uses are hampered by the difficulty in forming the active cyanoalkyl species through direct C–H bond cleavage.¹ While the robustness of acetonitrile towards C–H activation hinders the use of this

molecule as a substrate in catalytic applications, it is a great advantage in using acetonitrile as a solvent, as it allows many reactions to proceed using strong bases or other reactive species that would be unstable in more protic solvents such as water.^{2,3} Largely for this reason, acetonitrile is frequently the solvent of choice for equilibrium studies involving the reactions of transition metal hydrides, as the metal-hydride species and the reagents used to prepare them are often reactive towards other solvents.

Our group has been studying the formation and reactivity of d^8 transition metal hydride complexes with the formula $[\text{HM}(\text{triphos})(\text{PR}_3)]^{n+}$, which contain one triphosphine ligand and one monophosphine ligand (triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)$; $\text{PR}_3 = \text{PPh}_3, \text{PEt}_3, \text{PMe}_3$) to evaluate their viability as catalytic intermediates for reactions such as H_2 electrocatalysis and CO_2 reduction. Palladium triphosphine complexes of this type are notably active catalysts for the electrocatalytic reduction of CO_2 ,^{4,5} although the active catalyst species was found to be $[\text{Pd}(\text{triphos})(\text{NCCH}_3)]^{2+}$, formed upon dissociation of the monophosphine and coordination of solvent.⁶ Complexes with larger chelate bite angles, such as the trimethylene analogue of the triphos ligand, *i.e.* $\text{RP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2$, are inactive due to the formation of an inactive hydride complex.⁷ We sought to characterize the formation, structure, and thermodynamic hydricity of the analogous palladium hydride species with the catalytically active triphos ligand. For instance, it is not clear whether the monophosphine would remain bound, forming $[\text{HPd}(\text{triphos})(\text{PR}_3)]^+$ species analogous to the Co, Rh, and Ni metal hydrides we have been studying, or whether it would dissociate to form a $[\text{HPd}(\text{triphos})]^+$ species analogous to the catalytically inactive Pd hydride. To form these species and characterize their thermodynamic hydricities, we attempted to study their H_2 heterolysis equilibria using strong bases, which is a general method for generating hydrides of this type.^{3,8,9} Instead, we observed the formation of the cyanomethyl complex, $[\text{Pd}(\text{triphos})(\text{CD}_2\text{CN})]\text{BF}_4$, **1**, upon addition of the bases to the triphosphine complex in acetonitrile- d_3 . This result was unexpected, as the phosphazene and guanidine bases used in these studies are not basic enough to deprotonate free acetonitrile and have been used in other analogous studies in acetonitrile without similar side-reactions. Here we report the structures of **1** and an analogous complex, **2**, that contains a tridentate PN^{HP} ligand, $\text{HN}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, along with a discussion of the thermodynamic implications for the acidity and Pd-C bond energies.

2. Results and discussion.

2.1. Formation of palladium cyanomethyl complexes.

Our attempts to generate a palladium hydride with the formula $[\text{HPd}(\text{triphos})(\text{PPh}_3)]^+$ in H_2 heterolysis equilibria using guanidine and phosphazene bases are described in equation (1) of Figure 1, along with the structures of the bases used. No hydride formation was observed; instead, the $[\text{Pd}(\text{triphos})(\text{PPh}_3)]^{2+}$ precursor unexpectedly reacted with the base before the addition of H_2 , forming free PPh_3 and the cyanomethyl complex **1**, as shown in equation (2) of Figure 1. No further reaction was observed after addition of H_2 , and **1** was crystallized by layering the CD_3CN solution with diethyl ether.

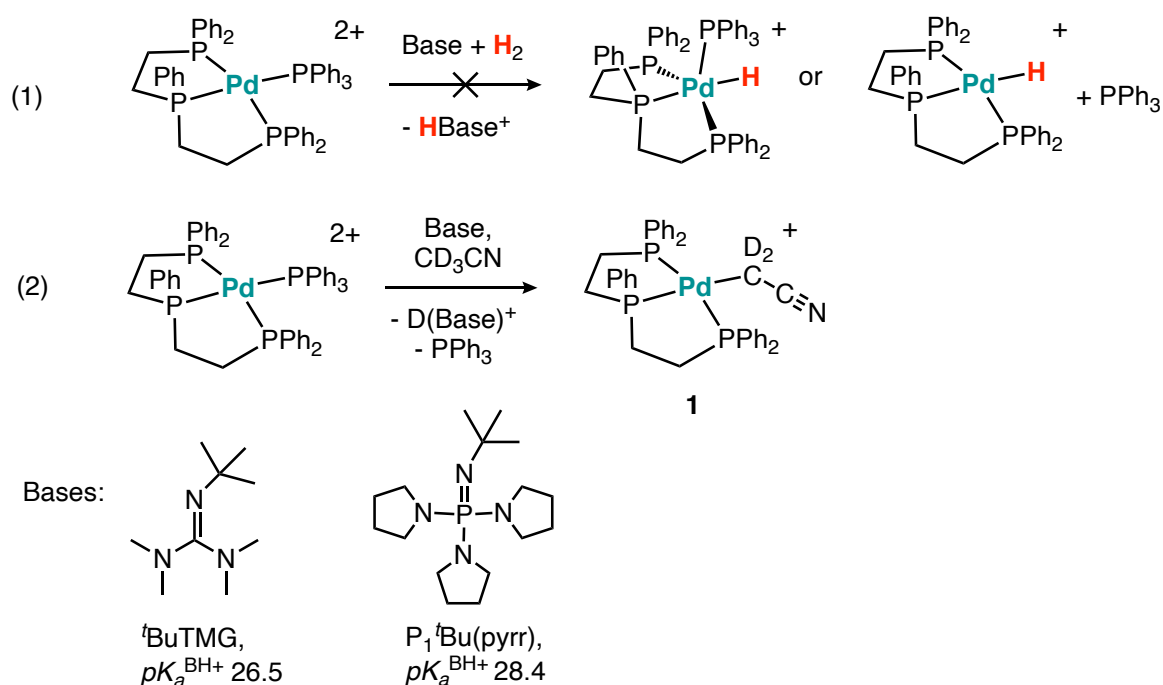


Figure 1 Formation of cyanomethyl complex **1**.

We observed a similar reaction for the palladium complex with the tridentate PN^{HP} ligand, ($\text{PN}^{\text{HP}} = \text{HN}[\text{CH}_2\text{CH}_2\text{PPh}_2]_2$), shown in Scheme 2; when we attempted to deprotonate the ligand to prepare the neutral complex with an anionic PNP ligand, $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)^-$, as shown in equation (3), we instead observed the formation of the cyanomethyl complex $[\text{Pd}(\text{PN}^{\text{HP}})(\text{CH}_2\text{CN})]\text{Cl}$, **2**, as shown in equation (4), after washing the product with acetonitrile. **2** was crystallized from an acetonitrile solution upon vapor diffusion with diethyl ether. X-ray crystal structures of both **1** and **2** were determined, although the data quality obtained from the crystals of **2** was poor, and the crystal structure is sufficient primarily for

the purposes of establishing the identity of the product and identifying a hydrogen-bonding interaction between the outer-sphere chloride and the N–H group of the ligand.

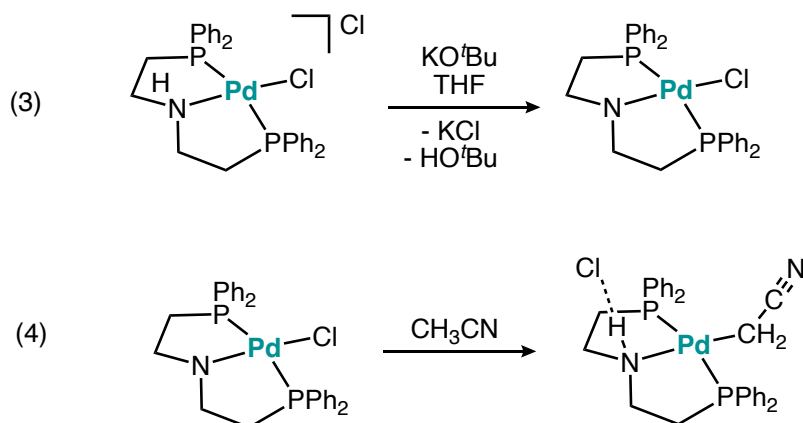
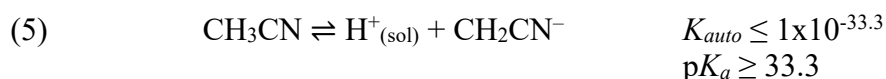


Figure 2 Formation of cyanomethyl complex **2**.

2.2. Acidity and thermodynamic results.

Beyond the structures of these cyanomethyl complexes, the significant scientific result demonstrated by these reactions is that coordination to these Pd centers makes the C–H bonds of acetonitrile molecules considerably more acidic than anticipated, as the bases used in these studies are much milder than those typically used to form metal-cyanomethyl complexes. This enhanced acidity is relevant to potential catalytic applications using cyanoalkyl nucleophiles. The pK_a of CH_3CN is defined by its autoionization constant, equation (5), where $\text{H}^+(\text{sol})$ is the solvated proton. A pK_a value of at least 33.3 ($K_{\text{auto}} \leq 1 \times 10^{-33.3}$) was painstakingly estimated by Chantooni and Kolthoff for equation (5) through conductivity measurements, but although this value is widely used, it was identified at the time as being a lower limit on the actual value.¹⁰ The measured value of 33.3 is likely to be too low due to the presence of impurities in the conductivity experiments. Schwesinger has since suggested that the true value may be as high as 44.¹¹ Morris proposed that a value of approximately 39 was likely to be correct, because strongly basic phosphazenes with $pK_a^{\text{BH}^+}$ values up to approximately 38 can be studied in this solvent (where $pK_a^{\text{BH}^+}$ refers to the pK_a of the conjugate acid of the base), but stronger bases decompose the solvent.²

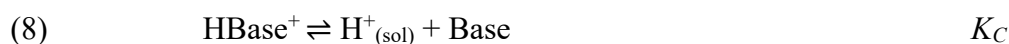
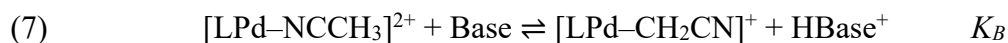
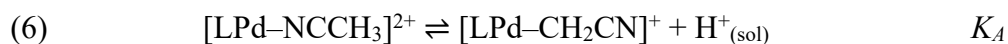


The high pK_a of acetonitrile has led to the development of very strong bases, such as the proazaphosphatranine series of Verkade's bases, $\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3\text{P}$, to generate the active cyanomethide anion as alternatives to *n*-butyllithium or other harsh and/or dangerous

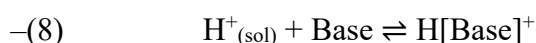
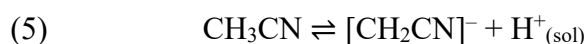
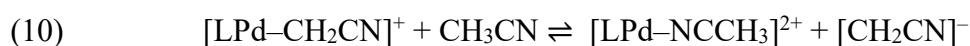
reagents.¹²⁻¹⁴ The strong bases used to deprotonate acetonitrile have limited the catalytic applications, as these bases are often reactive towards the electrophiles that are intended to react with the nucleophilic cyanomethyl group. As a result, many reactions involving direct deprotonation of nitrile substrates have been limited to activated nitriles, and alternative strategies have instead been developed to avoid the need to deprotonate acetonitrile, using activated species such as Me₃SiCH₂CN.^{15,16} It was previously recognized by Shibasaki that complexation of acetonitrile with a Lewis-acidic metal can stabilize the cyanomethyl species, allowing the weaker base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to be used successfully in catalytic amounts in the cyanomethylation of carbonyl compounds catalyzed by [CpRu(PPh₃)(MeCN)₂]⁺,^{17,18} a similar reaction using a nickel-pincer catalyst was reported by Ozerov.¹⁹ However, the degree of acidification of acetonitrile using transition-metal Lewis acids has not been quantified, and the cyanomethyl species are proposed to form in catalytic amounts as reactive intermediates. To the best of our knowledge, and as recently reviewed by Bissember *et al.*, stoichiometric deprotonation of acetonitrile to form a metal-cyanomethyl complex has been achieved only using hydroxide, alkoxide, or even stronger bases such as ⁿBuLi.²⁰ Lopez and Palomo ended their recent review of cyanoalkylation chemistry by emphasizing that "[i]n the context of metal-assisted deprotonation of alkylnitriles, predicting the ability of different metals to activate the nitriles towards deprotonation of the resultant complexes is difficult and thus research on this aspect would facilitate the design of new and more-efficient catalyst systems."¹ The guanidine and phosphazene bases used to generate the cyanomethyl species in this work have well-characterized p*K*_a^{BH⁺} values that are orders of magnitude less than free acetonitrile. As a result, they demonstrate that acetonitrile becomes more acidic by at least 8 p*K*_a units in the presence of the palladium-triphos and -PNP complexes here, with the uncertainty in the actual values being due to difficulties in establishing the p*K*_a of free acetonitrile itself.

The p*K*_a of a palladium-coordinated acetonitrile molecule is defined by equation (6), which can be viewed as the sum of equations (7) and (8). Therefore, $K_A = K_B \times K_C$, and $\text{p}K_a^{\text{Pd-NCCH}_3} = \text{p}K_a^{\text{BH}^+} - \text{p}K_{\text{eq}}$. The p*K*_a^{BH⁺} values for DBU, ^tBuTMG and P1^tBu(pyrr) are 24.3, 26.5, and 28.4, respectively, in acetonitrile.^{11,21,22} The former does not react with the palladium complexes described here to form a cyanomethyl complex to any observable degree while the latter two do so quantitatively, indicating that $K_B \ll 1$ for DBU and $\gg 1$ for ^tBuTMG; therefore, the p*K*_a^{Pd-NCCH₃} of the coordinated acetonitrile is likely to be approximately 25.

This represents a decrease of 8 pK_a units relative to the value of 33.3 established as a lower limit for free acetonitrile and a decrease of 14 pK_a units vs. the suggested value of 39.



It is also possible to use this data to estimate the Pd–C bond strength, or more technically the heterolytic bond dissociation free energy defined in equation (9), of the Pd-cyanomethyl complex. This Pd–C bond cleavage will actually occur as shown in equation (10), since the $[\text{LPd}]^{2+}$ fragment will bind another molecule of free solvent. Equation (10) in turn can be described as the difference between equation (5) and equations (7) and (8). The thermodynamic equivalence of equations (9) and (10) is evident in the equivalence of their equilibrium constant expressions, $K_9 = [\text{LPd}^{2+}][\text{CH}_2\text{CN}^-]/[\text{LPdCH}_2\text{CN}^+]$ and $K_{10} = [\text{LPd}(\text{NCCH}_3)^{2+}][\text{CH}_2\text{CN}^-]/[\text{LPdCH}_2\text{CN}^+]$, assuming the activity of the solvent is taken to be unity.



If the pK_a of acetonitrile is taken to be 33.3, and $K \approx 1$ for equation (7) using a base with $pK_a^{BH^+} = 25$, as indicated by the results above, then $K \approx 10^{-8}$ for equation (10), corresponding to a value of $\Delta G^\circ \approx +11$ kcal/mol for Pd–C bond cleavage. Using the higher estimated value of 39 for the pK_a of acetonitrile, $K_E \approx 10^{-14}$ and $\Delta G^\circ \approx +19$ kcal/mol. Clearly there is uncertainty in this estimate, due to the uncertainty in the pK_a of the solvent, but this strategy of determining heterolytic M–C bond cleavage energies through protonolysis places M–C and H–C bond energies on a single, self-consistent scale, using widely-used pK_a values as a reference. The experimental uncertainties should be more accurate in solvents with better-established thermodynamic data, such as water.

2.3. Spectroscopic and structural characterization of **1** and **2**.

The NMR spectra and crystal structures of **1** and **2** are representative of the expected C_s symmetry and overall square-planar geometry. The ^{31}P NMR spectrum of **1** in CD_3CN is broadly similar to other four-coordinate $[\text{Pd}(\text{triphos})\text{L}]$ complexes,²³ with a triplet at 100.86 ppm for the central phosphorus atom and a doublet at 48.00 ppm for the terminal phosphorus atoms, the latter of which are equivalent in solution as expected. The chemical shift of the central phosphorus atom, which is highly sensitive to the *trans* influence of the monodentate ligand, is shifted dramatically upfield relative to other $[\text{Pd}(\text{triphos})\text{L}]$ complexes, which have shifts for this phosphine between 110.3 ppm and 117.25 ppm for $[\text{Pd}(\text{triphos})(\text{CH}_3\text{CN})]^{2+}$.^{23,24} The P–P coupling constant of 18.6 Hz between the central and terminal phosphines is also much larger than in the other complexes, which range from 7.5 Hz in $[\text{Pd}(\text{triphos})(\text{NCCH}_3)]^{2+}$ to 10.0 Hz in $[\text{Pd}(\text{triphos})\text{Cl}]^+$. The chemical shift of the terminal phosphines, on the other hand, is only slightly different from the corresponding shifts in these complexes, which are between 53–54 ppm in all but the chloride, which appears at 45.5 ppm. Altogether, a much stronger *trans* influence is observed for the cyanomethyl complex relative to complexes with these other ligands, which range from strong-field (PPh_3) and moderately π -accepting, to weak-field and weakly donating, for CH_3CN and OTf , to π -donating in the case of Cl^- . The ^1H NMR spectra are not particularly informative, as the CD_2CN ligand does not have any protons, and the numerous aryl protons and diastereotopic ethylene resonances are overlapping multiplets that do not have any diagnostic signals. The ^{31}P NMR spectrum of **2** is very similar, showing a single peak for the phosphine ligands as a singlet at 47.88 ppm, very similar to the analogous terminal phosphines in **1**. The structure of **1** is shown in Figure 3. Crystallographic data for **1** and **2** are given in Table 1. The palladium complex has an overall distorted square planar structure similar to other $[\text{Pd}(\text{triphos})\text{X}]^+$ cations that have been crystallographically characterized.^{23,25–31} There is crystallographically-imposed mirror symmetry, matching the symmetry observed in solution but rare for solid-state structures of $[\text{M}(\text{triphos})\text{X}]$ complexes, which usually crystallize in chiral conformations due to the arrangements of the five-membered chelate rings. The chelate bite angle is $83.73(4)^\circ$, which is very similar to the aforementioned $[\text{Pd}(\text{triphos})\text{X}]^+$ cations but somewhat smaller than the $[\text{Pd}(\text{RP}[\text{CH}_2\text{CH}_2\text{PR}_2])(\text{NCCH}_3)]^{2+}$ complexes that have been structurally characterized; surprisingly, the structure of $[\text{Pd}(\text{triphos})(\text{NCCH}_3)]^{2+}$ has not been reported for comparison.⁷ The P1–Pd–C1 angle of $169.5(3)^\circ$ and P2–Pd–P2' angle of $163.86(6)^\circ$ are both distinctly bent, creating a slight tetrahedral distortion within the otherwise square planar geometry.

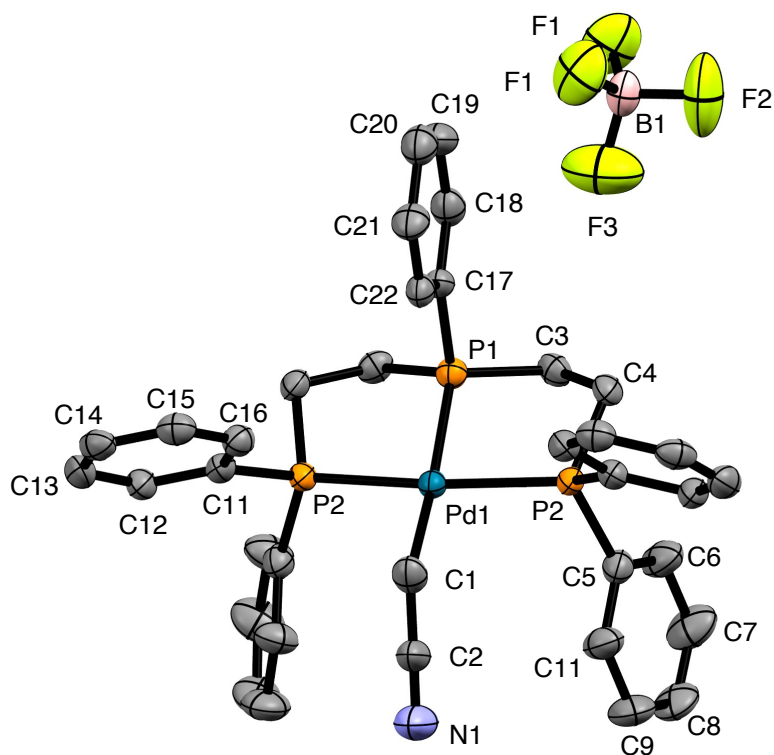


Figure 3 X-ray structure of **1** showing the atom-labeling scheme, with ellipsoids at 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1 Crystallographic and refinement data for **1** and **2**.

Species	1	2
Compound	[Pd(triphos)(CD ₂ CN)](BF ₄)(CD ₃ CN) ₂	[Pd(PN ^H P)(CH ₂ CN)]Cl
Empirical formula	C ₄₀ H ₃₃ BD ₈ F ₄ N ₃ P ₃ Pd	C ₃₀ H ₃₁ ClN ₂ P ₂ Pd
Formula weight	857.92	623.36
Temperature/K	173(2)	173(2)
Crystal system	tetragonal	orthorhombic
Space group	I4 ₁ md	Pbca
a/Å	23.8874(4)	20.4000(12)
b/Å	23.8874(4)	11.3362(13)
c/Å	12.6877(5)	24.3494(17)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å ³	7239.7(4)	5631.0(8)
Z	8	8
ρ _{calc} /cm ³	1.482	1.471

μ/mm^{-1}	0.696	0.89
F(000)	3288	2544
Crystal size/ mm^3	$0.1 \times 0.08 \times 0.08$	$0.17 \times 0.13 \times 0.04$
Radiation	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.392 to 54.958	6.33 to 50.052
Reflections collected	34741	15952
Independent reflections	4293	4913
R_{int}	0.0568	0.0770
R_{sigma}	0.0360	0.1075
Data/restraints/parameters	4293/1/229	4913/142/384
Goodness-of-fit on F^2	1.065	1.153
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0366$, $wR_2 = 0.0841$	$R_1 = 0.0930$, $wR_2 = 0.1612$
Final R indexes [all data]	$R_1 = 0.0492$, $wR_2 = 0.0920$	$R_1 = 0.1419$, $wR_2 = 0.1871$
$\Delta Q_{\text{max}}, \Delta Q_{\text{min}}/e \text{ \AA}^{-3}$	1.10/-0.58	1.60/-1.64

Computer Programs: Olex2 (Dolomanov, 2009),³² *CrysAlisPro* (Rigaku, 2018),³³ SHELXT2014 (Sheldrick, 2015),³⁴ SHELXL2014 (Sheldrick, 2015),³⁵ PLATON/SQUEEZE (Spek, 2015).³⁶

The unit cell of **1** has four Pd cations ($Z = 4$); for each cation there is an associated BF_4 anion and two symmetry-equivalent molecules of CD_3CN , the latter of which is disordered over two overlapping positions. The positions of the cocrystallized solvent molecules could be identified clearly from the electron density map, and they refined to chemically sensible geometries, albeit with extensive use of restraints. However, refinement of their thermal displacement parameters did not converge well even with the aforementioned restraints. Therefore, for the final refinement, the SQUEEZE function of the PLATON program³⁶ was used to remove the contribution of these solvent molecules from the structure. A total of 44 electrons, corresponding perfectly to the observed 2 molecules of CD_3CN per formula unit, was removed from a void space of 188 \AA^3 in the asymmetric unit, four such voids being found in total in the unit cell, 176 electrons and 8 solvent molecules overall. The void spaces lie in a channel running along the mirror planes of the unit cell, separated by Pd- CD_2CN units from different cations on either side, in the same locations that the poorly behaved solvent molecules were found in the initial refinement. The mirror plane in the middle of the unit cell bisects the molecule through the P-Pd- CD_2CN unit as well as through the BF_4 anion and the cocrystallized solvent molecules, making one-half of each molecule unique. No significant intermolecular interactions are observed. The BF_4 ion fits in a cleft above the metal center between the phenyl group of the central phosphorus atom and the

terminal C atom of the cyanomethyl group, and its position is therefore well defined, without any observable disorder.

There are five palladium-cyanomethyl complexes in the CSD, all of which are square-planar Pd(II) phosphine complexes analogous to **1**, but which are neutral, rather than cationic species: three complexes with the formula $[\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{CH}_2\text{CN})](\text{solvate})$,³⁷ $[\text{Pd}(\text{PCP})(\text{CH}_2\text{CN})]$, where PCP is a tridentate pincer ligand with an anionic C atom in the central position,³⁸ and the bis-cyanomethyl complex $[\text{Pd}(\text{dppe})(\text{CH}_2\text{CN})_2]$, where dppe is the diphosphine 1,2-(diphenylphosphino)ethane.³⁹ The cyanomethyl group is *cis* to the phosphines in each of these complexes, and the Pd–P distances of approximately 2.29–2.33 Å are nearly identical to the analogous Pd–P2 distances in **1**. These distances are also very similar to the Pd–P_{terminal} distances in $[\text{Pd}(\text{triphos})\text{X}]^+$ complexes with X = Cl, Br, I, NO₃, O₃SCF₃, and N-*p*-tosyl, all of which range from 2.31–2.34 Å.^{23,25–31} It is clear that there is no significant *cis* influence due to the cyanomethyl or any other X ligand. On the other hand, while the Pd–P1 distances in the known $[\text{Pd}(\text{triphos})\text{X}]^+$ complexes are all between 2.19–2.21 Å, indicating that the *trans* influences of these weak-field ions are all similar, the Pd–P1 distance in **1** is significantly longer, at 2.269(2) Å. This value is closer to those of the known $[\text{Pd}(\text{triphos})(\text{monophosphine})]^{2+}$ complexes, which are all very nearly 2.30 Å,^{24,40} consistent with the *trans* influence of the strongly σ -donating cyanomethyl group being stronger than those of the π -donating X ions but less than that of a π -accepting phosphine. For the other *trans* influence observed in this structure, the Pd–C distance of 2.173(8) Å in **1** is nearly 0.1 Å greater than in the $[\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{CH}_2\text{CN})]$ complexes, where the cyanomethyl is *trans* to the chloride, and slightly longer than the 2.136 Å in $[\text{Pd}(\text{PCP})(\text{CH}_2\text{CN})]$, where it is *trans* to an anionic carbon atom in the pincer complex. The distance in **1** is very similar to the two Pd–C distances in $\text{Pd}(\text{dppe})(\text{CH}_2\text{CN})_2$, where the C atoms are also *trans* to the phosphines of the dppe ligand. These distances again point to the very strong *trans* influence of phosphine donors over even very strongly sigma-donating C-donor atoms and especially over weak-field halides.

The cyanomethyl ligand is bent, with an *anti* arrangement with respect to the phenyl substituent across from the on the central phosphorus atom it is *trans* to. The C2–C1–Pd angle of 118.9(7)° is considerably larger than any of the other structurally characterized Pd-cyanomethyl complexes; the C–C and C–N distances are also both slightly shorter than in the other complexes. These differences may be related to the cationic nature of **1**, which may

withdraw electron density from the ligand, leading to more neutral $\text{N}=\text{C}=\text{CH}_2$ character rather than anionic $\text{NC}-\text{CH}_2^-$ character in the ligand.

The molecular structure of the cation in **2** is shown in Figure 4. The structure is broadly similar to that of **1**, with the major differences being the orientation of the cyanomethyl group and presence of an outer-sphere chloride anion. The Cl ion hydrogen-bonds tightly to the N–H group of the PNP ligand, with an H–Cl distance of 2.173(3) Å and an N–Cl distance of 3.14(1) Å. The cyanomethyl group is nearly eclipsed with the N–H---Cl hydrogen-bonding unit. The different orientation of this group may also be related to the significantly more linear N–Pd–C angle of 178.4(4)° compared to the bent P1–Pd–C angle in **1**. The Pd–P distances of 2.299(3) and 2.294(3) Å are very similar to those in **1**, but the Pd–C distance of 2.075(10) Å is approximately 0.1 Å shorter than in **1**, due to the apparently much weaker *trans* influence of the N atom vs the phosphine in **1**. The Pd–N distance of 2.129(8) Å, meanwhile, is ~0.06–0.07 Å longer than the comparable $[\text{Pd}(\text{PN}^{\text{H}}\text{P})\text{Cl}]^+$ cations, ~0.04–0.06 Å longer than in the Br^- or I^- complexes, and >0.1 Å longer than in the NO_3^- complex;^{41,42} these Pd–N bonds in the $\text{PN}^{\text{H}}\text{P}$ complexes are apparently more susceptible to the *trans* influence than the Pd–P bonds in the triphos complexes, and again they demonstrate a considerable *trans* influence for the cyanomethyl group.

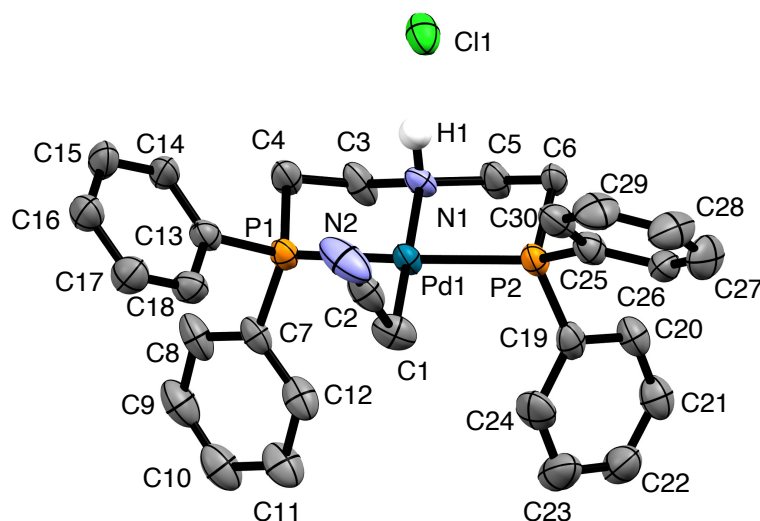


Figure 4 X-ray structure of **2** showing the atom-labeling scheme, with ellipsoids at 50% probability level. Hydrogen atoms and secondary disordered positions have been omitted for clarity.

3. Conclusions.

The studies described here demonstrate that square-planar palladium triphosphine and PNP complexes act as strong Lewis acids in acetonitrile, imparting a dramatically lower pK_a value to a coordinated solvent molecule. The coordinated acetonitrile ligands are deprotonated by bases with $pK_a^{BH^+}$ values greater than 24.3, forming well-defined, mononuclear cyanomethyl complexes. The increase in acidity is at least 8 pK_a units and likely as much as 14, with the uncertainty in these values originating from difficulties in measuring the autoionization constant of free acetonitrile. To the best of our knowledge, these reactions are the first stoichiometric demonstration of a cyanomethyl complex formed by deprotonating acetonitrile with a base whose $pK_a^{BH^+}$ is measurably lower than that of the free solvent. These results are relevant to catalytic cyanoalkylation reactions. Structurally, the cyanomethyl complexes have similar geometries to analogous complexes with other monodentate ligands, and the bond metrics indicate a *trans* influence for the cyanomethyl group that is considerably larger than halide or pseudo-halide ions but less than those of phosphine ligands.

4. Experimental.

All syntheses and experiments were conducted under an N_2 atmosphere, except diffraction experiments, which were carried out under dry air. $[Pd(\text{triphos})(PPh_3)](BF_4)_2^4$ and $[Pd(PN^H P)Cl]Cl^{41}$ were prepared according to literature methods. NMR spectra were recorded on a Jeol 300 MHz spectrometer. ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4 . All ^{31}P NMR spectra were proton-decoupled. All X-ray data was collected on a Rigaku XtaLab Mini (ROW) diffractometer using Mo- $K\alpha$ radiation. Crystals were mounted on a nylon loop using Paratone N oil. Experiments were carried out at 173 K. Absorption correction was applied using multi-scan methods (CrysAlisPro; Rigaku, 2018).³³ Initial structure solutions were found using SHELXT³⁴ and least-squares refinements were performed using SHELXL.³⁵ Hydrogen atoms were placed ideally.

Experiments forming **1** were conducted in CD_3CN solution in J-Young NMR tubes. In a typical experiment, $[Pd(\text{triphos})(PPh_3)](BF_4)_2$ (6.0 mg, 5.6 μmol) was dissolved in 0.55 mL of CD_3CN , transferred to the NMR tube, and a stoichiometric amount of the base was added. The solution turned from a beige color to bright yellow. H_2 was added, and the NMR spectra were collected for several days, over which time no further changes were observed. Crystals of **1** were then grown from a CD_3CN solution of **1** and $t\text{BuTMG}$ that had been layered with diethyl ether. In the structure of **1**, two acetonitrile solvates were removed from the refinement using PLATON/SQUEEZE as described above.³⁶

Experiments forming **2** were conducted in a Vigor glovebox under an N₂ atmosphere. A solution of [Pd(PNP)Cl]Cl (127 mg, 0.205 mmol) was dissolved in THF, and a solution of KOtBu (17.2 mg, 1.53 mmol) in THF was added. The reaction mixture was stirred overnight, and the reaction was filtered. The rusty red-colored solid was washed with THF, then extracted into MeCN. The rust-colored precipitate dissolved to give a bright orange color, and this solution was filtered. The filtrate was dried, giving 45.9 mg of yellow solid (47.5%). After crystallization from acetonitrile/diethyl ether, 35.4 mg of yellow crystals were obtained (37% yield). In the structure of **2**, the phenyl groups comprising C7-12 and C13-18 were disordered and refined using EADP and SADI restraints.

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