

Free and Metal-Coordinated (*N*-Isocyanimino)triphenylphosphorane: X-ray Structures and Selected Reactions

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An improved procedure for the synthesis of (*N*-isocyanimino)-triphenylphosphorane, $\text{C}\equiv\text{N}-\text{N}=\text{PPh}_3$ (**3**), is described. The X-ray structure analysis reveals an unusually small N–N–P angle $[115.2(2)^\circ]$ and an N–N bond order of only about 1.5, which indicates considerable $\text{C}\equiv\text{N}-\text{N}^+-\text{P}^+$ participation and electronically more-isolated functional groups (CN, P=N) in the isocyanide than, for example, in the isomeric $\text{N}\equiv\text{C}-\text{N}=\text{PPh}_3$ (**4**) [$\text{C}-\text{N}=\text{P} = 123.0(4)^\circ$, C–N bond order = 2.0]. In order to gain insight into the stereochemical consequences of metal coordination of **3**, an X-ray structural study of $[\text{Cr}(\text{CO})_5\text{C}\equiv\text{N}-\text{N}=\text{PPh}_3]$ (**5**) was also undertaken. Surprisingly, the central bond lengths (C–N, N–N) and angles (C–N–N) remain practically unchanged with noticeable coordination effects occurring only at the periphery of **5**, with the N–N–P angle $[112.3(2)^\circ]$ further decreased by 15° , the elongated (by 7σ) P–N bond, the somewhat shortened (by 4σ) P–C(Ph) bonds and even shorter C–H(Ph) bonds on the one side, and the well-known $\text{Cr}-\text{C}(\text{O})_{\text{trans}}$ contraction on the other. Treatment of **5** or its tungsten derivative with anhydrous Brønstedt and Lewis acids such as CF_3COOH , HCl, COS, phosgene or,

most efficiently, $[\text{PdCl}_2(1,5\text{-COD})]$ causes $\text{CN}\rightarrow\text{NC}$ isomerisation to give $[\text{M}(\text{CO})_5\text{N}\equiv\text{C}-\text{N}=\text{PPh}_3]$ [$\text{M} = \text{Cr}$ (**6**), W (**7**)]. In solution, $[\text{PdCl}_2(\text{CNPh}_3)_2]$ and $\text{Ph}_3\text{BCNNPPH}_3$ (**8**) slowly isomerize even without additional acid to give both free and Pd-coordinated **4** and $\text{Ph}_3\text{BNCNPPH}_3$ (**9**), respectively. In the presence of catalytic amounts of $[\text{PdCl}_2(1,5\text{-COD})]$, **3** is converted into **4** and the dimer $\text{Ph}_3\text{PN}-\text{C}(\text{CN})=\text{N}-\text{NPPH}_3$ (**10**) in an almost 1:1 ratio. The optimised geometries of the methyl derivatives of **3** and **4**, namely $\text{Me}_3\text{P}=\text{N}-\text{N}=\text{C}$ (**3c**) and $\text{Me}_3\text{P}=\text{N}-\text{C}\equiv\text{N}$ (**4c**), are in excellent agreement with the experimental data; major differences between the isomers (P–N–N angle, N–N bond length) are explained by the higher electronegativity of the isocyano group as compared to the CN substituent, which, in turn, is a better π -acceptor). The reaction path of the isomerisation of **3** to **4** (**3c** to **4c**) has also been studied computationally and been found to proceed via an $[(\text{P})=\text{N}^A-\text{N}=\text{C}^A(\text{N}^A-\text{C}^A)]$ cyclic transition state. The overall process is exothermic by 50 kcal mol^{-1} .

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Introduction

Despite occasional reports for almost 100 years now, *N*-isocyanides, i.e. species with the structural element $\text{C}\equiv\text{N}-\text{N}$, still remain an exotic class of compounds. This holds particularly true of the parent molecule, isodiazomethane, $\text{C}\equiv\text{N}-\text{NH}_2$ (**1**).^[1] Its mere naming as something which it is *not*, viz. diazomethane, reflects the uncertainties and difficulties connected with the discovery and understanding of

this very labile substance.^[2] Staudinger, in search of diisocyan, $\text{CN}-\text{NC}$, obviously was the first to get hold of **1**, and very remarkably assigned it the correct structure of an isocyanoamine.^[3] Later, for more than 30 years, alternative constitutions were favoured, and it was not until 1968 that Müller et al. returned to Staudinger's formula.^[2,4] In the mid-1970s, the first metal complexes of **1** were synthesised in our laboratory both from Müller's isodiazomethane solutions and, much more elegantly, from a stable, storable derivative, Wiberg's $\text{C}\equiv\text{N}-\text{N}(\text{SiMe}_3)_2$ (**2**), by hydrolysis at the protecting metal.^[5,6] The only disadvantage of **2** was its problematic accessibility, requiring many steps and costly low-temperature techniques. In 1980 we reported a novel precursor of **1** which is synthesised in a one-step procedure from cheap starting materials and actually proved to be a key substance in *N*-isocyanide chemistry.^[7,8] In the following we present an improved preparation of $\text{C}\equiv\text{N}-\text{NPPH}_3$ (**3**), its X-ray structure in comparison with that of its pentacarbonylchromium complex, and its metal-catalysed CN/NC-isomerisation and dimerisation reactions. In addition, quantum chemical calculations have been carried out to get more insight into the electronic and structural properties of

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[‡] Quantum chemical computations.

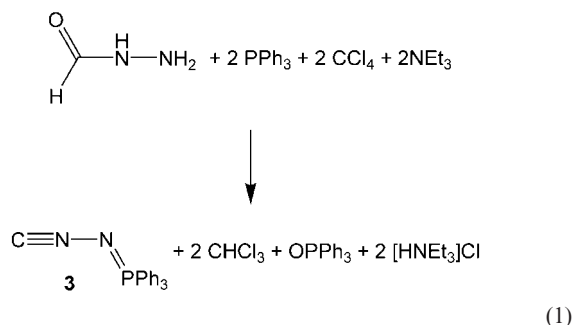
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compounds **3** and **4** and the reaction path of their respective isomerisation.

Results

(*N*-Isocyanimino)triphenylphosphorane: Synthesis and X-ray Structure

The title compound was prepared by reaction of *N*-formylhydrazine with two equivalents of Appel's three-component reagent, which serves two purposes, viz. dehydration of the formamido group and masking of the primary amine function [Equation (1)].^[7]



Repetition of the procedure as published, however, turned out to be difficult, and in only a few cases could yields of the claimed order of magnitude be reached. As reasons presumably responsible for this problem we have identified an incomplete reaction and decomposition of the desired product during work-up (vide infra). Taking this into account, in the modified procedure refluxing of the reaction mixture is prolonged and immediately followed by basic hydrolysis (with aqueous Na_2CO_3) of the highly acidic phosphorus(v) intermediates (e.g. $\text{Ph}_3\text{PCl}^+\text{Cl}^-$) and separation of the organic layer (containing **3**) from the aqueous one (see Experimental Section).

Single crystals suitable for an X-ray structure analysis were grown by slowly cooling a solution of **3** in warm ethanol. The molecule shows the expected bent structure at the imino nitrogen N1 (Figure 1). Structural investigations of iminophosphoranes generally reveal a considerable flexibility of this nitrogen as regards its hybridisation. $\text{P}=\text{N}-\text{X}$ angles ranging from 119° up to 137° indicate that this is primarily sp^2 with a tendency to higher s participation. The unusually small angle in **3** [$115.2(2)^\circ$] conversely points to more p -character (i.e. some $\text{C}\equiv\text{N}^+-\text{N}^--\text{P}^+\text{Ph}_3$ form), which causes the phosphorus and the isocyano nitrogen atoms to get as close as $2.494 \text{ \AA}$ which is actually the shortest nonbonding distance between non-hydrogen atoms in this crystal structure.

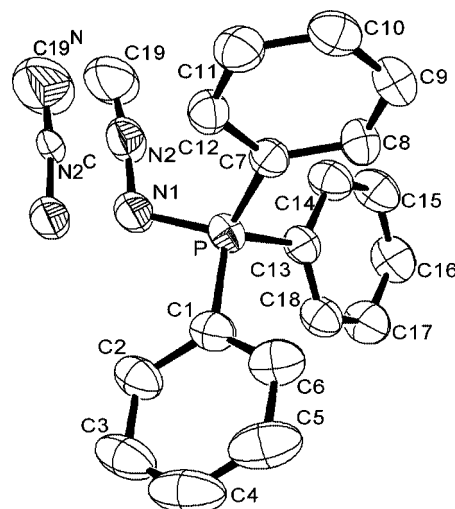
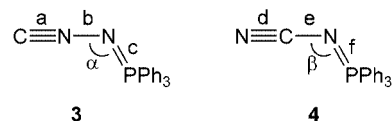


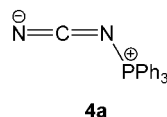
Figure 1. ORTEP drawing of the molecular structure of **3** (30% probability). The effect on the thermal ellipsoids of the functional group of a refinement cycle with interchanged scattering factors for C19 and N2 ("CN/NC test") is also shown. Both the abnormal blowing up of C19 (treated as an N atom) and the odd shrinkage of N2 (calculated as C) clearly exclude the cyanide form of **3**, as does the R value which increased by 0.34%. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: $\text{P}-\text{N1}$ 1.604(2), $\text{P}-\text{C}_{\text{av}}$ 1.797, $\text{N2}-\text{N1}$ 1.345(4), $\text{N2}-\text{C19}$ 1.154(4); $\text{P}-\text{N1}-\text{N2}$ $115.2(2)$, $\text{N1}-\text{N2}-\text{C19}$ $173.4(3)$.

Interestingly, the corresponding $\text{P}=\text{N}-\text{C}$ angle [$123.0(4)^\circ$] in the isomeric cyanoiminophosphorane **4** (Scheme 1) is much wider, while the $\text{C}\equiv\text{N}$ and $\text{P}=\text{N}$ bond lengths are identical with those in **3** within one or two standard deviations.^[9] Furthermore, the CN distances agree perfectly with the rated value for an ideal CN triple bond, and both PN bonds come very close to a true PN double bond ($1.57 \text{ \AA}$) as derived from experimental data.^[10] Another major difference occurs in the remaining bonds, however. The $\text{N1}-\text{N2}$ bond distance in **3** [$1.345(4) \text{ \AA}$] lies halfway between an NN single ($1.44 \text{ \AA}$) and an NN double bond ($1.24 \text{ \AA}$), while the $\text{C}-\text{N}(\text{imine})$ bond in **4**, which is formally a single bond, is only slightly longer than a typical CN double bond ($1.27 \text{ \AA}$). The two functional groups ($\text{C}\equiv\text{N}$ and $\text{P}=\text{N}$) are thus electronically more isolated in the isocyanide **3** than in the cyano isomer **4**, an observation which has been made many times in systems of the type $\text{C}\equiv\text{N}(\text{N}=\text{C})-\text{X}\cdots\text{Y}$. A more realistic description of the bonding in **4** – although not in **3** (!) – might therefore make use of a further resonance formula such as **4a**.



Scheme 1. Schematic formulae with selected bonding parameters (bond lengths in $\text{\AA}$): $a = 1.154(5)$, $b = 1.345(4)$, $c = 1.604(2)$, $a = 115.2(2)^\circ$; $d = 1.151(9)$, $e = 1.301(7)$, $f = 1.595(4)$, $\beta = 123.0(4)^\circ$.

Deviations from a tetrahedral configuration at the P atom in **3** are marginal. The phenyl rings show the well-known propeller-like arrangement with dihedral angles rel-



ative to the P–N1–N2–C19 plane of 18.3° (Ph1), 69.8° (Ph2) and –69.6° (Ph3).

The intermolecular contacts (≤ 3.5 Å) were also calculated. With the exception of a weak N $\cdots$ H–C bridge between a phenyl hydrogen and N1, which also shows strong intramolecular interactions with two hydrogen atoms, none of the contacts lies substantially below the sum of the corresponding van der Waals radii.

X-ray Structure of Pentacarbonyl[(*N*-isocyanimino)-triphenylphosphorane]chromium (**5**): Stereochemical Consequences of Metal Coordination

Metal coordination of a stable isocyanide is routine, and C $\equiv$ N–N=PPh₃ (**3**) is no exception. Preparation of the chromium complex **5** proceeds by substitution of THF in the photolytic intermediate [Cr(CO)₅THF];^[7,8] suitable crystals for the X-ray study were obtained from dichloromethane.

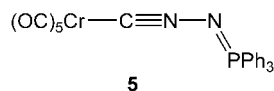


Figure 2 presents the overall geometry as expected for the combination of the functional *N*-isocyanide ligand **3** and the metal complex fragment Cr(CO)₅, together with selected bonding parameters. The first point of interest is the stereochemistry of the Cr(CO)₅ entity, which reflects the ligand properties of the incoming group. While all of the CO ligands experience the donating capacity of a typical isocyanide ligand, it is the *trans*-CO ligand which has to take the lion's share of the electronic charge transported onto the metal. In the present case the result is particularly striking: the Cr–(CO)_{trans} bond in **5** is shortened to 1.861(3) Å as compared, for example, to that in Cr(CO)₆ (1.918 Å) or those of Cr(CO)₅ adducts of several other functional isocyanides such as [Cr(CO)₅CNCH₂C(Me)(CH₂NC)₂] [1.882(2) Å],^[11] [Cr(CO)₅CNC $\equiv$ N] [1.913(4) Å],^[12] [Cr(CO)₅–CNC(=O)Ph] [1.899(3) Å],^[13] and [Cr(CO)₅CNC $\equiv$ CPh] [1.896(4) Å],^[14] while the average Cr–(CO)_{cis} distance in **5** only drops to 1.895 Å. A much less significant effect, yet one pointing in the same direction, is the corresponding lengthening of the C–O bonds, which again is more pronounced for (C–O)_{trans} [1.140(4) Å] than for the averaged (C–O)_{cis} (1.135 Å).

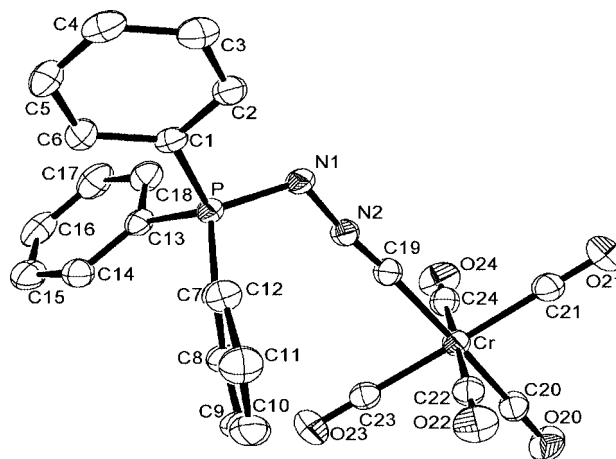


Figure 2. ORTEP drawing of the molecular structure of **5** (30% probability). The isocyanide nature of the ligand was ascertained by a “CN/NC test” (cf. caption of Figure 1), which resulted in unrealistic temperature factors and an increase of the *R* value by 0.66%. Selected bond lengths [Å] and angles [°]: P–N1 1.618(2), P–C_{av} 1.787, N2–N1 1.345(3), N2–C19 1.151(4), Cr–C19 2.031(3), Cr–C20_{trans} 1.861(3), (Cr–C_{cis})_{av} 1.895, (C20–O20)_{trans} 1.140(4), (C–O)_{cis,av} 1.135; P–N1–N2 112.3(2), N1–N2–C19 174.2(2), Cr–C19–N2 176.9(2).

The Cr–CN bond length is 2.031(3) Å, which fits well into the range of 2.00–2.05 Å determined so far for pentacarbonyl(*N*-isocyanide)chromium complexes. This is long in comparison with the corresponding values for [Cr(CO)₅(C-isocyanide)] complexes [*d*(Cr–CNC) < 2.00 Å] and clearly indicates a lower degree of π back-bonding.

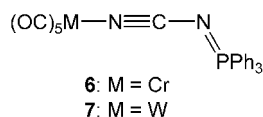
Turning to the new ligand itself, which, according to what we know from the stereochemistry of the CrC₆ surrounding, is a markedly better donor than common *C*-isocyanides, we were surprised to find its central skeleton practically unchanged: the C $\equiv$ N and N–N bond lengths are absolutely identical in **3** and **5**, and the 3 σ deviation in the quasi-linearity of the C–N–N atomic sequence is insignificant; again, coordination effects are noticed only at the periphery of CNNPPh₃ [as they appeared – most distinctly – at the other end of the molecule, namely the remote *trans*-CO ligand (see above)]: the more acute N–N–P angle of 112.3(2)° [–2.9° (15 σ)], which brings the P and N2 atoms even closer together, the slight elongation [by 0.014 Å (7 σ)] of the P–N bond and, remarkably, the somewhat shortened P–C(Ph) bonds [–0.010 Å (4 σ)]. All these data point to a considerable Ph₃P⁺–N[–]–N⁺C[M[–]] participation in the overall bonding in **5** by which extra electronic charge is transferred to M(CO)₅. Obviously, the N–N bond is not as insulating as inferred from a comparison with the nitrile (**4a**) earlier on. These findings are perhaps best understood in terms of Gutmann's “pile up” and “spill over” effects accompanying Lewis acid–Lewis base interactions.^[15]

Selected Reactions

CN/NC Isomerisations of (*N*-Isocyanimino)-triphenylphosphorane Complexes

The action of aqueous trifluoroacetic acid on CNNPPh₃ coordinated to pentacarbonyl-group VI metal fragments

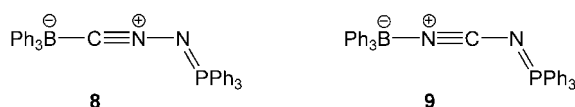
proceeds with hydrolysis of the (imino)N–P bond to give isodiazomethane complexes, occasionally in excellent yield (group VI metal = chromium).^[7,8] A totally different reaction occurs, however, when $[\text{Cr}(\text{CO})_5\text{CNNPPH}_3]$ (**5**) is treated with anhydrous acids: when allowed to stand for 1–2 days a solution of **5** in dichloromethane containing a few drops of CF_3COOH undergoes complete conversion of the isocyanide ligand into its nitrile isomer to form **6**.



The same effect can be achieved by passing a stream of dry HCl through a solution of **5**. While protic acids seem not to prompt the corresponding tungsten complex to isomerize, Lewis acids like COS and COCl_2 are effective with both metal complexes. Even more sophisticated Lewis acids such as $[\text{PdCl}_2(1,5\text{-COD})]$ work if the reaction is carried out under a CO atmosphere. Thus, under 1 bar of CO **5** isomerizes quantitatively within 3–4 days, whereas in a rotating autoclave under a CO pressure of 10 bar the transformation is complete in 24 h. Without carbon monoxide, Pd metal separates slowly from the solution, which then turns deep green. Complexes **6** and **7** were adequately characterised by their analytical and IR spectroscopic data (see Experimental Section); the data of **6** are in full agreement with the data reported for the compound which has earlier been synthesised directly by photolysis of hexacarbonylchromium in the presence of NCNPPH_3 .^[16]

At palladium(II), **3** isomerizes without the need for any additional acid. After two weeks two strong new bands appear at 2230 and 2180 cm^{-1} in the IR spectrum of a solution of $[\text{PdCl}_2(\text{CNNPPH}_3)_2]$ ^[8] in dichloromethane in place of the very weak original $\nu(\text{CN})$ (2200 cm^{-1}). Of these, the absorption at 2180 cm^{-1} can unambiguously be assigned to the free NCNPPH_3 , while the band at 2230 cm^{-1} fits into the range of palladium-coordinated nitrile species.

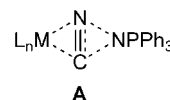
With equimolar amounts of triphenylboron, **3** forms an almost colourless crystalline adduct **8** which is air-stable and soluble in chlorinated hydrocarbons. In the IR spectrum, the weak CN stretch of the free ligand at 2067 cm^{-1} has been replaced by a new weak band at much higher wavenumbers (2230 cm^{-1}). As frequency shifts even of this order of magnitude are quite possible for isocyanide–BPh₃ adducts – for the corresponding (*N*-isocyanodialkylamine)triphenylboron species $\text{Ph}_3\text{B}-\text{CN}-\text{NR}_2$, $\Delta\nu(\text{CN})$ [$\nu(\text{CN})_{\text{complex}} - \nu(\text{CN})_{\text{free}}$] amounts to 135 cm^{-1} ^[17] – we can be sure that we are still dealing with the isocyanide isomer. In the end, this was unequivocally confirmed by its slow conversion in chloroform into **9**, which exhibits a very strong IR absorption at even higher wavenumbers (2280 cm^{-1}).



$\text{CN} \rightleftharpoons \text{NC}$ isomerisations in both directions are by no means rare.^[18] What is surprising here, though, is how spon-

taneously and smoothly they occur under the applied mild reaction conditions. It is true that these kinds of isomerisations are very common in cyanometal coordination polymers and are known to happen immediately by what has been termed a “flip-over” mechanism, however, the organic synthesis of nitriles by isomerisation of free *C*-isocyanides requires severe heating over a longer period.^[19] Obviously, the involvement of at least one metal (or metalloid, e.g. SiMe_3 ^[18,20]) is essential for the activation energy to be sufficiently small. Strangely enough, this is particularly born out by the functional *N*-isocyanide under consideration, which, as a free ligand, cannot be transformed into its isomer at all, either thermally, say by refluxing in THF or chloroform, or by protonation.

If we accept a synchronous mechanism with a “rotating” $\text{C}\equiv\text{N}$ species between the fixed metal and NPPH_3 groups, or, which comes down to the same thing, a migration of these groups about a stationary $\text{C}\equiv\text{N}$, perhaps via some bicyclic transition state of the type **A**, it seems plausible that the addition of an acid (Brønsted or Lewis) to the imino nitrogen greatly enhances the (less pronounced) migration tendency of the iminophosphorane group (as $\text{HN}=\text{PPh}_3$). At any rate, in the absence of an acid the $[\text{M}(\text{CO})_5\text{-CNNPPH}_3]$ complexes do not show any sign of isomerisation even after standing for weeks in various solvents.

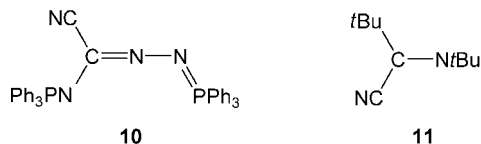


A closely related case of a $\text{CN} \rightarrow \text{NC}$ isomerisation to the one presented here is the rearrangement of a coordinated fulminate into an isomeric isocyanate ligand. This reaction occurred on attempted protonation of difulminato-bis(triphenylphosphane)platinum to produce the then unknown isofulminic acid ($\text{C}\equiv\text{N}-\text{OH}$) stabilized in a complex.^[21] Later, we studied the spontaneous isomerisation of $[\text{W}(\text{C}\equiv\text{N}-\text{O})(\text{CO})_5]^-$ and found it to be strongly solvent-dependent.^[22]

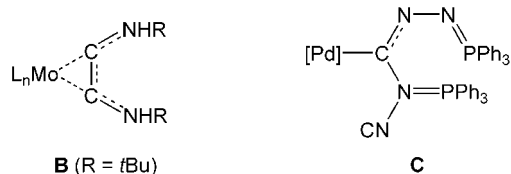
Catalytic Isomerisation and Dimerisation of **3**

From the findings discussed above, it was obvious that we should study the possibility of a catalytic isomerisation of **3** with traces of a metal component. As such, $[\text{PdCl}_2(1,5\text{-COD})]$ was chosen and found to produce complete disappearance of the weak $\nu(\text{CN})$ band at 2067 cm^{-1} within 20 h at ambient temperature. What appeared, however, were two absorptions at 2180 and 2220 cm^{-1} instead of the only one expected. Work-up finally resulted in two products: the isomeric (*N*-cyanoimino)triphenylphosphorane (**4**), which has already been synthesised by Appel and co-workers and was identified on the basis of its elementary analysis, its melting point and its IR data,^[23,24] and a second pale -yellow compound **10**, which was recrystallised from dichloromethane/diethyl ether and showed the same analytical composition but double the molecular mass. The IR spectrum with a

weak to medium intensity band at 2200 cm^{-1} [$\nu(\text{C}\equiv\text{N})$], a $\nu(\text{C}=\text{N})$ absorption at 1520 cm^{-1} and two $\nu(\text{P}=\text{N})$ features at 1110 [$\nu(\text{P}=\text{N}-\text{N})$] and 1300 cm^{-1} [$\nu(\text{P}=\text{N}-\text{C})$], as well as the ^{31}P NMR spectrum, which contains two singlets at $\delta = 24$ and 11 ppm , are in perfect agreement with the suggested structure for **10**.



A catalytic dimerisation of isocyanides has so far only been reported in one case, that of *tert*-butyl isocyanide with trace amounts of BF_3 to give **11**.^[25] On the other hand, there are numerous examples of stoichiometric C-C couplings of C-bonded species in the ligand spheres of metal complexes,^[26] with Lippard's reductive dimerisation of *tert*-butyl isocyanide ligands in $[\text{Mo}(\text{CN}t\text{Bu})_6]\text{I}$ to give **B** being among the first.^[27] Still, for the case at hand it seems most plausible to assume a mechanism **C** in analogy to that of the well-known metal-catalysed α -additions to isocyanides (or isocyanide insertions), which proceed via a primary nucleophilic attack at the metal-bonded isocyano carbon.^[28] Actually, all the necessary "instruments" are there: thus, we have shown that *N*-isocyanides are prone to nucleophilic attack even in less activating metal complexes,^[8,29] **3** carries a strong nucleophile in the form of the imino nitrogen, and N–N cleavage is a common occurrence in *N*-isocyanide chemistry.^[17,30,31]



Computational Section

Quantum chemical calculations were performed to gain a detailed insight into the electronic and structural properties of the compounds **3** and **4**. To simplify the problem, the phenyl substituents in **3** and **4** were replaced by methyl groups, and the geometries of the resulting compounds **3c** and **4c** were optimised at the B3LYP/6-311+G** level of theory. ZPEs were determined at the same level. The frequencies were also analysed at this level to confirm that the optimised geometries correspond to minima (NIMAG = 0) or first-order transition states (NIMAG = 1). A transition-state search was performed using the QST3 method. NBO analyses were performed at the above-mentioned level of theory. All computations were run using the Gaussian98W suite of programs and NBO 3.1, as implemented in G98W.^[32]

Discussion

Table 1 contains selected stereochemical parameters of compounds **3**, **3c**, **4** and **4c**. In general, the differences between the bond lengths and angles of the phenyl-substituted systems **3** and **4**, as obtained from X-ray analyses, and the data computed for the corresponding methyl species (**3c** and **4c**) are minor and easily explained by the exchange at P1 of phenyl for methyl (cf. Figure 3 and Table 1). Thus, the elongation of the P1–N1 bonds in **3c** and **4c** is clearly a consequence of the decreased electron-acceptor capacity of the trimethylphosphonio moiety. Other points of interest are the deviations between **3c** and **4c** (**3** and **4**, respectively), especially those of the P1–N1–X angles (**3**, **3c**: X = NC; **4**, **4c**: X = CN).

Table 1. Comparison of the experimental bonding parameters of **3** and **4** with those obtained from geometry optimisation (B3LYP/6-311+G**) (**3c**, **4c**).

Bond length [Å]	3	3c (<i>C_s</i>)	4	4c (<i>C_s</i>)
P1–N1	1.604	1.620	1.595	1.600
N1–N2	1.345	1.342		
N1–C1			1.301	1.318
C1–N2	1.154	1.176	1.151	1.167
Bond angle [°]				
P1–N1–N2	115.2	114.5		
P1–N1–C1			123.0	121.8

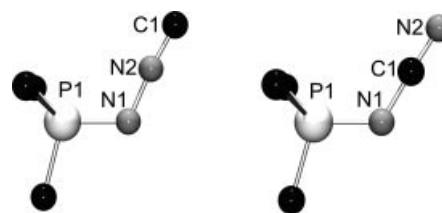


Figure 3. Representative structural elements in **3** (**3c**) (left) and **4** (**4c**) (right).

The exchange of N2 by the less electronegative C1 in **3c** (to give **4c**) changes the electronic nature of N1. NBO analyses assume N1 in both compounds to carry a lone pair of *p*-character oriented perpendicular to the symmetry plane of **3c** and **4c**. This results in an overall hybridisation of sp^2 for the remaining three substituents of N1 in this plane: the PMe_3 group, the second lone pair and the $-\text{NC}$ (**3c**) or $-\text{CN}$ (**4c**) group. The specific breakdown of the overall sp^2 hybridisation into the contributions of N1 to each bond results in the data listed in Table 2. The most noticeable changes are obviously caused by very different hybridisations of the lone pair and the bond to the (iso)ciano group, whereas the hybridisation of the N1–P1 bond remains nearly unchanged. The former can easily be explained by Bent's rule:^[33] electronegative substituents force the central atom (N1) to increase the *p*-character of the corresponding bond. The isocyano substituent in **3c** is clearly more electronegative than the cyano function in **4c**, which results in the very different orbital hybridisations of N1 in the two N1–X bonds (Table 2). As a result, the P1–N1–N2

angle in **3c** is smaller than the P1–N1–C1 angle in **4c**. In **3c**, both bonds (P1–N1 and N1–N2) have contributions from N1 hybridisations with *p* coefficients close to 3.0, hence the P1–N1–N2 angle is expected to be way below 120° (computed: 114.5°). In **4c**, the average hybridisation of the respective two bonds is $sp^{2.1}$ (cf. Table 2), which should give rise to an angle of about 120° (computed: 122°). These values are in excellent agreement with the corresponding X-ray data of the phenyl derivatives **3** (115°) and **4** (123°; Table 1).

Table 2. Orbital hybridisation of N1 based on NBO analyses (B3LYP/6-311+G**).

	3c (X = NC)	4c (X = CN)
N1–PMe ₃	$sp^{2.8}$	$sp^{2.5}$
N1–X	$sp^{2.9}$	$sp^{1.7}$
Lone pair (in plane)	$sp^{1.1}$	$sp^{1.9}$

As described above, the N1–N2 bond in **3** lies halfway between an N–N single and an N–N double bond, whereas the N1–C1 bond in **4** is much closer to a C–N double bond. The same observations are made in the case of the computed structures **3c** and **4c**, and can again be explained on the basis of NBO analyses: both lone pairs of N1 interact with the two mutually perpendicular π^* -orbitals of the C1–N2 bond. Since the π -bonds between C1 and N2 are polarized towards the nitrogen atom, the π^* -orbitals have larger coefficients at C1, and hence the cyano group in **4c** is a

much better π -acceptor than the isocyano function in **3c**. The respective donor–acceptor interactions were computed at the B3LYP/6-311+G** level resulting to be about 63 kcal mol^{−1} for **4c** and 33 kcal mol^{−1} for **3c**. The experimentally observed pronounced multiple-bond character of the N1–CN bond in **4** is thus confirmed computationally.

Finally, the reaction path of the isomerisation of **3** to **4** (**3c** to **4c**) was studied computationally using the QST3 method as implemented in Gaussian98W. The reaction profile is shown qualitatively in Figure 4, quantitative details are given in Table 3, and geometric parameters of TS1, TS2 and IM are given in Figure 5 (see also Supporting Information).

Table 3. Relative energies of the species in Figure 3 (B3LYP/6-311+G** incl. uncorrected ZPE).

	Relative energy [kcal mol ^{−1}]
3c	+50.3
TS1	+81.7
IM	+79.8
TS2	+82.1
4c	±0.0

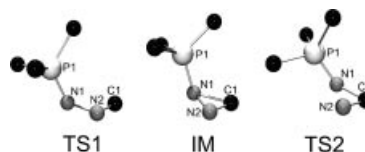


Figure 5. Geometrical data of TS1, IM and TS2 (bond lengths in Å). TS1: P1–N1 1.631, N1–N2 1.556, N1–C1 2.018, N2–C1 1.215; N1–N2–C1 92.7°. IM: P1–N1 1.646, N1–N2 1.613, N1–C1 1.681, N2–C1 1.234; N1–N2–C1 71.0°, N1–C1–N2 65.1°. TS2: P1–N1 1.629, N1–N2 1.861, N1–C1 1.597, N2–C1 1.215; N1–C1–N2 81.7°.

As shown in Figure 4, the reaction proceeds with formation of a new σ -bond between the $2p_z$ lone pair at N1 and the terminal carbon atom, via the transition state TS1 (E_a = 31.4 kcal mol^{−1}), to the cyclic intermediate IM. The latter reacts with cleavage of the N–N bond via TS2 (E_a = 2.3 kcal mol^{−1}) to the rearrangement product **4c**. The overall process is exothermic by 50.3 kcal mol^{−1} (cf. Table 3).

The experimentally observed lowering of the activation energy for the isomerisation by addition of Lewis acids can also be explained on this basis: the formation of donor–acceptor complexes between the intermediate IM and Lewis acids stabilizes the former by decreasing the repulsive interactions of lone pairs (see Figures 4 and 5).

Experimental Section

General Remarks: All experiments were performed under argon in dry, argon-saturated solvents. The (*N*-isocyanimino)triphenylphosphorane metal complexes [M(CO)₅CNNPPh₃] [M = Cr (**5**), W] and [PdCl₂(CNNPPh₃)₂] were prepared according to literature procedures.^[7,8] IR spectra were recorded on a Perkin–Elmer 621 or a Beckman IR 12 spectrometer. NMR spectra (³¹P) were recorded on a Jeol JNM-PS-100. Mass spectra were recorded on a Varian CH-5 (excitation energy 70 eV). Microanalyses (C,H,N) were obtained with a Heraeus CHN Rapid-Elementanalysator. Molecular

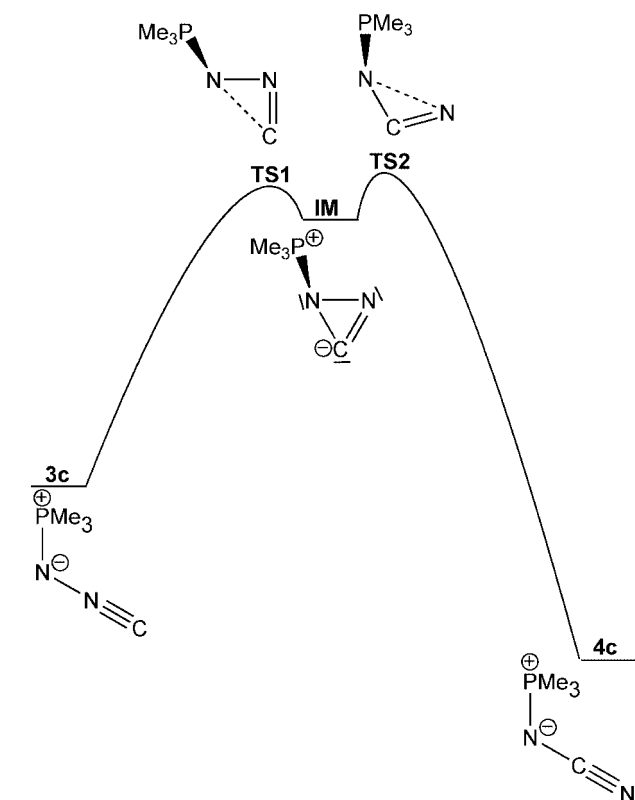


Figure 4. Reaction profile of the isomerisation of **3c** to **4c** at the B3LYP/6-311+G** level (including uncorrected ZPE at the same level).

weights were determined in CH₂Cl₂ solution using a Knauer Dampfdruck Osmometer, and melting or decomposition points were determined with a Büchi Model 510 melting point apparatus and are uncorrected.

Preparation of (*N*-Isocyanimino)triphenylphosphorane (**3**). Revised

Procedure: CH₂Cl₂ (600 mL), PPh₃ (157.4 g, 0.6 mol), NEt₃ (freshly distilled from KOH; 50.6 g, 0.5 mol) and formylhydrazine (dried in high-vacuum at 45 °C; 15.3 g, 0.25 mol) were placed in a reaction flask which had been dried with a heat-gun under high-vacuum. The slurry was then heated to 50–60 °C, and CCl₄ (77.0 g, 0.5 mol) was added dropwise over a period of about 30 min. The mixture was kept at 50–60 °C for at least 5–6 h. After cooling to room temp., 250 mL of a saturated aqueous Na₂CO₃ solution was added, the layers were separated, and the aqueous layer was washed with two 50-mL portions of CH₂Cl₂. The combined organic phases were dried with Na₂SO₄ and filtered. After evaporation of the solvent, the residue was dried under high vacuum, pulverised, stirred in 200 mL of ethanol/water (1:1.5) and collected on a frit. Recrystallisation from hot ethanol yielded 30.2 g (40%) of an orange-brown crystalline material (m.p. 159–160 °C, dec.). IR (KBr): $\tilde{\nu}$ = 2067 cm⁻¹ w [v(CN)]; 1117 s, 1099 sh [v(PN)]. C₁₉H₁₅N₂P (302.32): calcd. C 75.49, H 5.00, N 9.27; found C 75.69, H 4.99, N 9.40.

CN/NC-Isomerisation of Pentacarbonyl(*N*-isocyanimino)triphenylphosphorane]chromium (5**) with Protic Acids and COS:** A few drops (8–10) of CF₃COOH were added, with stirring, to a solution of [Cr(CO)₅CNNPPh₃] (**5**; 1.48 g, 3.0 mmol) in dry CH₂Cl₂ (25 mL). After standing for 48 h at room temp. the volatile components were removed under high vacuum and the residue was dissolved in a small amount of CH₂Cl₂ and chromatographed on silica gel in *n*-hexane (3.5 × 20 cm column) with a CH₂Cl₂/*n*-hexane (3.5:1) eluent. Slow evaporation of the bright yellow phase resulted in the cyano isomer **6** as yellow to green crystals.

Similar results were obtained by (a) passing a rapid stream of dry HCl through the above solution for a few seconds and keeping it at room temp. for 14 h, and (b) by treating a solution of [Cr(CO)₅CNNPPh₃] (1.48 g, 3.0 mmol) in THF (30 mL) with an excess of COS at 45 °C for 24 h and applying the same work-up procedure to the reaction mixtures. The yields (non-optimised) varied between 30 and 70% (see also below).

CN/NC-Isomerisation of Pentacarbonyl(*N*-isocyanimino)triphenylphosphorane]chromium (**5**) with [PdCl₂(1,5-COD)]. Preparation of Pentacarbonyl[(*N*-cyanimino)triphenylphosphorane]chromium (**6**):

(a) [Cr(CO)₅CNNPPh₃] (**5**; 990 mg, 2 mmol) and [PdCl₂(1,5-COD)] (290 mg, 1 mmol) were dissolved in 90 mL of toluene/CH₂Cl₂ (2:1) under a CO atmosphere and stirred for one week at room temp. Every two days the CO atmosphere was renewed. After evaporation of the solvent, the residue was extracted with diethyl ether. The extract was filtered and concentrated, and the product **6** crystallised on cooling to about –35 °C as yellow-green crystals. Yield: 60%.

(b) A mixture of **5** (1.98 g, 4.0 mmol) and [PdCl₂(1,5-COD)] (580 mg, 2.0 mmol) in 60 mL of toluene/CH₂Cl₂ (2:1) was placed in a 500-mL rotation autoclave and reacted under a CO pressure of 10 atm for 2 d. The work-up procedure was the same as in (a) and yielded 1.4 g (71%) of yellow-green crystalline **6**, m.p. 107 °C (dec.; ref.^[16] 102–106 °C). IR (KBr): $\tilde{\nu}$ = 2240 cm⁻¹ s [v(NC)]; 2065 s, 1920 vs, 1870 sh [v(CO)]; 1260 s, br. [v(PN)]. C₂₄H₁₅CrN₂O₅P (494.4): calcd. C 58.31, H 3.06, N 5.67; found C 58.49, H 3.07, N 5.55.

CN/NC-Isomerisation of Pentacarbonyl(*N*-isocyanimino)triphenylphosphorane]tungsten. Preparation of **7:** COCl₂ (30 mL of a 0.1 M solution in THF) was added to a solution of [W(CO)₅CNNPPh₃]

(940 mg, 1.5 mmol) in 30 mL of CH₂Cl₂. After stirring for 2 h at room temp., the solvent was removed in vacuo and the raw product was dissolved in a few millilitres of CH₂Cl₂. Cooling to about –35 °C gave 432 mg (48%) of **7** as yellow-green crystals, m.p. 125 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2230 cm⁻¹ s [v(NC)]; 2060 m, 1905 vs, br., 1870 sh [v(CO)]; 1280 s, br. [v(PN)]. C₂₄H₁₅N₂O₅PW (626.22): calcd. C 46.03, H 2.41, N 4.47; found C 45.89, H 2.39, N 4.62.

CN/NC-Isomerisation of (*N*-Isocyanimino)triphenylphosphorane at BPh₃

Preparation of [(*N*-Isocyanimino)triphenylphosphorane]triphenylborane (8**):** A solution of CNNPPh₃ (**3**; 906 mg, 3.0 mmol) in 35 mL of CH₂Cl₂ was added dropwise to a solution of BPh₃ (730 mg, 3.0 mmol) in 30 mL of CH₂Cl₂ at 0 °C. After stirring for 1.5 h at 0 °C the product was precipitated with petroleum ether and stored overnight at –18 °C to give **8** (1.2 g, 74%) as off-white crystals, m.p. 153 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2225 cm⁻¹ w [v(CN)]; 1190 sh, 1150 sh, 1120 vs, br. [v(PN)]. C₃₇H₃₀BN₂P (544.5): calcd. C 81.63, H 5.55, N 5.15; found C 81.63, H 5.87, N 4.88. Compound **8** is thermally stable in the solid state and can be kept under nitrogen at room temp.

CN/NC Isomerisation of [(*N*-Isocyanimino)triphenylphosphorane]triphenylborane. Preparation of [(*N*-Cyanimino)triphenylphosphorane]triphenylborane (9**):** A solution of **8** (1.09 g, 2.0 mmol) in 10 mL of CHCl₃ was stored for 2 weeks at room temp. After evaporation of the solvent the crude material was treated with ethanol. The insoluble white powder (**9**) was filtered off and dried in high vacuum. Yield: ca. 600 mg (55%). IR (KBr): $\tilde{\nu}$ = 2280 cm⁻¹ vs, 2085 sh [v(NC)]; 1350 s, 1320 sh [v(PN)]. C₃₇H₃₀BN₂P (544.5): calcd. C 81.63, H 5.55, N 5.15; found C 80.03, H 5.80, N 5.14.

Catalytic Isomerisation and Dimerisation of (*N*-Isocyanimino)triphenylphosphorane (3**). Preparation of (*N*-Cyanimino)triphenylphosphorane (**4**) and (CNNPPh₃)₂ (**10**):** A catalytic amount of [PdCl₂(1,5-COD)] (29 mg, 0.1 mmol) was added, with stirring, to a solution of CNNPPh₃ (**3**; 3.25 g, 10.75 mmol) in 40 mL of CH₂Cl₂. Stirring was continued for 20 h at room temp., after which time the solvent was removed in vacuo and the residue stirred in 30 mL of ethanol for 1 h. The insoluble yellow product was filtered off and recrystallised from CH₂Cl₂/Et₂O to give 1.6 g (50%) of pure **10**, m.p. 221 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2220 cm⁻¹ w [v(NC)]; 1300 s, br., 1275 sh, 1130 sh, 1110 s, br. [v(PN)]; 1540 s, 1480 w, 1140 s, 1040 sh, 1030 s. C₃₈H₃₀N₄P₂ (604.60): calcd. C 75.49, H 5.00, N 9.27, P 10.25; found C 75.81, H 5.05, N 9.21, P 10.14. Mol. mass calibrated against PPh₃: 616.

The brown ethanolic solution was evaporated to dryness and the solid residue was dissolved in 10 mL of warm CH₂Cl₂. Compound **4** (1.45 g, 45%) separated in the form of a light-brown powder at 0 °C, m.p. 188 °C (dec.). [ref.^[23,24] 192–196 °C (dec.)]. IR (KBr): $\tilde{\nu}$ = 2180 cm⁻¹ vs [v(NC)]; 1270 s, br. [v(PN)]. C₁₉H₁₅N₂P (302.3): calcd. C 75.49, H 5.00, N 9.27; found C 74.73, H 5.07, N 9.18.

X-ray Structure Determinations: Single crystals of **3** were obtained by slowly cooling a warm ethanol solution of **3**; those of **5** were grown from dichloromethane. Crystallographic data of **3** and **5** were collected on a Philips PW1100 diffractometer in the ω –2 θ scan mode using Ag-K α radiation (λ = 0.5596 Å) and a graphite monochromator (Table 4). The phase problem in **3** was solved by direct methods, and that of **5** by applying the heavy atom approach. Neither absorption nor extinction corrections were carried out. In both cases, all hydrogen positions could be obtained from ΔF syntheses yet were not included in the final cycles of refinement. All calculations were carried out using the program system SHELX-76^[34] with scattering factors for neutral atoms taken from the literature.^[35] The molecular plots were produced with the ORTEP program.^[36]

Table 4. Crystal data and structure refinement of **3** and **5**.

	3	5
Empirical formula	C ₁₉ H ₁₅ N ₂ P	C ₂₄ H ₁₅ CrN ₂ O ₅ P
Formula mass	302.3	494.4
Crystal size [mm]	0.4 × 0.3 × 0.15	0.4 × 0.3 × 0.2
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> [Å]	9.680(2)	12.817(5)
<i>b</i> [Å]	16.602(4)	15.431(3)
<i>c</i> [Å]	10.356(2)	12.536(4)
β [°]	110.55(1)	116.03(4)
<i>V</i> [Å ³]	1558.38	2227.86
<i>Z</i>	4	4
$\rho_{\text{calcd.}}$ [Mg m ⁻³]	1.288	1.473
$\mu_{(\text{Ag-K}\alpha)}$ [cm ⁻¹]	0.94	2.80
<i>F</i> (000)	632	1008
Temperature [K]	293	233
2 θ range for data collection [°]	13.62–49.42	3.10–47.64
Reflections collected	9661	10721
Independent reflections	2180	4921
<i>R</i> _{int} [%]	0.0511	0.0419
Observed reflections	1835 [<i>I</i> ≥ 2.5 σ (<i>I</i>)]	3691 [<i>I</i> ≥ 2.5 σ (<i>I</i>)]
Weighting scheme	$w = 1/[\sigma^2(F_o) + 9 \times 10^{-5} F_o^2]$	$w = 1/[\sigma^2(F_o) + 10^{-6} F_o^2]$
<i>R</i> ₁ / <i>wR</i> ₂ [<i>F</i> > 4 σ (<i>F</i>)]	0.0439/0.0426	0.0409/0.0397

CCDC-279551 (for **3**) and -279552 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Gaussian98W archive entries and cartesian coordinates of all computed species.

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