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Isocyanide-functionalised phosphines: an uncharted field

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While numerous functional phosphines have been reported, investigated, and applied to date, phosphines equipped with an additional isocyanide moiety have received only limited attention. This frontier article provides an overview of the chemistry of these compounds, which has not yet been comprehensively reviewed. In particular, different types of phosphinoisocyanides (*viz*., isocyanide-tethered phosphines as well as compounds featuring the direct P–NC bond) and routes towards them, in addition to the reactivity, coordination behaviour, and transformations of these molecules in both their native and coordinated forms, are discussed. In particular, this overview focuses on the synthesis, reactivity, and coordination properties of phosphines bearing the isocyanide moiety at the organic (aliphatic or aromatic) or organometallic (ferrocene) scaffold. Also discussed is the chemistry of isocyanophosphines of the R_2PNC type that arise, in metal-coordinated form (as C-donors), *via* reactions between cyano complexes and chlorophosphines. All these compounds have remarkable synthetic potential that mainly stems from the specific reactivity of isocyanides, which readily undergo diverse addition and insertion reactions, thereby providing access to, *e.g.*, complexes with monodentate and P,C-chelate or bridged phosphinoisocyanide ligands and structurally unique carbene complexes.

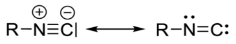
Introduction

Triorganophosphines[1] are indispensable ligands for coordination chemistry and catalysis by transition metal complexes, useful reagents in organic synthesis, and efficient organocatalysts.[2] The attractiveness of phosphines lies in an elaborate synthetic methodology that makes them broadly accessible, as well as the possibility to fine-tune their donor (basicity) and steric properties through organic substituents.[3] Besides changing the hydrocarbyl substituents attached to the phosphorus atom, the family of phosphines can be significantly expanded by incorporating additional "functional" groups into their structures. This strategy broadens design possibilities for phosphine ligands because the introduced groups can, among others, act as additional donor sites, changing the overall coordination behaviour, alter the polarity and solubility of the compounds, and serve as reactive groups that provide access to other hybrid phosphines through their synthetic modifications. Numerous hybrid phosphines have been reported, featuring additional nitrogen-based, sulfonate, carboxylate, and other groups.[4] However, despite the considerable progress, some areas remain less explored, including phosphines bearing an isocyanide moiety.

Organic isocyanides are reactive molecules,[5] whose unique chemistry reflects their partial carbene character (Fig. 1).[6] Despite interesting and useful reactivity, however, the development of their chemistry and practical applications has been hindered by their repugnant penetrating odours (especially for volatile compounds).

Of particular relevance to coordination chemistry is the ability of isocyanides to coordinate transition metals as σ-donor/π-acceptor ligands,[7] which are isoelectronic with CO. In addition, isocyanides readily add nucleophiles or insert into metal–carbon bonds, which can be advantageously applied in the preparation of metal carbene complexes.[8]

As stated above, phosphines bearing an isocyanide functional group remain rare. This can be partly attributed to difficulties related to their synthesis,[9] mainly to the sensitivity of the phosphine groups, which can react with the agents typically used to prepare isocyanides or under the conditions used to obtain them. Although only a handful of compounds have been reported to date, rich and unconventional reactivity has already been reported. This frontier article highlights the unique chemistry of phosphinoisocyanides to encourage further research focused on these disregarded yet attractive



$$R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}| \longleftrightarrow R{-}\ddot{N}{=}C:$$

Fig. 1 Two major resonance forms of an isocyanide molecule.

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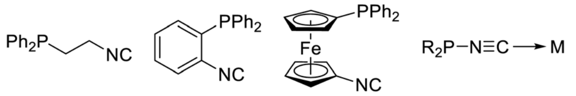


Fig. 2 Representative examples of phosphinoisocyanides reported to date (M is a transition metal).

compounds. Attention is paid to isocyanide-tethered triorganophosphines as well as to phosphinoisocyanides featuring the direct P–NC bond that arise by transformations of coordinated cyanide ligands in transition metal complexes (Fig. 2).

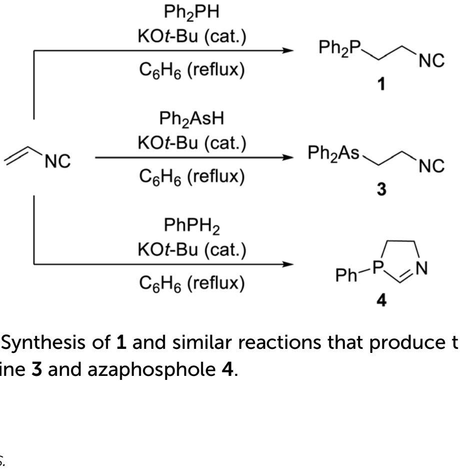
The chemistry of isocyanide-functionalised phosphines

Early developments

Very likely the first, intentionally prepared and explored phosphinoisocyanide was (2-isocyanoethyl)diphenylphosphine (**1**). This compound, reported in a communication in 1971[10] and a full report three years later,[11] was obtained by base-catalysed addition of diphenylphosphine across the double bond in vinylisocyanide[12] (Scheme 1). The reaction was performed in the presence of a catalytic amount of potassium *tert*-butoxide in refluxing benzene, and the product was isolated by vacuum distillation and obtained as a viscous liquid in 53% yield. An analogous route was previously used to prepare the isomeric nitrile, $Ph_2PCH_2CH_2CN$ (**2**), from acrylonitrile. This reaction, however, proceeded spontaneously without any catalyst.[13]

A similar method was successfully applied for the preparation of the corresponding arsine, $Ph_2AsCH_2CH_2NC$ (**3**; 31% yield). In contrast, the reaction involving phenylphosphine resulted in an air-sensitive, oily product, analysed as $C_9H_{10}NP$, lacking the isocyanide group according to the IR spectra. This compound was formulated as 3-phenyl-4,5-dihydro-3*H*-1,3-azaphosphole (**4**), arising from the addition of a P–H bond across vinylisocyanide and subsequent intramolecular cyclisation by the addition of the second P–H bond.[14]

Compound **1** was characterised using ^{1}H NMR and IR spectroscopy, mass spectrometry, elemental analysis, and molecular weight determination by osmometry. The diagnostic CN stretching vibration in the neat sample was detected at 2154 cm^{-1}.



Scheme 1 Synthesis of **1** and similar reactions that produce the corresponding arsine **3** and azaphosphole **4**.

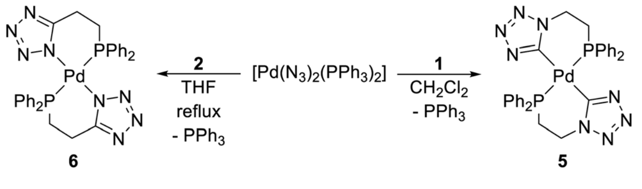
In both early reports,[10,11] only preliminary coordination experiments with [Cr(nbd)(CO)$_4$] (nbd = norbornadiene) were reported for **1**. The reaction performed in benzene with equimolar amounts of these educts yielded a multinuclear complex tentatively formulated as [Cr$_3$(CO)$_{12}$(**1**)$_4$], with three *cis*-Cr(CO)$_4$ units bridged by two phosphinoisocyanide ligands and coordinated by additional monodentate **1** at both terminal Cr atoms, based on elemental analysis, IR spectra, and molecular weight determination. Arsine **3** reacted similarly.[10,11]

A decade later,[15] isocyanide **1** emerged as part of a panel of donor-substituted nitriles tested in cycloaddition reactions with Rh(I), Ir(I), Pd(II), and Pt(II) azide complexes,[16] particularly for comparison with the structurally related nitrile **2**. Thus, the reaction of [Pd(N$_3$)$_2$(PPh$_3$)$_2$] with an excess of **1** in dichloromethane yielded phosphinotetrazolate complex **5** as a colourless precipitate (80% yield; Scheme 2). A similar reaction with nitrile **2** produced isomeric compound **6**. However, while the reaction with **1** proceeded swiftly, affording **5** within a few minutes at ambient temperature, the cycloaddition of **2** required a longer reaction time and elevated temperature (refluxing THF for 3 days; yield of **6**: 75%). The formulation of the tetrazolate complexes was supported only by elemental analysis; no additional characterisation data were provided.

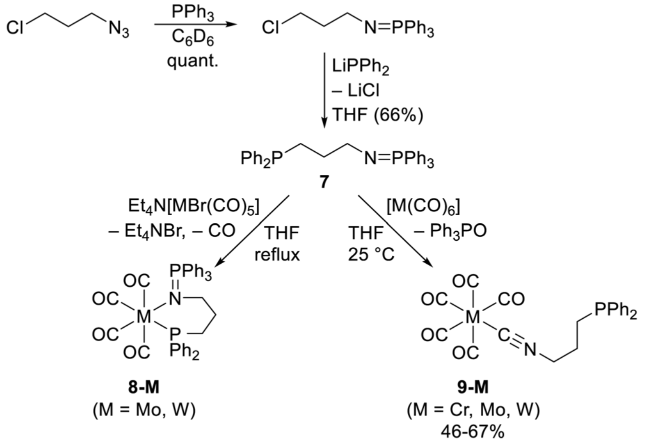
Analogous reactions between **1** and [Pt(N$_3$)$_2$(PPh$_3$)$_2$], [Pd(N$_3$)(CN)(PPh$_3$)$_2$], and [Pd(N$_3$)(CH$_2$CN)(PPh$_3$)$_2$] resulted in product mixtures. According to spectroscopic analysis, the authors reported that cycloaddition occurred even in these cases (as determined from a decreased intensity of the azide vibrations in the IR spectra), but the species formed contained "isocyanide ligands".[15]

Complexes with phosphinoisocyanides formed from phosphinoiminophosphorane proligands

The first defined *complexes* with phosphinoisocyanide ligands were obtained by a rather unusual, indirect route from phosphine-iminophosphorane **7**, which is accessible by standard functional group manipulation.[17] In a thermally induced reaction with Et$_4$N[MBr(CO)$_5$] (M = Mo, W), this compound yielded the expected P,N-chelate complexes [M(CO)$_4$(**7**-κ^{2}P,N)] (**8-M**, M = Mo, W; Scheme 3). However, similar reactions with homoleptic carbonyl complexes, [M(CO)$_6$] (M = Cr, Mo, W), afforded products with C-bound phosphinoisocyanide ligands, [M(CO)$_5$(Ph$_2$P(CH$_2$)$_3$NC-κC)] (**9-M**, M = Cr, Mo, W). The presence of the coordinated isocyanide moiety in **9-M** was inferred from



Scheme 2 Reactions of isomeric phoshinoisocyanide **1** and phosphinonitrile **2** with a Pd(II)-azide complex.



Scheme 3 Synthesis of iminophosphorane **7** and its reactions, which produce iminophosphorane and phosphinoisocyanide complexes.

the spectroscopic data ($\nu_{NC} \approx 2174$ cm^{-1} and δ_C(NC) 163, 153, and 143 ppm for M = Cr, Mo, and W, respectively), whereas the ^{31}P NMR spectra exhibited resonance due to the uncoordinated phosphine moiety ($\delta_P \approx -18$ ppm). The conversion of **7** to the phosphinoisocyanide ligand was explained by nucleophilic attack of the iminophosphorane moiety on the metal-bound CO and subsequent elimination of triphenylphosphine oxide (formally an aza-Wittig reaction[18]).

The reaction of **7** with [(η^5-C_5H_5)FeI(CO)$_2$] took a similar course, resulting in a cationic P,C-chelate complex [(η^5-C_5H_5)Fe(CO)(Ph$_2$P(CH$_2$)$_3$NC-κ^{2}C,P)]I (**10**; ν_{NC} 2089 cm^{-1}, δ_C(NC) 184, δ_P 54) and triphenylphosphine oxide. Complex **10** underwent smooth anion exchange with NH$_4$[PF$_6$] to yield [(η^5-C_5H_5)Fe(CO)(Ph$_2$P(CH$_2$)$_3$NC-κ^{2}C,P)][PF$_6$] (**10a**; see the molecular structure in Fig. 3) and, more significantly, reacted with *n*-propylamine under amine addition across the coordinated isocyanide group to selectively produce P-chelating diaminocarbene complex **11** (Scheme 4).[17]

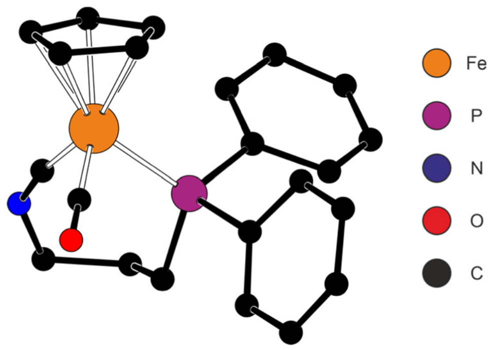
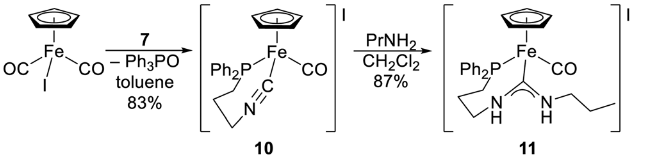


Fig. 3 View of the complex cation in the structure of [(η^5-C_5H_5)Fe(CO)(Ph$_2$P(CH$_2$)$_3$NC-κ^{2}C,P)][PF$_6$] (**10a**). The diagram was drawn using the data deposited at the CCDC (deposition number: 1307387). One of two crystallographically independent cations is shown. Positions of the hydrogen atoms were not reported.



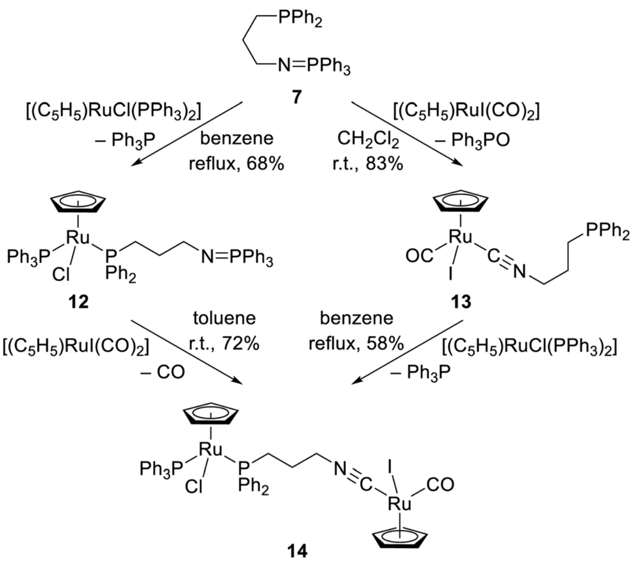
Scheme 4 Synthesis of P,C-chelating phosphinoisocyanide complex **10** and its conversion to diaminocarbene complex **11**.

The fundamental role of the carbonyl ligands in transformation of the phosphorane moiety of **7** was proven *via* reactions with isoelectronic (η^5-cyclopentadienyl)ruthenium(II) complexes (Scheme 5). While the reaction of **7** with [(η^5-C_5H_5)RuI(PPh$_3$)$_2$] resulted in displacement of one PPh$_3$ ligand to afford **12**, that with [(η^5-C_5H_5)RuCl(CO)$_2$] produced isocyanide complex **13**. Compounds **12** and **13** could be transformed into the P,C-bridged dinuclear complex **14** after reaction with the "other" Ru precursor (Scheme 5).[17]

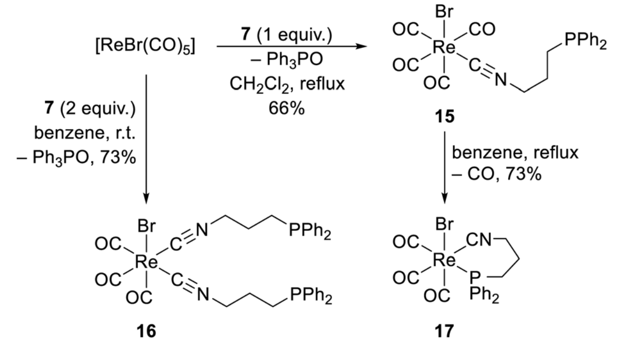
Similar proligand transformations were observed during the reaction of **7** with [ReBr(CO)$_5$], which produced isocyanide complexes **15** (ν_{NC} 2222 cm^{-1}) and **16** (ν_{NC} 2137 cm^{-1}), depending on the reaction stoichiometry (1 : 1 or 2 : 1) (Scheme 6). Upon heating in benzene, complex **15** underwent thermally induced intramolecular displacement of one CO ligand, producing P,C-chelate complex **17** (ν_{NC} 2219 cm^{-1}).

In a reaction with [Re$_2$(CO)$_{10}$], compound **7** also yielded isocyanide complex **18**, which transformed into P,C-bridged complex **19** after irradiation with a medium-pressure mercury lamp (Scheme 7). Subsequent oxidative cleavage of the Re–Re bond with bromine produced "ligand-bridged" dinuclear compound **20**.[17]

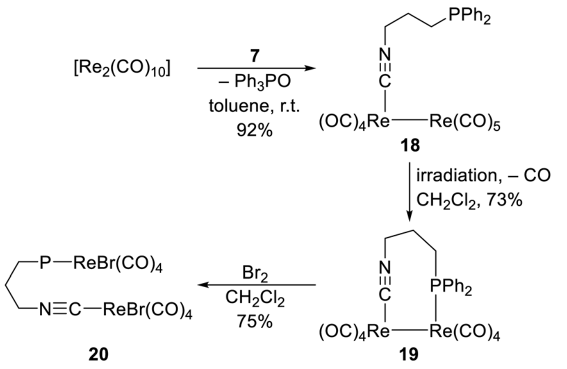
More recently,[19] the reaction of an iminophosphorane proligand with [(η^5-C_5H_5)FeI(CO)$_2$] followed by nucleophilic



Scheme 5 Synthesis and mutual interconversion of (η^5-C_5H_5)Ru complexes from **7**.

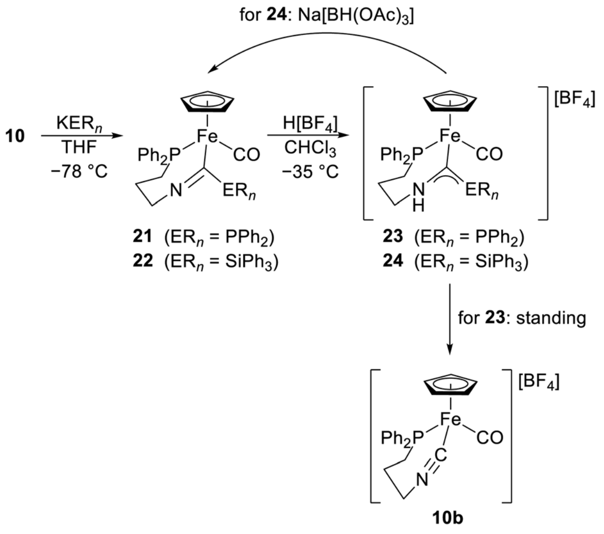


Scheme 6 Synthesis and reactions of Re(I)-carbonyl complexes with phosphinoisocyanide ligands formed from iminophosphorane **7**.



Scheme 7 Dinuclear Re(I) complexes with a phosphinoisocyanide ligand coordinated in different modes.

addition across the Fe-bound isocyanide group was utilised to prepare a pair of phosphino-amino and silyl-amino carbene complexes (Scheme 8). In particular, the addition of $KPPh_2$ or $KSiPh_3$ to complex **10** in THF at −78 °C generated imidoyl complexes **21** and **22** in 80% and 28% yields (δ_C(imidoyl) = 214.3 and 234.4 ppm), respectively. Subsequent protonation with $H[BF_4]$ at −35 °C produced the respective carbene complexes **23** and **24** in essentially quantitative yield (δ_C(carbene) = 276.4 and 299.4 ppm, respectively). However, while silylcarbene **24** could be isolated as a stable yellow solid, the phosphinocarbene **23** decomposed even at −35 °C under the liberation of Ph_2PH and regeneration of the parent isocyanide complex (now as a $[BF_4]^-$ salt **10b**) within several hours. Silylcarbene **24** converted slowly back to **22** after the action of $Na[BH(OAc)_3]$ under vacuum.[20]



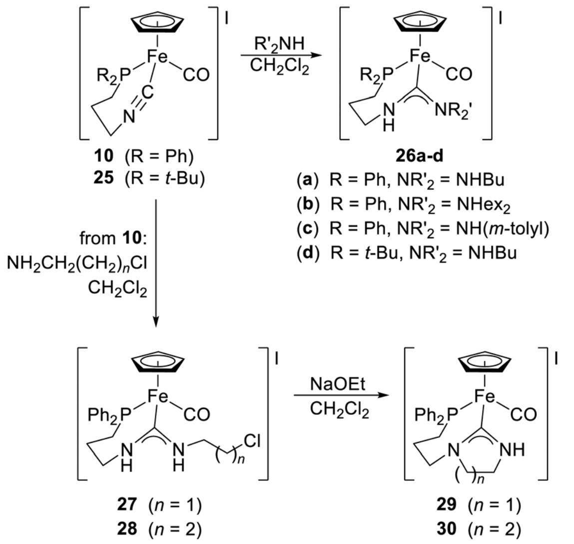
Scheme 8 Synthesis of carbene complexes from phosphinoisocyanide complex **10**.

In subsequent work,[20] complex **10** and an analogous compound bearing a di-*tert*-butylphosphino substituent (**25**) were used to prepare a series of protic diaminocarbene complexes **26a–d** by the addition of amines (Scheme 9, yields ≈90%). Compounds with cyclic carbene groups (**29** and **30**) were obtained similarly from suitable ω-chloroalkyl amines and subsequent base-induced cyclisation.

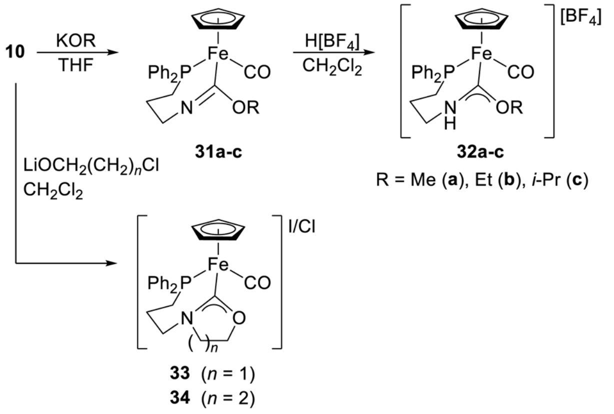
The family of reported compounds was expanded to include additional oxy-amino carbenes **32a–c**, resulting in high yields *via* the addition of KOR and subsequent protonation with $H[BF_4]$, similar to the preparation of silyl- and phosphino-substituted carbenes. Compounds with cyclic carbene moieties **33** and **34** were obtained in one step using ω-chloroalkyl alkoxides as the reagents (Scheme 10). In addition to the standard spectroscopic and analytical characterisation, the representative compounds were structurally authenticated using single-crystal X-ray diffraction analysis and further analysed computationally with emphasis on changes in their electronic structure.

Isocyanide-tagged triarylphosphines

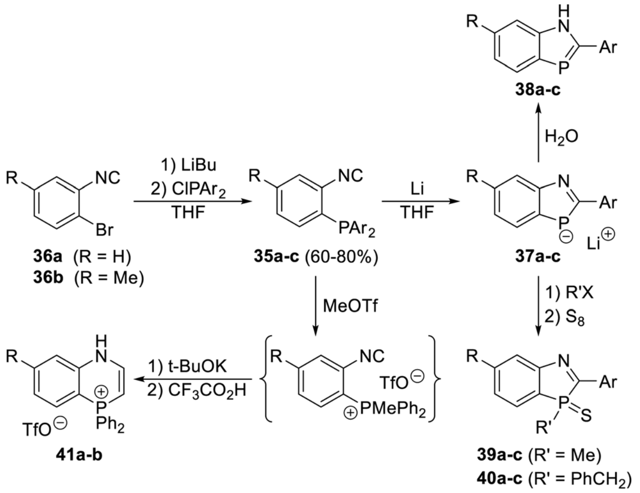
In 2015,[21] Duan and Mathey reported the preparation of isocyanide-substituted triarylphosphines **35a–c** (Scheme 11).



Scheme 9 Synthesis of diaminocarbene complexes from **10** and **25** (Bu = *n*-butyl, Hex = *n*-hexyl).



Scheme 10 Preparation of oxy-amino carbene complexes from **10**.



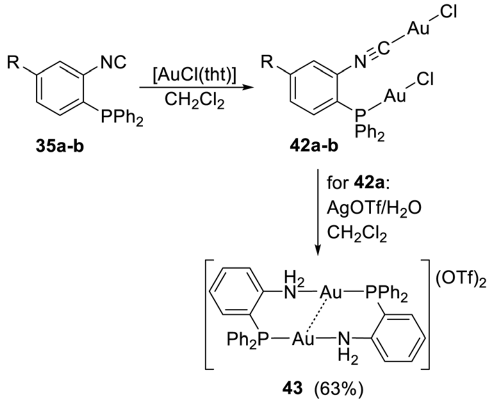
Scheme 11 Synthesis and reactions of isocyanide-substituted triarylphosphines [R/Ar = H/Ph (**a**), Me/Ph (**b**), and H/*p*-tolyl (**c**)].

These compounds were obtained from substrates with a preinstalled isocyanide moiety, namely, by lithiation of 2-bromoaryl isocyanides **36a–c** and subsequent quenching of the nonisolated lithio intermediate with chlorophosphines. DFT calculations of **35a** have shown that the frontier molecular orbitals were delocalised. However, while the HOMO included the phosphorus lone pair and no contribution from the isocyanide moiety, the LUMO included the isocyanide π* orbital and no orbitals localised at the phosphorus atom. This finding suggested complementary reactivity for the two functional groups.

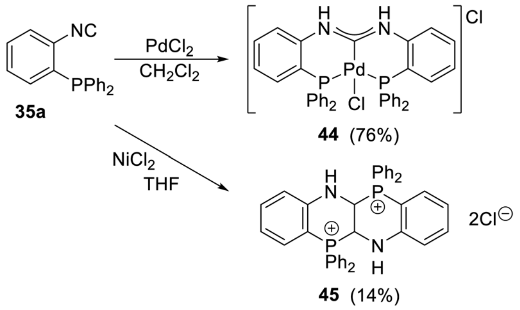
When they were treated with lithium metal in THF, compounds **35a–c** cyclised into azaphospholides **37a–c**. These intermediates were hydrolysed to 2-aryl-1*H*-1,3-benzazaphospholes **38a–c** or, alternatively, alkylated with reactive alkyl halides ($PhCH_2Br$ and MeI) and thionated to yield 3-alkyl-2-aryl-3*H*-1,3-benzazaphosphole sulfides **39a–c** and **40a–c**. Methylation of **35a–b** with methyl triflate produced phosphonium salts, which reacted successively with potassium *tert*-butoxide and with trifluoroacetic acid to afford phosphorinium salts **41a–b** (Scheme 11).

The reaction of **35a–b** with 2 equiv. of [AuCl(tht)] (tht = tetrahydrothiophene) produced bis(chlorogold) complexes **42a–b** (Scheme 12). In the crystal state, complexes **42a–b** assembled in centrosymmetric dimeric arrays interconnected by pairs of weak intermolecular aurophilic contacts[22] (3.46 Å for **42a** and 3.21 Å for **42b**). Chloride removal from **42a** with AgOTf in dichloromethane produced dimeric gold(I) phosphinoamine complex **43**, whose structure was stabilised by intramolecular aurophilic interactions according to X-ray diffraction analysis (Au⋯Au = 3.00 Å). The transformation of the ligand molecule was explained by hydrolysis of the isocyanide group to formamide, followed by further hydrolysis or, alternatively, a decarbonylation step, ultimately producing a phosphinoamine.

The reaction of **35a** with $PdCl_2$ in CH_2Cl_2 resulted in carbene complex **44** (Scheme 13; the molecular structure in shown in Fig. 4), very likely *via* accidental hydrolysis of the isocyanide group to an amine in one ligand and subsequent addition of the amine to the isocyanide moiety of a second ligand, either free or coordinated to Pd. A different reaction was observed with $NiCl_2$ in THF, producing insoluble dibenzazaphosphorinium salt **45**, albeit in a low yield.



Scheme 12 Synthesis of Au(I) complexes from **35a** and **35b** [R = H (**a**), Me (**b**)]. Intramolecular Au⋯Au interaction in the molecule or **43** are indicated by a dashed line.



Scheme 13 Reactions of **35a** with $PdCl_2$ and $NiCl_2$.

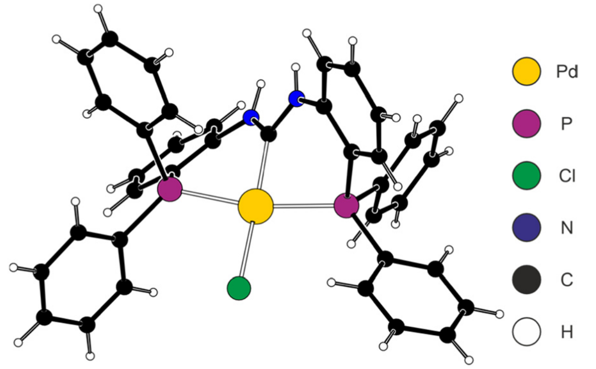
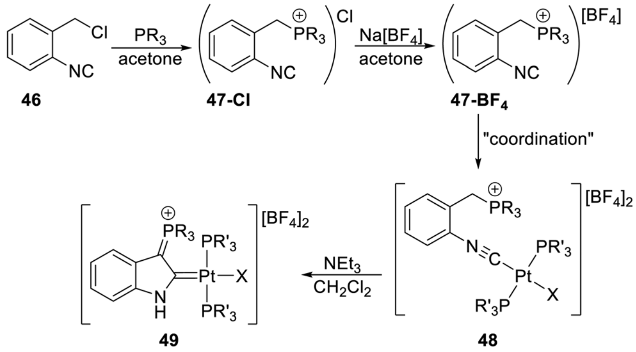


Fig. 4 View of the complex cation in the structure of **44**·CH_2Cl_2. The diagram was generated from the data deposited at the CCDC (deposition number: 1063708).

In this context, the peculiar reactivity of phosphonium salts with isocyanoaryl substituents investigated by Michelin and coworkers is also worth mentioning (Scheme 14). The phosphonium salts were obtained by the standard alkylation of tertiary phosphines with 1-(chloromethyl)-2-isocyanobenzene (**46**)[23] (a similar reaction in the presence of LiBr produced the corresponding bromide salts) and were converted to the less hygroscopic tetrafluoroborate salts **47-BF$_4$** by subsequent anion exchange. These salts were used to prepare a series of standard Pt(II)-isocyanide complexes **48**, which underwent smooth cyclisation into ylide-substituted indol-2-ylidene complexes **49** in the presence of triethylamine as a mild base.[24]

Ferrocene-based phosphinoisocyanide

Ferrocene-based phosphinoisocyanide **50** was reported in 2017.[25] Its preparation (Scheme 15) was based on the standard formylation of 1′-(diphenylphosphino)-1-aminoferrocene (**51**) and dehydration of the intermediate formamide. First, however, it was necessary to find a reliable route towards the phosphinoamine precursor.[26] Notably, ferrocene cannot be directly nitrated because of facile oxidation to the cationic ferrocenium. Hence, the standard procedure for the preparation of anilines, which consists of nitration and reduction, could not be applied.[27] For the preparation of **51**, a method based on sequential lithiation/fuctionalisation of 1,1′-dibromoferrocene (**52**)[28] and azide intermediates was devised. This route, however, required additional protection of the already present phosphine moiety to avoid unwanted Staudinger reaction.[29] The approach applied initially employed phosphine sulfide intermediates (route A in Scheme 15). In the first step, bromide **52** was lithiated and phosphinylated to produce phosphine bromide **53**[28b] and subsequently thionated with elemental sulfur to afford phosphine sulfide **53S**. An analogous lithiation/functionalisation step was used to introduce an azide group to give **54S**. The reaction of this rather unstable intermediate with Raney® nickel proceeded under the reduction of both the phosphine moiety and the azide group to yield an intermediate amine, which was converted *in situ* to formamide **55**. Unfortunately, the transformation of **54S** into **55** typically proceeded in low yields (<30%) and was accompanied by the reductive removal of the phosphorus substituent[30] to produce FcNHCHO as a side product (Fc = ferrocenyl).



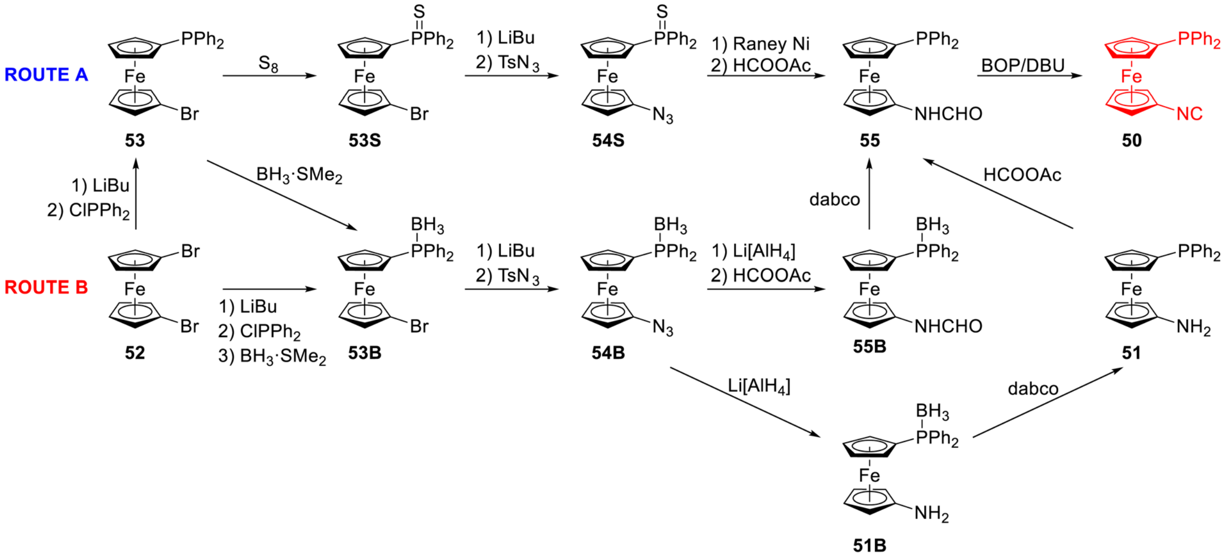
PR_3	PR'_3	X
PMe_nPh_{3-n} (n = 0–3)	PPh_3	Cl
PMe_3	PMe_nPh_{3-n} (n = 1, 2)	Me
PMe_3	$Ph_2PCH{=}CHPPh_2$ (*cis*)	Cl
$P(CH_2Ph)_nPh_{3-n}$ (n = 1–3)	PPh_3	Cl

Scheme 14 Synthesis of isocyanides with phosphonium methyl substituents and their conversion to Pt(II) isocyanide and carbene complexes.

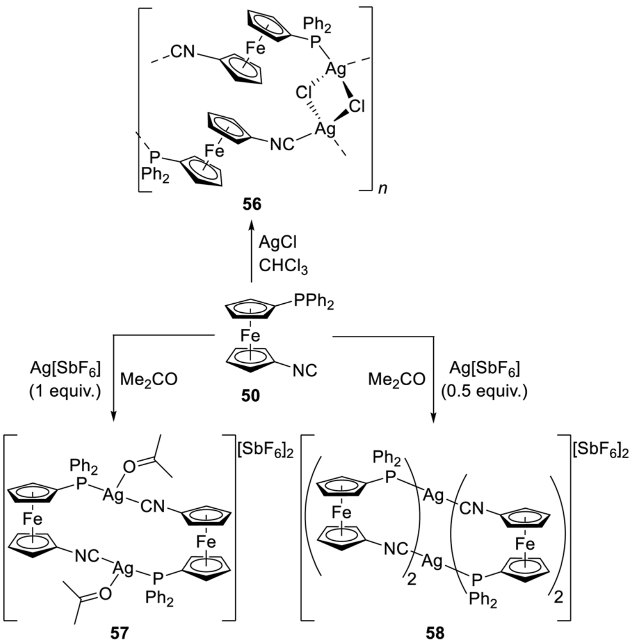
To alleviate these problems, an alternative procedure (route B) was designed involving BH_3-protected intermediates.[31] In this case, adduct **53B** was converted to P-protected azide **54B** and, subsequently, to formamide **55B**. Deprotection with 1,4-diazabicyclo[2.2.2]octane (dabco),[32] ultimately produced formamide **55**. Albeit longer, the "borane route" was better yielding and provided a reliable access to amine **51** and its P-protected form **51B**, which could also be converted to **55**.

Dehydration of **55** into the targeted isocyanide **50** was achieved in good yield (71%) using Castro's reagent (*viz.*, (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate, BOP)[33] and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as a base. The use of conventional reagents such as $POCl_3/NEt_3$ or $COCl_2$/i-Pr_2NH resulted in decomposition.

Compounds **50** and **51** were completely characterised by spectroscopic and electrochemical methods, and their molecular structures were determined by X-ray diffraction analysis. Phosphinoisocyanide **50** was subsequently examined as a hybrid phosphine ligand for group 11 metal complexes.[25] Unfortunately, reactions of **50** with the Cu(I) precursors CuCl and $[Cu(MeCN)_4][BF_4]$ did not yield any defined products. The reaction with AgCl (AgCl : **50** = 1 : 1) in chloroform yielded insoluble coordination polymer **56** built up from dimeric $Ag_2(\mu\text{-}Cl)_2$ units interlinked by P,C-bridging phosphinoisocyanide ligands into infinite linear ribbons (Scheme 16). Complexes with P,C-bridging **50** were also obtained from reactions with $Ag[SbF_6]$, which produced disilver(I) complexes **57** and **58** depending on the metal-to-ligand ratio. Complex **57**, obtained with 1 equiv. of ligand per silver atom, was a symmetrical dimer containing an additional side-on-bonded acetone ligand. When 2 equiv. of **50** were employed, the reaction produced symmetrical, quadruply P,C-bridged disilver(I) complex



Scheme 15 Synthesis of 1′-(diphenylphosphino)-1-isocyanoferrocene (**50**).



Scheme 16 Ag(I) complexes obtained from **50**.

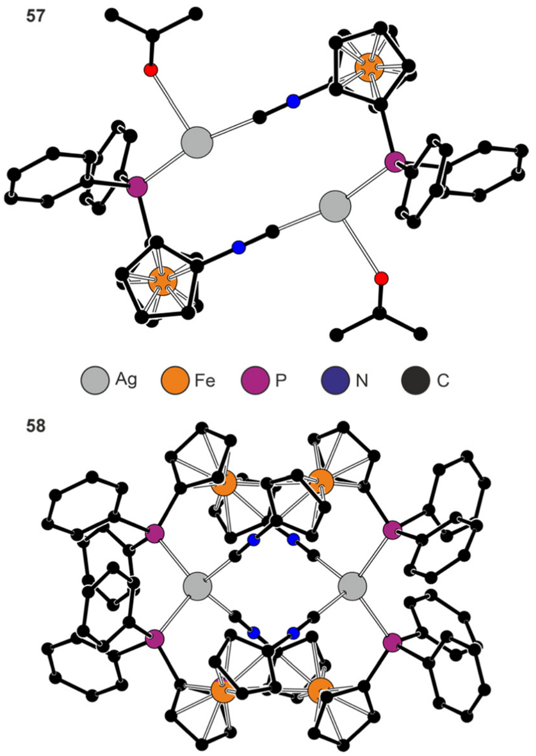
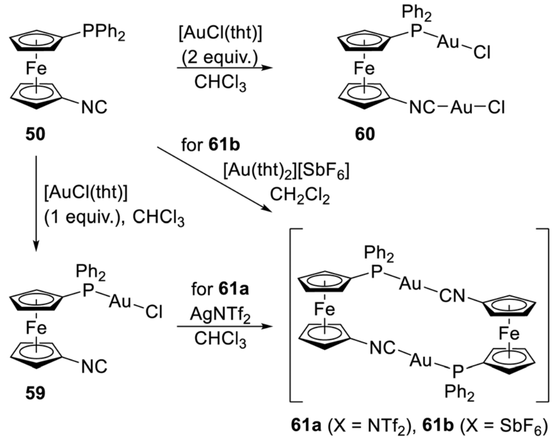


Fig. 5 Views of the complex cations in the structures of $\mathbf{57}\cdot 3Me_2CO$ and **58**. The diagrams were drawn from the original data. Hydrogen atoms are omitted for clarity. CCDC deposition numbers: 1558586 and 1558587.

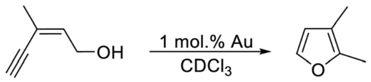
58, wherein the Ag(I) ions had identical distorted tetrahedral P_2C_2 donor sets. The molecular structures of **57** and **58** are presented in Fig. 5.

The interaction of **50** with [AuCl(tht)] as an AuCl surrogate also produced two different complexes depending on the ligand amount (Scheme 17), *viz*. the “phosphine” complex **59** and the digold(I) complex **60**. Subsequent chloride removal with $AgNTf_2$ converted **59** to another digold(I) complex **61a**, featuring equivalent, linear dicoordinate gold(I) centres. Similar compound **61b** with a different counterion was obtained directly from **50** and $[Au(tht)_2][SbF_6]$. The Au⋯Au separation in the structurally characterised cation of **61b** (5.44 Å) suggested the absence of intramolecular aurophilic interactions.

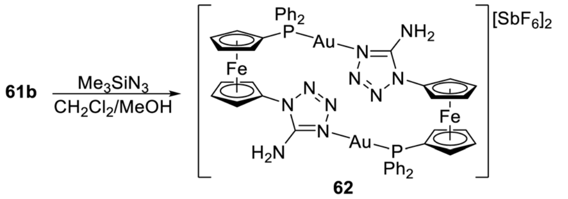
Because analogous dimers resulting from the isomeric phosphinonitrile ligand,[34] $[Au_2(\mu(P,N)\text{-}Ph_2PfcCN)_2]X_2$ (fc =



Scheme 17 Preparation of Au(I) complexes featuring **50** as a ligand (NTf_2^- = bis(trifluoromethanesulfonyl)imide anion, tht = tetrahydrothiophene).



Scheme 18 Au-catalysed cyclisation of (*Z*)-2-methylbut-1-en-3-yn-1-ol into 2,3-dimethylfuran.



Scheme 19 Reaction of **61b** with *in situ*-generated HN_3.

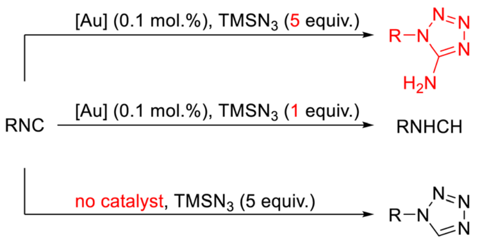
ferrocene-1,1′-diyl, X = SbF_6, $N(SO_2CF_3)_2$), yielded highly active gold(I) catalysts,[35] the catalytic properties of complex **61** were evaluated in the model gold-mediated cyclisation of (*Z*)-2-methylbut-1-en-3-yn-1-ol into 2,3-dimethylfuran (Scheme 18).[36] Unlike the nitrile complexes, however, compounds **61a–b** did not exhibit appreciable catalytic activity under otherwise similar reaction conditions. This difference was attributed to a hindered dissociation of the dimeric cation, very likely representing the catalyst activation step. Indeed, DFT calculations performed for the isomeric species $[Au_2(\mu(P,C)\text{-}Ph_2PfcNC)_2]^{2+}$ and $[Au_2(\mu(P,N)\text{-}Ph_2PfcCN)_2]^{2+}$ suggested that the dissociation of the isocyanide complex was approximately 12 kcal mol^{-1} greater than that of the nitrile complex (39 *vs.* 27 kcal mol^{-1}).

Subsequent work[37] focused on the reactivity of the dimeric Au(I) complexes towards azides to determine whether the coordinated isocyanide group will enter into cycloaddition reactions to possibly produce any tetrazolate species (*vide supra*). Unexpectedly, the reaction with (trimethylsilyl)azide ($TMSN_3$) in dichloromethane/methanol converted **61b** to another dinuclear complex **62** containing a pair of equivalent, P,N-bridging 1-(1′-(diphenylphosphino)ferrocen-1-yl)-5-aminotetrazole-κ^2P, N^4 ligands (Scheme 19). Apparently, the Au-bound isocyanide group underwent a twofold addition of HN_3 *in situ* formed from $TMSN_3$ and methanol, which was originally added to dissolve the poorly soluble precursor **61b**.

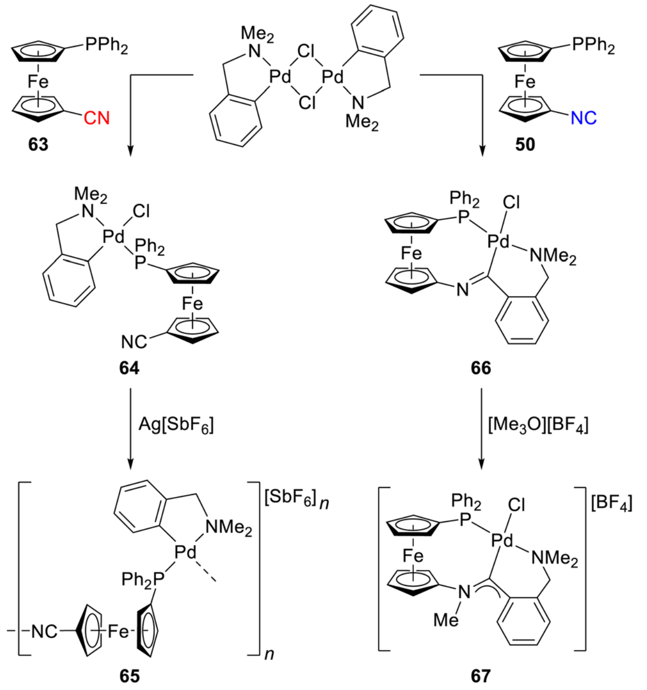
This serendipitous discovery prompted a systematic study to determine whether the conversion of isocyanides to difficult-to-access 5-aminotetrazoles can be achieved with other substrates and, mainly, in a catalytic manner. Reaction tests revealed that as little as 0.1 mol% of the commonly used Au(I) complex $[Au(PPh_3)(MeCN)][SbF_6]$ can convert a range of aliphatic and aromatic isocyanides (RNC) and $TMSN_3$ (5 equiv.) to the corresponding 1-*R*-1*H*-tetrazol-5-amines rapidly and in high yields (usually >90%; Scheme 20). When the amount of $TMSN_3$ was reduced to 1 equiv., the reaction produced only the respective cyanamide RNHCH, whereas the reaction without any catalyst yielded 1-*R*-1*H*-tetrazoles *via* a known cycloaddition reaction.[38] In other words, three different products could be obtained selectively and in high yields from the same starting materials depending on the presence or absence of the gold catalyst and the amount of $TMSN_3$ added to the reaction mixture (Scheme 20).

Another study[39] compared the coordination behaviours of isocyanide **50** and the abovementioned isomeric phosphinonitrile Ph_2PfcCN (**63**) in Pd(II) complexes. The compounds were already differentiated *via* reactions with $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene), representing a $PdCl_2$ source. While **63** reacted cleanly to provide the bis(phosphine) complex $[PdCl_2(\mathbf{63}\text{-}\kappa P)_2]$, a similar reaction with isocyanide **50** produced an intractable mixture, consistent with the complicated reactivity of phosphinoisocyanide **35a** (*vide supra*).

Dissimilar behaviour of **50** and **63** was also noted in the reactions of these compounds with $[(L^{NC})Pd(\mu\text{-}Cl)]_2$, where L^{NC} is the cyclometalated 2-[(dimethylamino-κN)methyl]phenyl-κC^1 ligand. Interaction of **63** with this dimer resulted in cleavage of the chloride bridges to produce the phosphine complex $[(L^{NC})PdCl(\mathbf{63}\text{-}\kappa P)]$ (**64**), which converted to linear coordination polymer **65** propagating *via* P,N-bridging **63** after halogen removal (Scheme 21). In contrast, the reaction with **50** proceeded under the insertion of the isocyanide group into the



Scheme 20 Divergent reactions of isocyanides with *in situ*-generated hydrazoic acid. All reactions were performed in dichloromethane/methanol. The noncatalysed reaction required considerably longer reaction times than the Au-mediated formation of aminotetrazoles did. [Au] = $[Au(PPh_3)(MeCN)][SbF_6]$.



Scheme 21 Reactions of $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ with the isomeric phosphinoferrocene nitrile **63** and isocyanide **50** (L^{NC} = 2-[(dimethylamino-κN)methyl]phenyl-κC^1). All reactions were performed in dichloromethane.

Pd–C bond to afford imidoyl complex **66**. Its subsequent methylation with Meerwein salt yielded the cationic, P-chelating aminocarbene complex **67**.[40]

While compounds **66** and **67** were clearly differentiated by their NMR signatures (*e.g.*, by the ^{13}C NMR shifts of the Pd-bound carbon atoms; δ_C 199.5 and 232.0, respectively; both signals were observed as doublets because of coupling with the phosphine moiety), their molecular structures were markedly similar (Fig. 6). Still, however, small differences in the bond lengths suggested a stronger Pd–C bond and a weaker C–N bond in the carbene complex.

The experimental geometries of **66** and **67** were well reproduced by theoretical calculations, which also revealed that the Pd–C bond in both complexes could be described as a single bond. The conversion of **66** into **67** resulted in electron density accumulation in the Pd–C bond region, suggesting strengthening of the Pd–C bond in the carbene complex, consistent with the structural data. Furthermore, the analysis revealed that the N═C bond retained a double character during the conversion, but its polarisation towards N increased after carbene formation.

In cyclic voltammetry, the complexes underwent reversible oxidation assigned to the ferrocene/ferrocenium redox couple. Nonetheless, the redox potential determined for **66** was lower than that of **67**, which is consistent with the cationic nature of the carbene complex (0.20 *vs.* 0.69 V *vs.* the ferrocene reference). In addition, carbene complex **67** exhibited an irreversible multielectron reduction, presumably corresponding to the Pd(II) → Pd(0) redox transition.

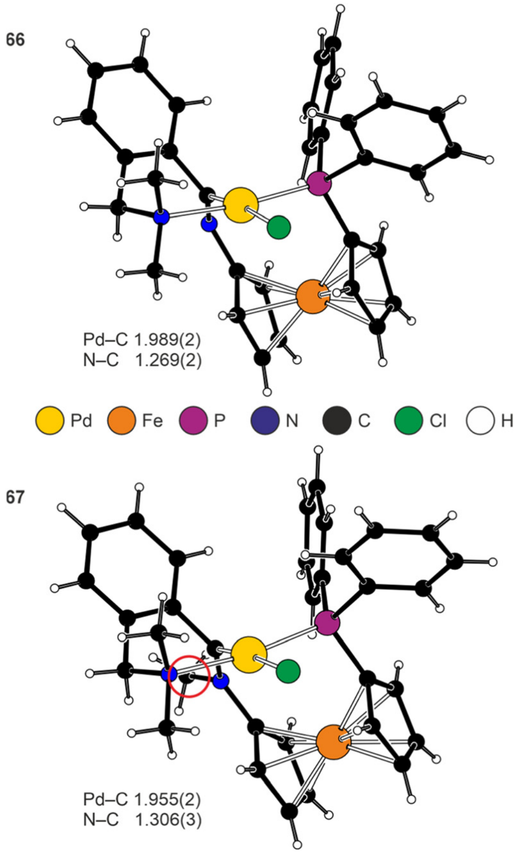
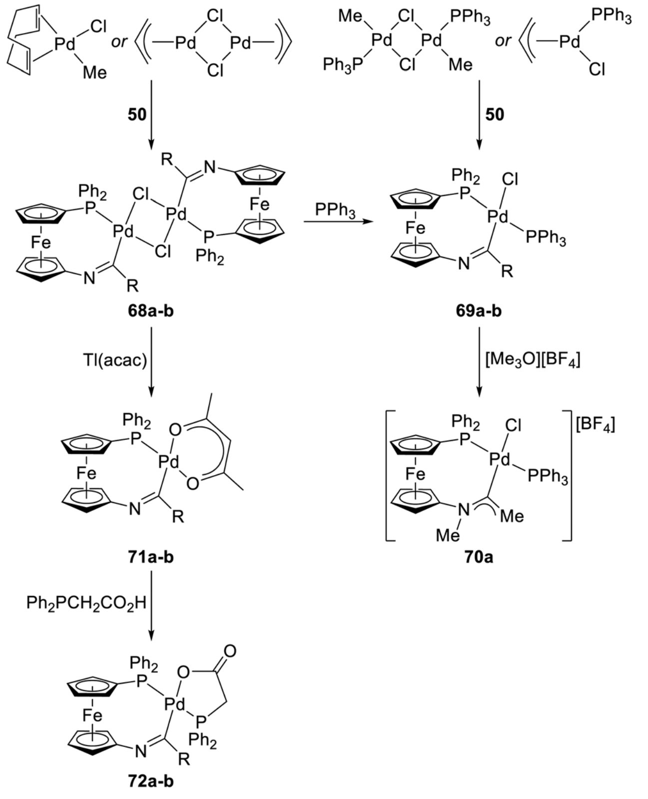


Fig. 6 Structure diagrams of **66** and **67**·3CHCl$_3$. The methyl group in the structure of the carbene complex is indicated by a red circle. The $[BF_4]^-$ anion and the solvent molecules in the structure of **67**·3CHCl$_3$ are omitted for clarity. CCDC deposition numbers: 1857564 and 1857565.

Similar reactions were accomplished with complexes possessing nontethered σ-methyl ligands. Two types of products were obtained, *viz.* the chloride-bridged dimer **68a** and the monopalladium complex **69a**, depending on the presence of the phosphine co-ligand (Scheme 22). The monopalladium complex **69a** was smoothly transformed into the carbene complex **70a** by methylation. Analogous reactions with η^3-allyl precursors were successful only in the first step, producing imidoyl complexes **68b** and **69b** under concomitant η^3-to-η^1 haptotropic isomerisation of the allyl ligand. The subsequent methylation was unselective, resulting in an inseparable product mixture.

The dimeric imidoyl complexes served as convenient entries for bis-chelating complexes **71a–b** *via* reactions with thallium(I) acetylacetonate, Tl(acac). The subsequent reaction with (diphenylphosphino)acetic acid proceeded under proton transfer and chelate coordination of the formed acetate[41] to afford **72a–b**; for **72b**, this reaction was accompanied by double bond isomerisation at the allyl substituent.

Notably, whereas complexes **68a–b** resulted as a mixture of chemically similar isomers (presumably *cis* and *trans*), only one species was obtained after dimer cleavage with PPh$_3$ (for the Pd-methyl complex also during the carbene formation).

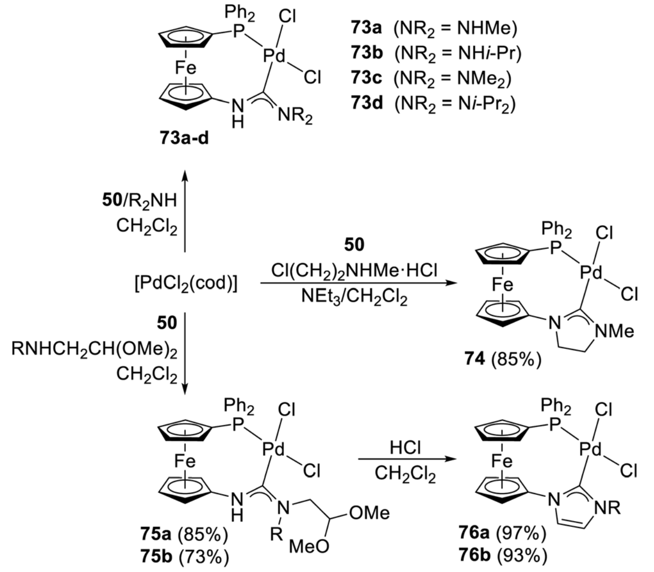


Scheme 22 Reactions of phosphinoisocyanide **50** with Pd–methyl and Pd–allyl complexes and transformations of the primary products (all reactions in dichloromethane) [R = Me (**a**) or $CH_2CH{=}CH_2$ (**b**); for **72b**: R = CH=CHMe].

This observation corresponds to the notion that groups with a strong *trans* effect[42] become destabilised when they occupy mutually *trans* positions.[43] In **69a–b** and **70a**, the C- and P-ligands exerting the largest *trans* influence are indeed found in the *cis* position. Even so, the imidoyl groups in **72a–b** are located *trans* to the carboxylate oxygen.

The reaction of **50** with $[PdCl_2(cod)]$ proceeded under the formation of an ill-defined insoluble material (*cf.* the behaviour of **63**). In the presence of primary or secondary amines, however, the reaction yielded P-chelate diaminocarbene Pd(II) complexes **73a–d** (Scheme 23),[44] which were isolated as air-stable solids in moderate to good yields (≈35–65%) by column chromatography. With suitably substituted amines, the reaction led to cyclic diaminocarbene complexes **74** and **76a–b** (Scheme 23).

All compounds were completely characterised, including structure determination for **73b** (Fig. 7), **73c**, **74**, and **76a**. In all the structures, the ferrocene cyclopentadienyls remained parallel (tilt angles < 6°), but the pivotal $P{-}C(C_5H_4)$ and $N{-}C(C_5H_4)$ bonds were mutually rotated by 5–13° from an eclipsed conformation to create a donor pocket suitable for the $PdCl_2$ moiety. The coordination was further aided by rotation of the carbene NCN unit from the plane of its parent cyclopentadienyl ring by ≈40–45°.



Scheme 23 Synthesis of P-chelating Pd(II) diaminocarbene complexes [for **75** and **76**: R = Me (**a**), i-Pr (**b**)].

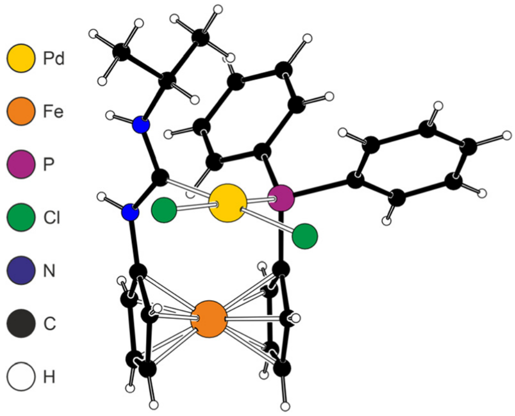
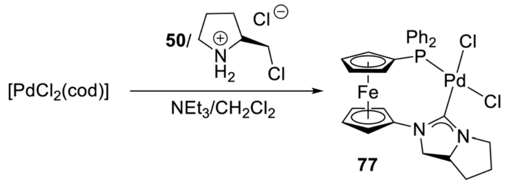


Fig. 7 Molecular structure of **73b**·$CHCl_3$ (only one of the two structurally independent molecules is shown). CCDC reference number: 1922546.

Cyclic voltammetry measurements performed for model compounds **73c**, **74**, and **76a** revealed reversible (quasireversible for **73c**) oxidations attributable to ferrocene-centred redox transitions. This assignment was corroborated by DFT calculations showing that electron removal occurs exclusively at the ferrocene unit, despite the conjugated nature of the compounds. Notably, the redox potentials of the first oxidation were lower ($E^{\circ\prime}$ = 0.28 V for **73c**, 0.35 V for **74**, and 0.48 V for **76**) than the potential determined for $[PdCl_2(dppf\text{-}\kappa^2P,P')]$ ($E^{\circ\prime}$ = 0.58 V) under similar conditions, indicating a higher electron density at the ferrocene unit in the carbene complexes (the potentials are expressed relative to the ferrocene/ferrocenium reference; dppf = 1,1′-bis(diphenylphosphino)ferrocene).

An additional complex with a chiral carbene moiety, compound **77** (Scheme 24), was obtained by the reaction with (*S*)-2-



Scheme 24 Synthesis of carbene complex **77** with a chiral carbene ligand (triethylamine is used to convert the chiral amine hydrochloride into the free base).

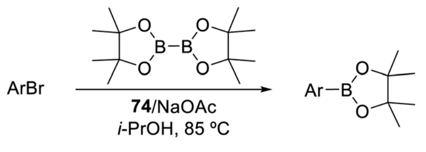
(chloromethyl)pyrrolidine, accessible from (*S*)-proline. The compound was obtained as a mixture of two diastereoisomers differing in axial chirality at the ferrocene unit, which has a fixed conformation because of stable and rigid chelate coordination. The stereoisomers were separated by chromatography and characterised using electronic circular dichroism spectroscopy, and the dominant product was structurally authenticated as an (S,R_{ax}) isomer.

The Pd(II)-carbene complexes were further applied as stable and defined precatalysts for Pd-mediated Miyaura borylation[45] of aryl bromides with bis(pinacolato)diboron (Scheme 25). In this reaction, the imidazole-based carbene complexes performed best, achieving virtually complete conversion of 4-bromotoluene as the model substrate into the corresponding pinacol ester without unwanted biaryl coupling (1 mol% Pd, 85 °C, 1 h reaction time). Reaction scope tests performed with the easily accessible complex **74** confirmed its favourable catalytic properties and wide applicability of this catalytic system.

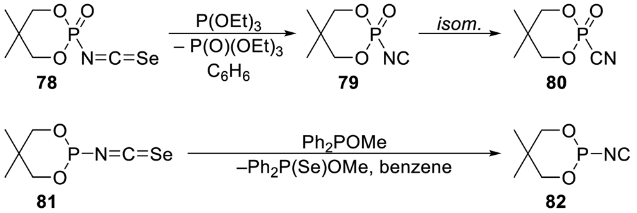
Phosphinoisocyanides with a P–NC bond

Compounds comprising a direct P–NC linkage also remain scarce,[46] partly due to facile isomerisation of isocyanides R_2PNC into their thermodynamically favoured "nitrile isomers" R_2PCN. To prepare compounds with a P–NC bond, Stec and coworkers performed deselenylation of 2-isoselenocyanato-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (**78**) with triethyl phosphite (Scheme 26).[47] The reaction produced an unstable P-isocyanide **79**, showing the CN stretching vibration at 2080 cm^{-1} and the ^{31}P NMR resonance at δ_P 34.5, detected as a 1 : 1 : 1 triplet due to interaction with ^{14}N. However, this isocyanide was found to rapidly isomerise to the cyano derivative **80** (IR: 2210 cm^{-1}, δ_P 28.5 in benzene).

In an attempt to prepare the P(III) analogue (Scheme 26),[48] crude 2-isoselenothiocyanato-1,3,2-dioxaphosphorinane **81** was similarly treated with methyl *P*,*P*-diphenylphosphinite (Ph_2POMe) in benzene. In this case, however, the reaction led to $Ph_2P(Se)OMe$ and nitrile **82** (IR: 2170 cm^{-1}, δ_P: −100.7), most likely due to a rapid isomerisation following the deselenylation step. The nitrile was isolated in a 60% yield.



Scheme 25 Pd-catalysed borylation of aryl bromides with bis(pinacolato)diboron.

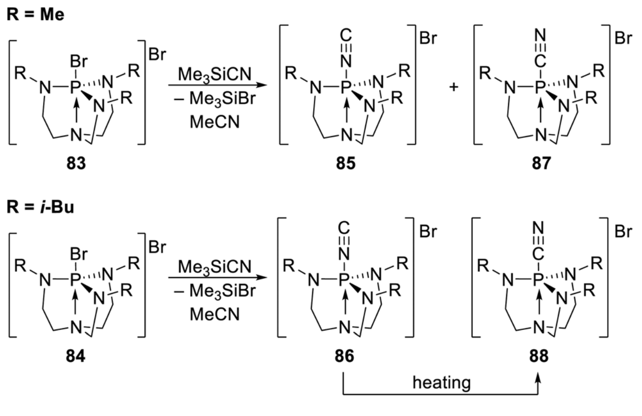


Scheme 26 Synthesis and reactions of (iso)cyanodioxaphosphorinanes.

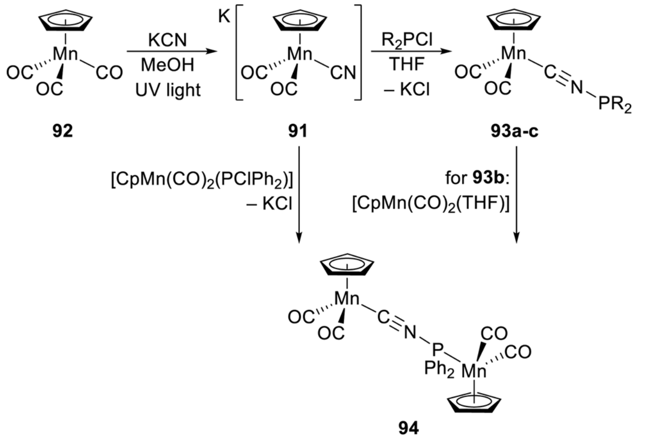
Three decades later, Verkade *et al.*[49] reported an analogous transformation in the molecules of azaphosphatranes (Scheme 27). Specifically, the reactions of P–Br derivatives **83** and **84** with (trimethylsilyl)cyanide were shown to produce P–NC products **85** and **86**. While the less sterically encumbered compound **85** was isolated only as a mixture with the isomeric cyanide **87** (the **85** : **87** ratio was 90 : 10), isocyanophosphine **86** could be isolated in pure form and characterised by spectroscopic methods (IR: ν_{NC} 2088 cm^{-1}; δ_C(NC): 176.5, doublet with $^2J_{PC}$ = 27 Hz) and single-crystal X-ray crystallography. The compound was stable as a solid when stored under an inert atmosphere. Nevertheless, upon heating, it also transformed to the isomeric cyanide **88**. A quantitative isomerisation of the sterically stabilised **86** was achieved upon heating the sample at 80 °C in acetonitrile for 120 h; considerably faster reactions were observed in the presence of a Lewis acid.

The first complexes featuring phosphinoisocyanides R_2PNC as ligands were obtained by electrophilic functionalisation of (cyano)carbonylmetallate complexes. In 1979, Behrens *et al.*[50] investigated the reactivity of the carbonylate complex Na[$Mn_2(CO)_9(CN)$] (**89**) towards a panel of electrophiles. The reaction involving this educt and Ph_2PCl was shown to produce isocyanophosphine complex [$Mn_2(CO)_9(CNPPh_2$-κC)] (**90**).

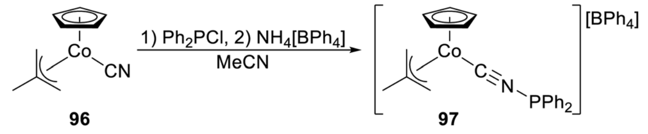
Independently and practically simultaneously, Höfler and Kemp described[51] that cyanometallate K[(η^5-C_5H_5)Mn(CO)$_2$(CN)] (**91**), accessible from cymantrene (**92**) and KCN,[52]



Scheme 27 Synthesis and isomerisation of isocyano-aminophosphines.



Scheme 28 Synthesis and reactions of phosphinoisocyanide complexes **93a–c** [R = Et (**a**), Ph (**b**) and OEt (**c**)]. The preparation of **93a–c** was carried out at low temperature (−40 to −80 °C); the syntheses of **94** were performed in tetrahydrofuran (THF).



Scheme 29 Synthesis of Co-isocyanophosphine complex **97**.

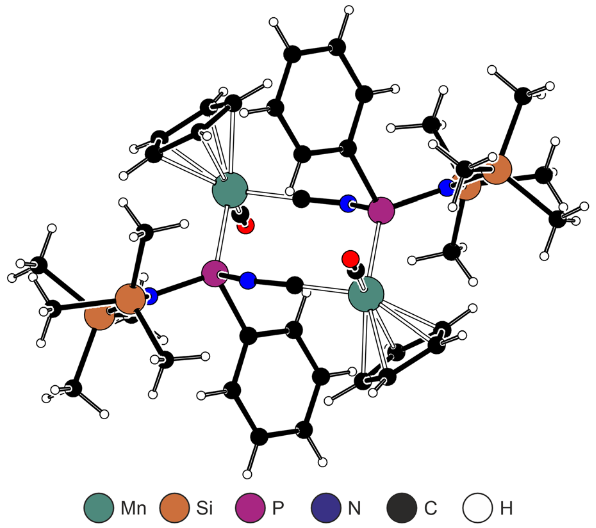
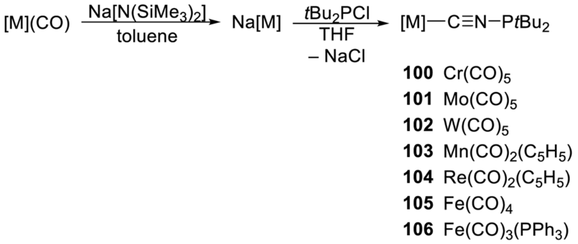


Fig. 8 View of the molecular structure of the dimeric complex **99**. The central $\{Mn_2C_2N_2P_2\}$ ring adopts a chair conformation; the Mn–CN distance and the Mn–C≡N angle are 1.789(2) Å and 175.9(2)°, respectively. The diagram was drawn using the data deposited with the CCDC (deposition no. 1163989).



Scheme 30 Simplified reaction scheme illustrating the preparation of complexes **100–106**.

reacts with chlorophosphines to produce isocyanide complexes **93a–c** in good yields (49–73%; Scheme 28). The compound with the terminal diphenylphosphino group (**93b**) reacted with $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$ to give the dinuclear complex **94**, which was alternatively obtained from **91** and the chlorophosphine complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(PClPPh_2)]$. All compounds and the related isocyanoarsine complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(CNAsPh_2\text{-}\kappa C)]$ (**95**), obtained similarly from **91** and Ph_2AsCl, were studied by spectroscopic methods (IR and NMR spectroscopy, mass spectrometry).

A follow-up study by Behrens and coworkers[53] focused on compound **93b**, and the related isocyanoarsine complexes $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(CNAsMe_2\text{-}\kappa C)]$ (**95-Mn**) and $[(\eta^5\text{-}C_5H_5)Re(CO)_2(CNAsMe_2\text{-}\kappa C)]$ (**95-Re**). Attempts to convert these compounds into cationic nitrosyl complexes with $NO[PF_6]$ failed, leading to decomposition. For **93b**, characteristic ^{13}C NMR resonances were observed for Mn-bound CO (δ_C 227.4) and the isocyanide ligand (δ_C 212.4); an IR band attributed to the CN stretching mode was observed at 2020 cm^{-1} (in a dichloromethane solution).

Later on, an analogous transformation was described with the neutral (cyclopentadienyl)cobalt cyanide complex **96**, which converted into isocyanide complex **97** upon reacting with $ClPPh_2$ and subsequent anion exchange (Scheme 29).[54] In a similar vein, the Mn(I) complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2\{CNP(Ph)N(SiMe_3)_2\text{-}\kappa C\}]$ (**98**) was prepared from $Na[(\eta^5\text{-}C_5H_5)Mn(CO)_2(CN)]$ (**89a**) and $((Me_3Si)_2N)PhPCl$. This complex was shown to spontaneously (albeit only partly) convert into P,C-bridged dimer $[\{\mu(P,C)\text{-}Ph(N(SiMe_3)_2)PNC\}\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ (**99**) under liberation of CO.[55] The molecular structure of **99** is shown in Fig. 8. The formation of the dimeric complex was manifested by a shift of the ν_{CN} band from 2015 cm^{-1} (**98**, in cyclohexane) to 2040 cm^{-1} (**99**, in dichloromethane).

Very recently, this chemistry was revived by Kirk and Hill,[56] who prepared a series of isocyanophosphine complexes using a generally similar route (Scheme 30). The starting carbonylates were generated from the corresponding neutral carbonyl complexes ($[M(CO)_6]$, M = Cr, Mo, W; $[Fe(CO)_5]$, $[Fe(CO)_4(PPh_3)]$ and $[(\eta^5\text{-}C_5H_5)M(CO)_3]$, M = Mn, Re) and $Na[N(SiMe_3)_2]$ in toluene. Their subsequent reaction with $t\text{-}Bu_2PCl$ produced the isocyanophosphine complexes **100–106** in good yields (over 70%). Similar reactions between $Na[W(CO)_5]$ and heavier pnictines $t\text{-}Bu_2ECl$ (E = As and Sb) afforded the respective complexes with homologous isocyanopnictine ligands, $[W(CO)_5(C{\equiv}NEtBu_2\text{-}\kappa C)]$; attempts to prepare the Bi congener failed.

The complexes were studied by spectroscopic methods, X-ray diffraction analysis, and DFT calculations. In their IR spectra, they exhibited diagnostic bands due to the carbonyl ligands and the isocyanide unit ($\nu_{CN} \approx 2030–2110\ cm^{-1}$); ^{13}C NMR signals of the isocyanide groups were observed at δ_C 172–206. Structure diagrams for the representative compounds **102** and **106** are presented in Fig. 9.

Compounds **100–104** were found[57] to undergo [3 + 2] cycloaddition reactions with acetylenedicarboxylic acid dimethyl ester, an electron-poor alkyne, forming carbene complexes with 2,3-azaphospholyl-1-idene ligands (Scheme 31). A similar reaction was observed with $CF_3C{\equiv}CCO_2Et$, while methyl propiolate, ethyl 2-butynoate, and common dienophiles such as maleic anhydride, tetracyanoethylene, and *in situ*-generated benzyne did not react.

The carbene complexes displayed ^{13}C NMR signals at δ_C 289.7, 281.5, and 266.5 for the group 6 metal complexes **107**, **108**, and **109**, respectively, and at δ_C 289.6 and 247.5 for the (η^5-C_5H_5)M complexes **110** and **111**. Together with the results of DFT calculations performed on model species, this indicated that the carbene ligands in the newly prepared compounds are more π-acidic than the conventional N-heterocyclic carbenes (NHCs) and cyclic aminoalkyl carbenes (CAACs). Complexes **107–111** exhibited solvatochromism, which was more pronounced for the group 6 metal complexes. This phenomenon was also theoretically investigated. Analysis of the frontier molecular orbitals has shown that while the three highest occupied molecular orbitals are predominantly metal-centred, the LUMO is based on the heterocyclic carbene ligand with contributions from all ring atoms.

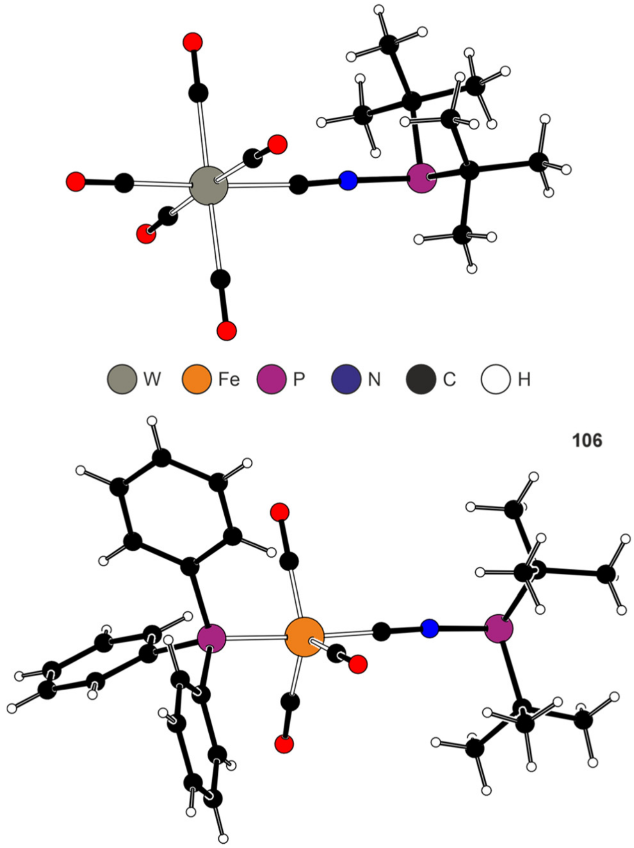
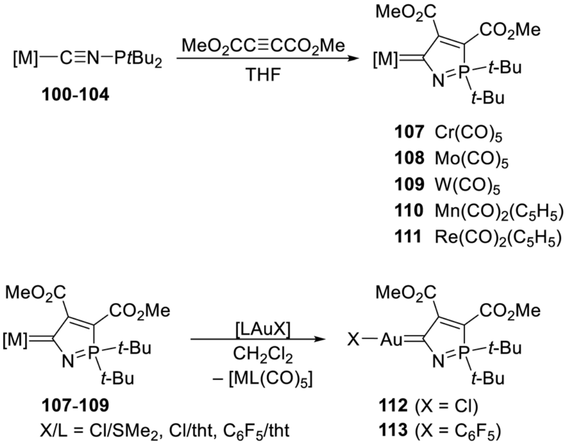


Fig. 9 Views of the complex molecules in the structures of **102** and **106**·C_6H_{14}. The diagrams were drawn using the data deposited with the CCDC (deposition no. 2403979 and 2403974).



Scheme 31 Cycloadditions reactions of isocyanophosphine complexes **100–104** and transmetalation of the group 6 carbene complexes to Au(I) (tht = tetrahydrothiophene).

Compounds **107–109** transmetalated to gold (Scheme 31). The Mo-complex **108** was the most efficient for carbene transfer due to a rapid reaction, which was explained by a larger localisation of one of the higher-lying occupied molecular orbitals (HOMO−3) on the carbene carbon atom as compared to the Cr and W analogues. Attempts to isolate products of transmetalation from **109** to Rh(I), Rh(III), Pd(II) or Pt(II) were not successful.

Summary and outlook

This article highlights the multifaceted chemistry of hybrid phosphines equipped with an additional isocyanide substituent attached either to the organic backbone of the phosphine molecule or directly to the phosphorus atom, which have received only limited attention thus far. Nevertheless, even the few phosphinoisocyanides reported to date exert remarkable reactivities and coordination behaviour, stemming from the particular combination of the two chemically distinct functional parts.

As hybrid ligands, phosphinoisocyanides combine two soft, σ-donor and π-acceptor groups, and can thus coordinate as unidentate P- and C-donors or P,C-chelating and bridging ligands. However, the two groups differ substantially in their steric profiles (*viz.* ψ-tetrahedral phosphine group *vs.* the linear isocyanide unit), which results in the peculiar coordination behaviour (*e.g.*, reduced tendency towards the formation of chelate complexes, which can only occur if the organic part is sufficiently flexible and the donor groups are distant). Apart from the formation of simple and P,C-bridged complexes, the facile insertion and (cyclo)addition reactions involving the (coordinated) isocyanide group provide convenient access to structurally unique carbene complexes in which the carbene unit is tethered to the metal centre by the phosphine moiety. Of note are also the recent studies focused on compounds with the direct P–NC bond, which remained long elusive. All these aspects render phosphinoisocyanides appealing for further studies and applications.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software, or code were included, and no new data were generated as part of this review.

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1 According to IUPAC recommendation, hydrocarbyl derivatives of PH_3 should be called phosphanes. This contribution, however, adheres to the older nomenclature (phosphines), which is still in use, *e.g.*, by *Chemical Abstracts* and is recognised as an alternative to the IUPAC recommendation.

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