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Heterocyclic Carbenes

Phosphinoisocyanide/Alkyne Cycloaddition: Generation of Azaphospholylidene (NPHC) Ligands

*Ryan M. Kirk and Anthony F. Hill**

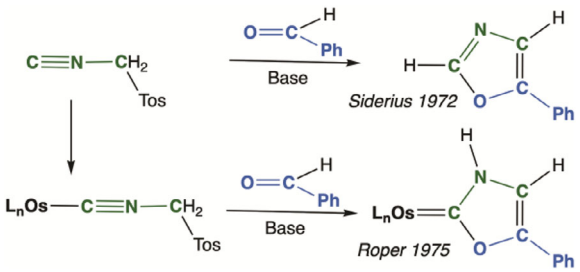
Abstract: Phosphinoisocyanide complexes undergo facile [3 + 2] cycloaddition reactions with activated alkynes to afford the first azaphospholylidene complexes which are rare examples of *N,P*-heterocyclic carbenes (NPHC). In addition to quantifying the donor/acceptor properties of this new class of carbene, their transmetalation reactions are also described.

Pnictogenoisocyanide complexes of the form $[L_nM(C{\equiv}N\text{-}ER_2)]$ (E = P, As or Sb) have recently become available for a diverse range of transition metals (Cr, Mo, W, Mn, Re, and Fe),[1] following earlier sporadic reports of phosphinoisocyanide derivatives of manganese and rhenium, which were identified on the basis of limited spectroscopic data.[2–5] Nothing is yet known about the reactivity profile of these unusual ligands beyond one report of the bimolecular decomposition of an unstable example to form a $\mu{:}\sigma(C),\sigma(P)$-bridged complex.[5] The *intentional* appending of extraneous metal centres to the pnictogen is a process to which we will soon return[6] and whilst this is tangential to the present discussion, suffice to say such processes are a manifestation of nucleophilicity on the part of the pnictogen. Herein, we report the first examples of cycloaddition reactions of phosphinoisocyanides. With activated alkynes, these proceed in a remarkably facile and expedient manner to afford rare examples of *N,P*-heterocyclic carbene[7–9] (NPHC) complexes for a range of metals. These NPHC (2,3-azaphospholyl-1-idene) ligands may in turn be transferred between metal centres.

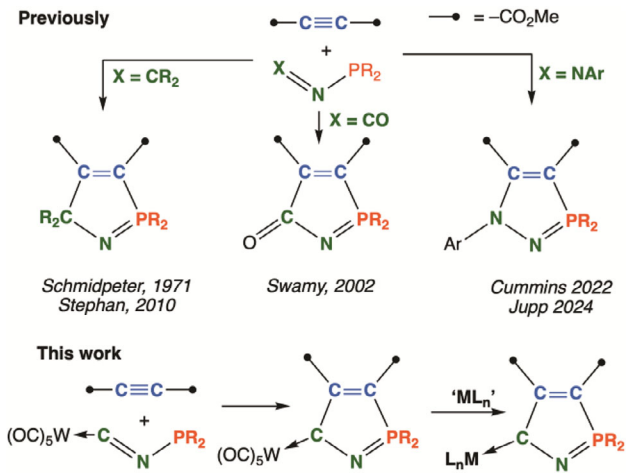
Isocyanides are prolific participants in a variety of cycloaddition reactions, however the outcomes may be varied when the isocyanide is first coordinated to a metal centre in which case *N*-heterocyclic carbenes may arise (Scheme 1).[10,11]

Thus 100 years after Tschugajeff prepared, unrecognised as such, the first isocyanide-derived carbene complex, isocyanides remain key synthons in the development of *N*-heterocyclic carbene complex chemistry.[12,13] The dearth of heteroatom-functionalised isocyanides, free or coordinated, has meant that such cycloaddition reactions have rarely extended to other types of heterocycles. With a range of phosphinoisocyanide complexes now in hand,[1] we have now explored their reactions with activated alkynes and other dipolarophiles, cognisant that encouraging precedent is provided by isolobal methylenimino-, isocyanato- and azo-phosphines (Scheme 2).[14–18]

The reactions of dimethylacetylene dicarboxylate (DMAD, $MeO_2CC{\equiv}CCO_2Me$) with $[L_nM(C{\equiv}NP^tBu_2)]$ [L_nM = $(OC)_5Cr$ **1$_{Cr}$**, $(OC)_5Mo$ **1$_{Mo}$**, $(OC)_5W$ **1$_W$**, (η^5-C_5H_5)$(OC)_2Mn$ **1$_{Mn}$**, (η^5-C_5H_5)$(OC)_2Re$ **1$_{Re}$**] resulted in the immediate formation of intense blue (Cr, Mn) or purple (Mo,



Scheme 1. Cycloaddition reactions of a free[10] versus coordinated[11] isocyanide.



Scheme 2. Cycloadditions of various phosphines.[14–18]

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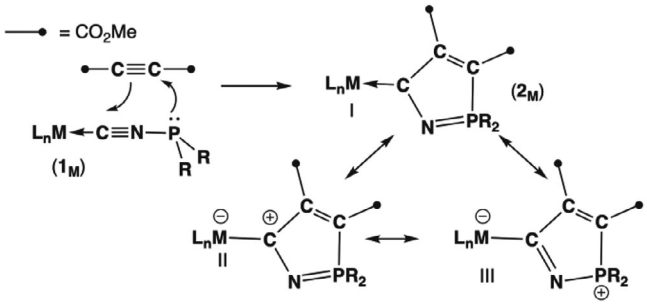


Scheme 3. Synthesis and canonical descriptions of NPHC complexes $\mathbf{2_M}$. R = ^{t}Bu; L_nM = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $Mn(CO)_2(\eta^5\text{-}C_5H_5)$, $Re(CO)_2(\eta^5\text{-}C_5H_5)$.

W, Re) solutions. Flash column chromatography followed by crystallisation afforded all five products in excellent (>80%) yields. Subsequent analysis revealed them to be the novel *N,P*-heterocyclic carbene (NPHC) complexes [L_nM(CNP^{t}Bu$_2$CR = CR)] (R = CO_2Me, collectively $\mathbf{2_M}$), which feature previously unknown[8] 2,3-azaphospholyl-1-idene ring systems (Scheme 3). These arise from a formal [3 + 2]-cycloaddition between the nucleophilic C≡N─P linkage and the electrophilic acetylenic unit. This process is most-likely not concerted, but rather involves initial Michael-type nucleophilic attack by the phosphorus of $\mathbf{1_M}$ at one alkyne carbon, followed by ring-closure of the resulting zwitterionic betaine. Numerous examples of nucleophilic attack by phosphines on DMAD have been reviewed and a similar two-step process is invoked for the [2 + 3] cyclo-addition reactions of azophosphines with activated alkynes.[17,18,19] The extensive unsaturation of these NPHC ligands combined with their inferred π-acidity would be expected to allow intense metal-to-ligand charge transfer, which is presumed to be the source of the vibrant colours of $\mathbf{2_M}$ (*vide infra*). At present, no analogous cyclisation reaction has been observed between DMAD and the heavier arsino- and stibinoisocyanide complexes [W(C≡NE^{t}Bu$_2$)(CO)$_5$] (E = As, Sb),[1] the pnictogens of which are presumed to be insufficiently nucleophilic to attack the alkyne. Likewise, neither unactivated alkynes RC≡CR (R = Me, Ph) nor the strong dipolarophiles tetracyanoethene, maleic anhydride, 4-phenyl-1,2,4-triazole-3,5-dione, benzyne (as $Me_3SiC_6H_4OTf$-2/F$^-$), methylpropiolate, and ethylbutynoate underwent cycloaddition reactions with [W(C≡NP^{t}Bu$_2$)(CO)$_5$] ($\mathbf{1_W}$). A regioselective (94:6) cycloaddition was however observed between $\mathbf{1_W}$ and ethyltrifluorobutynoate, preferentially placing the CF_3 adjacent to the λ^5-phosphorus centre in the complex [W{CNP^{t}Bu$_2$C(CF_3) = C(CO_2Et)(CO)$_5$}] ($\mathbf{3_W}$). This selectivity presumably reflects the greater electrophilicity of the CF_3-substituted (f^- = 0.27, Z_C = −0.08 a.u.) *cf.* ester-adjacent (f^- = 0.07,Z_C = −0.03 a.u.) carbon in frontier orbital-controlled nucleophilic attack at the alkyne. The iron(0) complexes [Fe(C≡NP^{t}Bu$_2$)(CO)$_3$(L)] (L = CO, PPh_3)[1] *did* visibly react with DMAD in CH_2Cl_2 solution, though only poorly soluble, so-far unidentified, materials were observed.

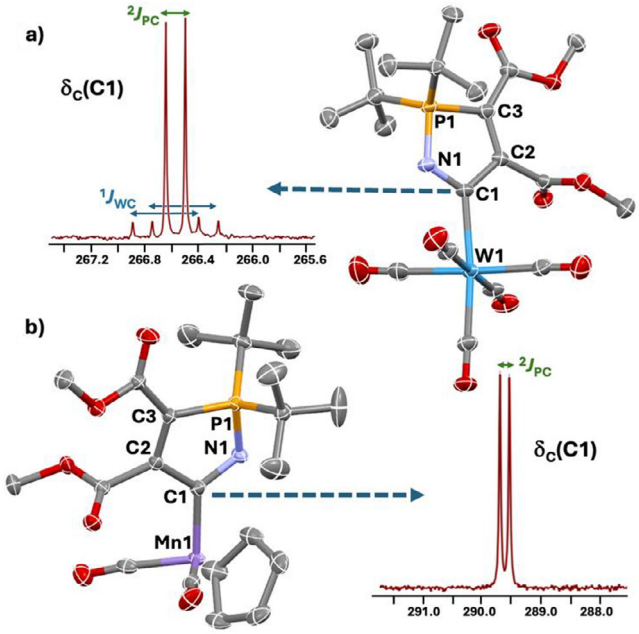
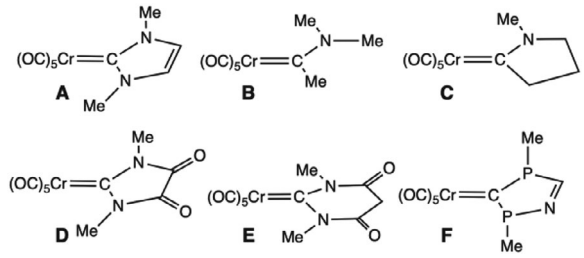


Figure 1. The molecular structures of a) $\mathbf{2_W}$ and b) $\mathbf{2_{Mn}}$ in crystals (Hydrogen atoms omitted, 50% displacement ellipsoids). Selected distances (Å) and angles (°): $\mathbf{2_W}$ W1-C1 2.222(3), C1-C2 1.545(4), C2-C3 1.343(3), C3-P1 1.801(3), P1-N1 1.667(3), N1-C1 1.319(4), N1-C1-C2 111.6(3), C1-C2-C3 114.3(2), C2-C3-P1 105.6(2), C3-P1-N1 96.3(1), P1-N1-C1 112.1(2). $\mathbf{2_{Mn}}$ Mn1-C1 1.923(1), C1-C2 1.530(2), C2-C3 1.352(2), C3-P1 1.805(1), P1-N1 1.637(1), N1-C1 1.347(2), N1-C1-C2 110.7(1), C1-C2-C3 115.1(1), C2-C3-P1 104.6(1), C3-P1-N1 97.0(1), P1-N1-C1 112.1(1). Inset: Vignettes of the high frequency carbene resonance region of $^{13}C\{^1H\}$ NMR spectra of $\mathbf{2_W}$ and $\mathbf{2_{Mn}}$.

Spectroscopic data for all six $\mathbf{2_M}$ and $\mathbf{3_W}$ are provided in the Supporting Information, however some features call for comment: Sharp ^{31}P NMR peaks between 100–110 ppm are observed for the Group 6 species, shifted slightly to lower frequency (80–100 ppm) for the Group 7 examples; the strong $^1J_{NP}$ coupling evident for the linear $\mathbf{1_M}$ precursors[1] is all but extinguished upon cyclisation (*sp*-N,C → *sp*^{2}-N,C). Solution IR spectra include four ($\mathbf{2_{Cr}}$, $\mathbf{2_{Mo}}$, $\mathbf{2_W}$, $\mathbf{3_W}$) or two ($\mathbf{2_{Mn}}$, $\mathbf{2_{Re}}$) terminal ν_{CO} absorptions but are devoid of the characteristic weak ν_{CN} stretch observed for $\mathbf{1_M}$ at ~2100 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectra the metal-bound carbene signals manifest between 290–240 ppm (to considerably higher frequency of conventional NHC complexes[20–23]). These move to lower frequency in the series $\mathbf{2_{Cr}} \approx \mathbf{2_{Mn}} > \mathbf{2_{Mo}} > \mathbf{2_W} \approx \mathbf{3_W} > \mathbf{2_{Re}}$ (loosely correlating inversely with metal π-basicity) with $^2J_{PC} \approx 30$ Hz (and for $\mathbf{2_W}$, $^1J_{WC} \approx 100$ Hz; Figure 1a Inset). The pair of disparate vinylic ring-carbon resonances appear at ~160 and ~120 ppm ($J_{PC} \approx 50$ and 55 Hz, respectively); that to higher frequency with marginally smaller J_{PC} is assigned to the carbene-adjacent carbon atom. The high frequency chemical shift of this resonance is attributed to the atom's substantial involvement in the LUMO(s) of $\mathbf{2_M}$ (*vide infra*) with the attendant contribution to the paramagnetic component of the shielding tensor.

The solid-state molecular structures of all six NPHC complexes, $\mathbf{2_M}$ and $\mathbf{3_W}$, were determined crystallographically.[24] Those of $\mathbf{2_W}$ and $\mathbf{2_{Mn}}$ being representative are shown in

Table 1: Calculated[a] parameters for model N and P heterocyclic carbenes[b]



	Natural charge[c]			Löwden bond order		Bond length		f^- (C)
	Z_C a.u.	Z_M a.u.	Z_N a.u.	M = C –	C–N –	M=C Å	C–N Å	a.u. a.u.
A	+0.13	+0.38	−0.40	0.77	1.41	2.140	1.365	0.028
B	+0.07	+0.39	−0.40	0.82	1.68	2.115	1.323	0.293
C	+0.07	+0.37	−0.40	0.84	1.66	2.079	1.319	0.303
D	+0.22	+0.39	−0.50	0.91	1.31	2.060	1.382	0.146
E	+0.22	+0.41	−0.51	0.80	1.36	2.154	1.379	0.209
F	−1.03	+0.42	[d]	0.88	[e]	2.047	[f]	0.191
2_{Cr}'	+0.00	+0.39	−0.94	0.90	1.69	2.033	1.333	0.018
2_{Mo}'	+0.03	−0.25	−0.93	0.93	1.71	2.187	1.333	0.055
2_{W}'	−0.03	+0.08	−0.93	0.98	1.70	2.186	1.333	0.059

[a] DFT:B97X-D/6–31G*/LANL2Dζ. [b] For a similar treatment of a more extensive library of 29 carbenes bound to the "Mn(CO)$_2$(η^5-C$_5$H$_5$)" fragment in addition to other C$_1$ p-acidic ligands see Table S1, Supporting Information. [c] 1 a.u. = 0.1602 × aC. [d] $\boldsymbol{Z_P}$ = +0.97. [e] Mean LBO(C—P) = 1.29. [f] Mean **r**(C—P) = 1.756 Å.

Figure 1 whilst $\mathbf{2_{Cr}}$, $\mathbf{2_{Mo}}$, $\mathbf{2_{Re}}$, and $\mathbf{3_W}$ are detailed in the Supporting Information.

The three Group 6 complexes are isomorphous ($P2_1/n$) and effectively isostructural, differing only very slightly in the relative rotations of the M(CO)$_5$ centres. Though not isomorphous ($\mathbf{2_{Mn}}$: $P2_1/c$; $\mathbf{2_{Re}}$: P-1), the Group 7 "piano–stool" structures are also essentially isostructural. The M1-C1 bonding distances ($\mathbf{2_{Cr}}$ 2.086(1) Å; $\mathbf{2_{Mo}}$ 2.225(2) Å; $\mathbf{2_W}$ 2.222(3) Å; $\mathbf{2_{Mn}}$ 1.923(1) Å; $\mathbf{2_{Re}}$ 2.037(3) Å) fall within conventional bounds for the plethora of structural data available for Group 6 and 7 "Fischer-type" carbenes.[24] The azaphospholylidene rings are planar (maximum vertex extrusion < 1°) and relatively sterically unimposing (%V_{bur} = 22%–26%). Interatomic lengths correspond to C1-C2 single (~1.53 Å), C2 = C3 double (~1.34 Å), and C3-P1 single (~1.80 Å) bonds. The enhanced π-basicity of the Group 7 metals relative to the pentacarbonyl ligated Group 6 centres might be expected to somewhat reduce the significance of the zwitterionic canonical forms **II** and **III** (Scheme 3) and possibly also accounts for their lower frequency ^{31}P resonances.

Optimised geometries (DFT:ωB97X-D/6–31G*/LANL2Dζ/gas-phase)[25–27] for the computationally pruned model complexes [L$_n$M(CNPMe$_2$CR = CR)] (R = CO$_2$Me, $\mathbf{2_M}$**'**, ^{t}Bu replaced by Me for computational economy) are given in the Supporting Information and these correspond well to the experimentally determined geometries for the real complexes $\mathbf{2_M}$. As a representative example, the atomic charges, Löwden bond orders, condensed atom Fukui indices[28,29] and frontier orbitals of interest for $\mathbf{2_M}$**'** (M = Cr, Mo, W) are given in Table 1 and Figure 2 alongside those for a selection of relevant carbenes, *viz*. Öfele's archetypal NHC complex [Cr{= C(NMeCH)$_2$}(CO)$_5$] (**A**),[30] Fischer's acyclic alkyl–aminocarbene [Cr{= C(NMe$_2$)Me}(CO)$_5$] (**B**),[31] Bertrand's cyclic alkyl amino carbene (**C**, CAAC);[32,33] two exemplary π-acidic diamido carbenes (**D**, **E**, DAC),[34] and a model for Bertrand's *P*-heterocyclic carbene (**F**).[35–38] A similar treatment of a wider library of 29 carbene complexes of the type [Mn(=CR$_2$)(CO)$_2$(η^5-C$_5$H$_5$)] is provided in the Supporting Information (Table S1).

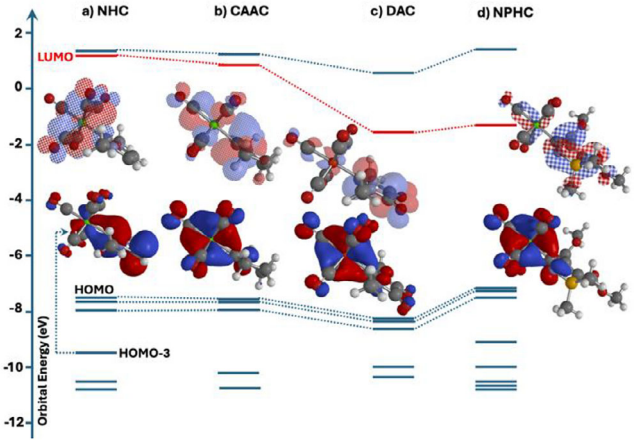


Figure 2. Selected frontier orbitals of interest for the carbene complexes a) [Cr = C(NMeCH)$_2$}(CO)$_5$] (A), b) [Cr(=CNMeC$_3$H$_6$)(CO)$_5$] (C); [Cr{= C(NMeCO)$_2$}(CO)$_5$] D) and c) [Cr{= CNPMe$_2$(CCO$_2$Me)$_2$}(CO)$_5$] ($\mathbf{2_{Cr}}$**'**); DFT:ωB97X-D/6–31G*/LANL2Dζ).

Frontier molecular orbitals for the free carbenes are provided in the Supporting Information (Figure S11), from which it is apparent that the energy of the σ-donor HOMO of the various carbene types (**A**-**C** is rather invariant (*ca* −6.5

to −7.6 eV). In contrast, the π-acceptor orbital energies span some 4.3 eV, from + 3.84 eV for the negligibly π-acidic NHC dimethylimidazolylidene and the reputedly π-acidic free diamidocarbenes **E** (+0.23 eV) and **D** (−0.88 eV) with the NPHC :CNPMe$_2$CRCR (R = CO$_2$Me, LUMO = −0.42 eV) being intermediate between **D** and **E**. The azaphospholylidene is therefore a potent π-acceptor ligand with a comparatively modest HOMO–LUMO gap (*ca* 6.1 eV). Notably the LUMO is only partially carbene-C based, with substantial contributions from all atoms of the heterocycle. The photochemical implications of this are considered below.

Taken together, the computational results indicate that the net acceptor ability for the carbene ligand increases in the order **A** < **B** = **C** < **2$_{Cr}$'** which reflects *both* the comparatively low energy of the LUMO (enhancing Cr→C retro-donation) and the HOMO which is the lowest in energy for the three free carbenes (Supporting Information), thereby mitigating σ-basicity. For these complexes the energies of the HOMO, HOMO-1 and HOMO-2 sets are rather similar, while there is a clear stabilisation of the LUMO for **2$_{Cr}$'**. This raises an intriguing possibility, given that complexes of NHC, CAAC, and Fischer aminocarbenes are characteristically impervious to nucleophilic attack at the carbene carbon. That said, while azaphospholylidene complexes may well be prone toward nucleophilic attack, a consideration of both natural charges (charge-control) and atom-condensed Fukui functions (FMO-control) for atoms in the heterocycle (Figure S12, Supporting Information) suggest that the carbene carbon is *not* the sole electrophilic site within the heterocycle.

The endearing colours of **2$_M$** (blue to purple) are curious; Group 6 pentacarbonyl "Fischer-type" carbene complexes are invariably generally mundane hues of yellow or orange. Furthermore, all of the **2$_M$** complexes displayed pronounced solvatochromism, for example: **2$_{Mo}$** is blue in cyclohexane, purple in dichloromethane, and magenta in acetonitrile (see Figure 3b inset).

The electronic spectra of all **2$_M$** were measured in several solvents of varying dipole (0.0–3.44[39]); pertinent data are summarised in Figure 3 (see also Table S2 and spectra, Supporting Information). The large molar extinction coefficients ($\varepsilon \approx$ 4000–7000 Lmol^{-1} cm^{-1}) coupled with the general observation that the three highest occupied molecular orbitals are primarily metal-based while the LUMO is predominantly ligand heterocycle-based (Figure 2) leads to the conclusion that the colour arises from MLCT transitions, a supposition confirmed by TD-DFT analysis (Supporting Information). The negative solvatochromism manifest as hypsochromic (blue) shifts with increasing solvent polarity suggests *destabilisation* of the excited state molecule (**2$_M$***) in higher dielectric media. The calculated dipoles, *e.g.*, for the ground (^1S: 10.83 D) and excited states (^1S*: 1.97 D) for **2$_{Mo}$** are consistent with MLCT to a *less polar* excited state that is stabilised by *less* polar media. The hypsochromic shifts are most pronounced for the Group 6 complexes ($\Delta\lambda_{max}$ = 70–90 nm) and while similar behaviour is observed for (less polar) **2$_{Mn}$** and **2$_{Re}$**, this is much less dramatic ($\Delta\lambda_{max} \sim$ 20 nm).

Group 6 Fischer-type carbenes have on occasion been shown to transmetalate to later transition metals, in particular gold(I),[40–45] most likely *via* heterobimetallic

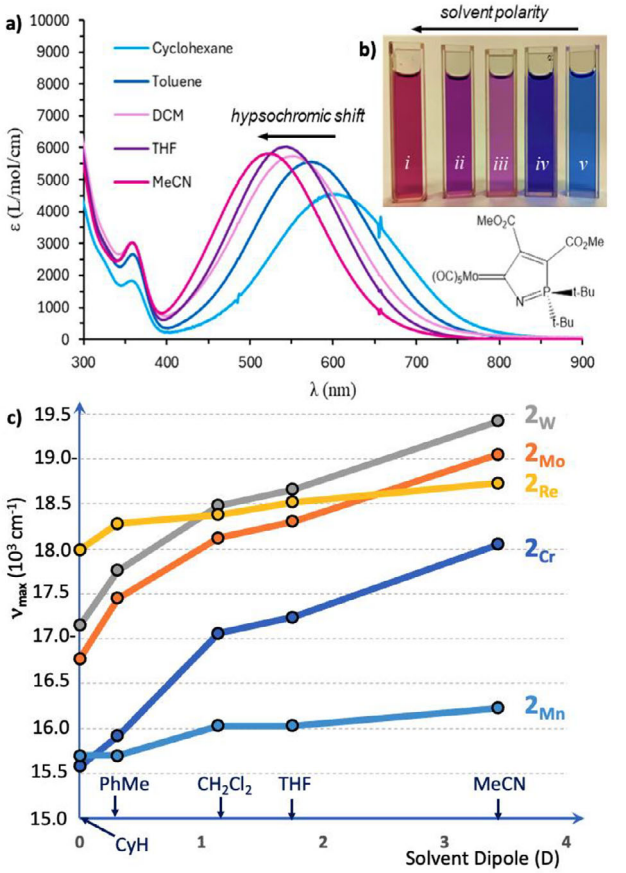
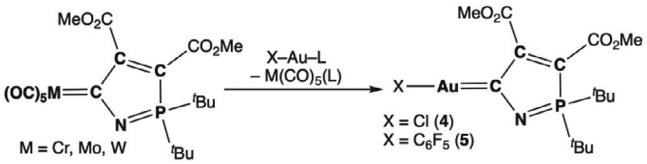


Figure 3. a) Electronic spectra and b) photograph of **2$_{Mo}$** (0.10 mmolL^{-1}) measured in (*i*) acetonitrile, (*ii*) THF, (*iii*) CH_2Cl_2, (*iv*) toluene (PhMe) and (*v*) cyclohexane (CyH) with data from Table S3 (Supporting Information). c) Solvatochromism for the complexes **2$_M$** (M = Cr, Mo, W, Mn, Re), Frequency (10^3 cm^{-1}) for ν_{max} versus solvent dipole (D).[39]



Scheme 4. Synthesis of Gold(I) Azaphospholylidene Complexes. X-Au-L = [AuCl(SMe$_2$)], [AuCl(THT)], [Au(C$_6$F$_5$)(THT)].

μ_2-carbene intermediates[46–50] akin to [WPt{μ-C(OMe)Ph}(CO)$_5$(PMe$_3$)$_2$][49] and [WAu(μ-CHPh)(CO)$_2$(PPh$_3$)(η^5-C$_5$H$_5$)],[50] rather than free carbenes. All three Group 6 carbenes react with [AuCl(L)] (L = SMe$_2$ or THT, tetrahydrothiophene) in CH_2Cl_2 at ambient temperature to afford a mixture of [M(L)(CO)$_5$] and the new yellow–orange gold(I) complex [Au(CNP^{t}Bu$_2$CRCR)Cl] (R = CO$_2$Me **4**, Scheme 4, Figure 4). In practise, **2$_{Mo}$** emerged as the preferred transmetalation agent since complete consumption of both reagents required only ~60 min (*via* TLC), whereas **2$_{Cr}$** and **2$_W$** called for extended reaction times (> 24 h). The increased reactivity of **2$_{Mo}$** is predicated upon the higher-lying HOMO-3 of **2$_{Mo}$'** which is considerably localised on the carbene donor atom relative to **2$_{Cr}$'** and **2$_W$'**. Of the three group 6 complexes,

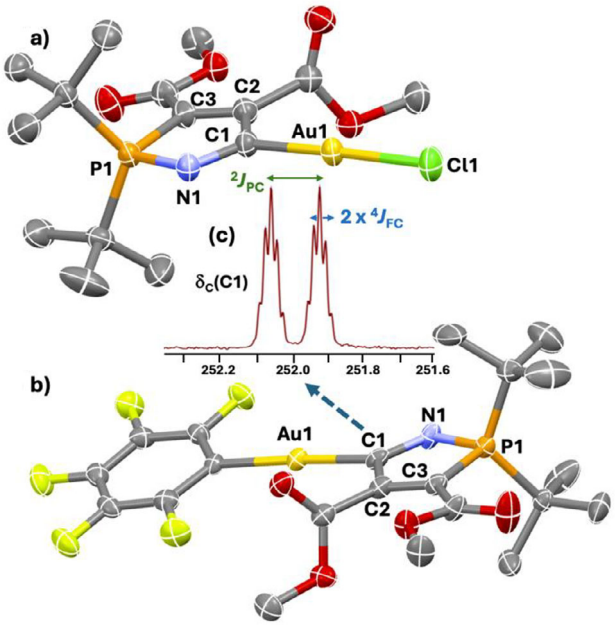


Figure 4. The molecular structures of gold(I) azaphospholylidene complexes in crystals of (a) **4** and (b) **5**·CH_2Cl_2 (Hydrogen atoms and solvate omitted, 50% displacement ellipsoids). Selected distances (Å) and angles (°): **4** Cl1-Au1 2.291(1), Au1-C1 1.988(4), C1-N1 1.305(4), N1-P1 1.681(3), P1-C3 1.811(3), C3-C2 1.345(5), C2-C1 1.517(5), Cl1-Au1-C1 178.1(1), C2-C1-N1 114.2(3), C1-N1-P1 110.5(2), N1-P1-C3 96.1(2), P1-C3-C2 105.2(3), C3-C2-C1 113.9(3); **5** Au1-C1 2.000(5), C1-C2 1.531(7), C2-C3 1.341(7), C3-P1 1.808(4), P1-N1 1.678(4), N1-C1 1.305(6), N1-C1-C2 112.4(4), C1-C2-C3 115.3(4), C2-C3-P1 104.4(4), C3-P1-N1 96.5(2), P1-N1-C1 111.4(4). Inset: vignette of the $^{13}C\{^1H\}$ NMR spectrum of **5** highlighting the carbene resonance with J_{FC} and J_{PC} coupling.

2_{Mo}' carries the largest negative charge on the metal (−0.25 a.u.) which presumably also facilitates gold addition.

The complex **4** proved to be rather fragile, decomposing upon anaerobic chromatography thereby precluding purification, although crude samples containing $[M(L)(CO)_5]$ could nonetheless be characterized by NMR spectroscopy: in **4**, a shift of the ^{31}P signal to 116.2 ppm is noted (in CD_2Cl_2; *cf.* 109.6 ppm for **2** $_W$) and the carbene ^{13}C shift is observed at 227.0 ppm (*cf.* 266.5 ppm for $\mathbf{2_W}$ in C_6D_6) with $^2J_{PC} \approx 26$ Hz; all other signals appear in their usual positions. Single crystallographic quality crystals of **4** were obtained from a crude sample. A similar reaction between $\mathbf{2_{Mo}}$ and $[Au(THT)(C_6F_5)]$ in CH_2Cl_2 provided the analogous but considerably more robust complex $[Au(CNP^tBu_2CRCR)(C_6F_5)]$ (R = CO_2Me **5**) alongside $[Mo(THT)(CO)_5]$. Spectroscopic data were generally unremarkable (CD_2Cl_2: δ_P = 118.9; δ_C = 252.0, $^4J_{CF}$ ~4, $^2J_{PC} \approx 26$ Hz) other than to note the appreciable $^4J_{CF}$ coupling observed for the carbene resonance, which is however typical of other 'AuC_6F_5 carbene adducts.[40–45] Attempts to transfer the NPHC ligand of $\mathbf{2_{Mo}}$ to various Rh^I, Rh^{III}, Pd^{II} or Pt^{II} substrates invariably resulted in decolorisation however the intended products have so far defied isolation.

In conclusion, 2,3-azaphospholylidenes represent a new class of *N,P*-heterocyclic carbene (NPHC) ligands, the viability of which has been demonstrated by examples based on six metals from Groups 6, 7 and 11. Furthermore, the group 6 examples have been shown to serve as transmetalating agents for the installation of these ligands on other metal centers. Spectroscopic and computational data suggest that these new ligands show considerably greater π-acidity than conventional NHC or CAAC ligands, approaching that of alkylidenes and diamidocarbenes.

Supporting Information

The authors have cited additional references within the Supporting Information.[46–68]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Cycloaddition · Heterocyclic carbene · Isocyanide · Phosphorus heterocycles · Transmetalation

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Communication

Heterocyclic Carbenes

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Phosphinoisocyanide/Alkyne Cycloaddition: Generation of Azaphospholylidene (NPHC) Ligands

Rare examples of nitrogen phosphorus heterocyclic carbene (NPHC) complexes of group 6 and 7 metals arise from a facile [3 + 2] cycloaddition of phosphinoisocyanides (L_nM-$CNPR_2$) with activated alkynes. The NPHC ligands are shown to be comparatively π-acidic and the group 6 examples undergo facile transfer of the intact carbene to gold(I) centres.