Synthesis and electronic structure of the first cyaphide-alkynyl complexes

Article (Accepted Version)


This version is available from Sussex Research Online: http://sro.sussex.ac.uk/id/eprint/48848/

This document is made available in accordance with publisher policies and may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher’s version. Please see the URL above for details on accessing the published version.

Copyright and reuse:
Sussex Research Online is a digital repository of the research output of the University.

Copyright and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable, the material made available in SRO has been checked for eligibility before being made available.

Copies of full text items generally can be reproduced, displayed or performed and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.
The novel complexes trans-{Ru(dppe)₂(C≡CR)(C≡P)} (R = CO₂Me, C₆H₄OMe), the first to incorporate cyphamide as part of a conjugated system, are obtained in facile manner. The electronic structure of these compounds is probed by X-ray, DFT and UV/Vis studies.

Low coordinate phosphacarbons (e.g. RC≡P, R₂CaPR₂') have long been a source of intrigue, being isolobal and isoelectronic analogues of more familiar carbo-centric and nitrogenous species, yet still embodying appreciable dichotomies. For instance, the chemistry of phosphaalkynes and phosphaalkenes is dominated by the high-energy \( \pi \)-systems (HOMO) akin to classical alkynes and alkenes, yet the lone pairs remain accessible (cf. nitrides and imines) to engage in reactivity,\(^7\) albeit that those of phosphaalkynes are appreciably stabilised. Such varied facets render low-coordinate phosphacarbons attractive moieties to incorporate into electro-active and conducting molecules as a means of moderating orbital distributions and energies, and thus the molecular electronic properties. Indeed, this is illustrated by numerable examples\(^3\) of phosphaalkene\(^4\) and phosphole-based\(^5\) systems, which exhibit electrochemical and photo-electronic responses in comparison to carbo-centric and nitrogen-doped analogues.

In respect of phosphaalkynes, however, such application has yet to be realised, a direct corollary of a lack of intrinsic kinetic stability within the C≡P moiety and resulting difficulties in accessing appropriate derivatives. Indeed, even complexes of the notionally simple cyphamide ligand (C≡P\(^{-}\)), a direct analogue of the ubiquitous cyanide, have long evaded isolation.\(^6\) Though first observed by Angelici in 1992, in the complex \( '\text{Cl(Et}_2\text{P)}_2\text{Pt(C≡P)}' \),\(^7\) later trapped as \([\text{Cl(Et}_2\text{P)}_2\text{Pt}(-\text{η}^1\text{-C≡C≡P})\text{Pt}(\text{Et}_2\text{P})]_2\),\(^8\) only in 2006 was Grützmacher able to isolate the first unequivocal example of a terminal cyphamide complex, \( [\text{RuH(dppe)}_2\text{(C≡P)}] \) (1),\(^9\) obtained from the \( \text{η}^1\)-phosphaalkyne complex \([\text{RuH(dppe)}_2\text{(P=CSiPh)}_3]^+\) (2') by base-induced desilylative rearrangement.\(^9,10\) Since first observed by this seminal report, no further examples have been described, though Russell and co-workers recently inferred the \textit{in situ} formation of trans-\([\text{Mo(dppe)}_2\text{(C≡P)}(\text{P=CSiMe})_3] \),\(^11\) albeit unisolated.

We are interested in the chemical and electronic properties of organometallics that comprise low-coordinate phosphacarbons,\(^12\) particularly those involving metal-centred conjugation. To this end, Grützmacher`s methodology presented an intriguing opportunity. Herein, we report the synthesis and isolation of the first compounds to incorporate the cyphamide ligand as part of an extended \( \pi \)-system; we also outline preliminary investigations into the electronic structure of these molecules.

The ruthenium alkynyl complexes \([\text{Ru(dppe)}_2\text{(C≡CR)}\text{Cl}] \) (R = CO₂Me \( 3,13 \), \( p\)-C₆H₄OMe \( 4 \)) were converted \textit{in situ} to the respective triflate salts by reaction with AgOTf, subsequent treatment with \( \text{Me}_2\text{SiC≡P} \) affording \([\text{Ru(dppe)}_2\text{(P=CSR}_{3}\text{Me}_2)(\text{C≡CR})]^+\) (R = CO₂Me \( 5 \), \( p\)-C₆H₄OMe \( 6 \)) in good yields (Scheme 1).

\[ \text{Scheme 1. Reagents and conditions: (i) AgOTf, CH}_3\text{Cl}_2; \text{(ii) P=CSR}_{3}\text{Me}_2, \text{CH}_3\text{Cl}_2/C\text{-H}_2; \text{(iii) KO'Bu, thf;}} \]

The identities of \( 5 \) and \( 6 \) follow convincingly from multinuclear NMR spectroscopic data. Thus, the \(^1\)P\(^{[\text{1}]}\)H NMR spectra exhibit quintet and doublet resonances (\( 5' \): \( \delta_\text{p} 108.6; \( 6' \): \( \delta_\text{p} 113.1 \)) in 1:4 ratio, with mutual couplings of ca 30 Hz. A singlet resonance corresponding to the \( \text{SiMe}_3 \) group is apparent in the \(^1\)H NMR spectra, in each case integrating consistently with the dppe backbone, and exhibiting correlation (HMBC) with a characteristic doublet in the \(^13\)C\(^{\text{[1]}\text{H}}\) NMR spectra (\( \delta_\text{C} \approx 190 \)) attributed to the phosphaalkynic centre, and thus confirming the \text{P=CSR}_{3}\text{Me}_2\text{, moiety. Retention of the alkynyl functionality is similarly confirmed, as is the presence of triflate (\( \delta_\text{p} \approx 78.9 \)), while bulk purity was established by microanalysis. The spectroscopic data resemble those reported...
for 2', differences in chemical shift being attributable to a more electron withdrawing nature for the metal fragments of 5' and 6', and thus differing polarization of the alkynyl P and C centres.

The molecular connectivity was further supported by isolation of X-ray quality crystals of 5.OTf, obtained by slow cooling of a saturated CDCl₃ solution of the salt (Figure 1). The cation exhibits the anticipated geometry, with the trans-disposed alkynyl and phosphalkyne adopting near perfect linearity (\(\angle\text{C-Ru-P} = 177.0(3)\), \(\angle\text{Ru-C}_2\text{C} = 178.0(10)\); \(\angle\text{Ru=PC} = 175.7(4)\) °); this contrasts the situation observed in 2' and Jones' [RuH(dppe)\(_2\)(η\(^-\)P=CM)]\(_2\),\(^{15,16}\) both of which exhibit appreciably bent geometries for the phosphalkyne unit (\(\angle\text{Ru=PC}=165.5\(2\))\(^\circ\)) and 153.7(2) ° respectively, attributed to steric encumbrance. The internal geometry of the 5' unit is largely unremarkable; the C-P linkage (1.528(11) Å) is comparable to those of 2' (1.530(3) Å)\(^{17}\) and Russell's trans-[Mo(dppe)\(_2\)(η\(^-\)P=CSiMe\(_3\))]\(_2\) (1.540(2) Å),\(^{15}\) which are consistent with prior examples.\(^{15,16}\) A somewhat short C=C distance is noted. (1.153(15) Å; cf. 1.16 – 2.25 Å from a CCDC search)\(^{17}\), but is mirrored in the parent alkynyl 3 (1.136(10) Å), and presumably results from disorder within this unit.

\[\text{acyphide,} \text{Since failed to reveal any intermediates, or significantly slow the reaction.}\]

\[\text{diffraction study (Figure 2).}\]

\[\text{Figure 2. Molecular structure of 8. Hydrogen atoms omitted and phenyl rings reduced for clarity; 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg.; Ru(1)-C(31) 2.082(11), C(96)-P(5) 1.528(11), C(96)-Si(1) 1.858(12), C(91)-C(92) 1.545(15), C(92)-C(93) 1.450, P(5)-C(96)-Si(1) 178.3(6), C(95)-P(5)-Ru(1) 175.7(4), P(5)-Ru(1)-C(91) 177.0(3), C(96)-C(92)-C(93) 171.91(14), C(2)-C(3)-C(4) 178.5(4).}\]

\[\text{In the solid state, 8 exhibits slight distortion from linearity (\(\angle\text{Ru}-\text{C}_2\text{C}=174.4(3)\); \(\angle\text{Ru}-\text{C}_2\text{C}=172.3(2)\) °), as previously noted for other trans-bisalkynyls.}^{19}\] A shorter C-P(1) (1.544(4) Å) and very slightly longer Ru-C(1) (2.065(4) Å) bond are noted as compared with 1 (1.573(2) and 2.057(2) Å respectively), presumably reflecting diminished \(\delta_d\) \(\rightarrow\) \(\pi^{*}_{(\text{SiP})}\) retrodonation within 8, due to the competing trans-alkynyl. It is, however, noteworthy that DFT studies\(^\text{18}\) indicate greater linearity within the conjugated system of 8, together with a longer C-P linkage (1.58 Å), a situation that is mirrored for 7; this would perhaps imply incidence of packing effects in the solid state.

The frontier orbitals of 7 and 8 (Figure 3) are similar to those typically seen in alkynyl and bis(alkynyl) complexes.\(^{20}\) Thus, the HOMO and HOMO-1 in each case derive from the out-of-phase mixing of the Ru (d\(_{xy}\) and d\(_{xz}\)) and C=C(π) and C=P(π) orbitals, with an appreciable contribution from the cyaphide moiety. This is most pronounced for 7 (50 % \(\pi_{(\text{SiP})}\) and 35 % Ru) in which the electron-withdrawing methylpropionate ligand contributes only ca 10% to either orbital. In contrast, the more donating C=CC\(_3\)H\(_2\)OMe ligand contributes significantly to the HOMO of 8 (24 % \(\pi_{(\text{SiP})}\), 17 % \(\pi_{(\text{Ru})}\) and 30 % Ru, 24 % \(\pi_{(\text{C-P})}\)), leading to reduced involvement of the cyaphide, which in turn dominates the orthogonally-lying HOMO-1 (43 % \(\pi_{(\text{SiP})}\), 35 % Ru, 14 % \(\pi_{(\text{C-P})}\)), lying 0.2 eV lower in energy (cf. 0.01 eV for 7). The LUMO of each molecule is appreciably separated from the HOMO (ΔE \= 3.45 eV \(\text{σ}^0\) and 3.77 eV \(\text{σ}^0\)) and centred on the dppe ligands (ca 75 %) and Ru d\(_{xy}\) orbital (25 %), with appreciable Ru-P antibonding character. Higher energy orbitals (up to LUMO+10) are almost exclusively ligand (dppe) based, while the C-P \(\pi^0\) orbitals do not contribute appreciably until LUMO+18/19; the C=C (and for 8 Ar) \(\pi^0\) orbitals feature from LUMO+11.

\[\text{Figure 1. Molecular structure of 5' in crystals of 5.OTf, DCM solvate. Hydrogen atoms are omitted and phenyl rings reduced for clarity; 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg.; Ru(1)-C(31) 2.082(11), C(96)-P(5) 1.528(11), C(96)-Si(1) 1.858(12), C(91)-C(92) 1.545(15), C(92)-C(93) 1.450, P(5)-C(96)-Si(1) 178.3(6), C(95)-P(5)-Ru(1) 175.7(4), P(5)-Ru(1)-C(91) 177.0(3), C(96)-C(92)-C(93) 171.91(14), C(2)-C(3)-C(4) 178.5(4).}\]
It is noteworthy that the lone-pair of the cyaphide moiety is appreciably stabilised with respect to the π-system, lying ca 1.6 eV below the HOMO (HOMO-6 in 7, HOMO-7 in 8). In each case, NBO calculations reveal the lone-pair to be held in an orbital of ca 75 % s and 25 % p character, with polarisation of the C≡P moiety in the sense Pδ−. In this regard, the cyaphide closely resembles classical phosphaalkynes.

Both 7 and 8 were further studied by a combination of UV/Vis spectroscopy and TD-DFT (calculating the first 100 excited states; see ESI for details). Both exhibit strong absorptions around 250 nm (40000 cm⁻¹) arising from Ligand→Ligand charge transfer (LLCT) between the π-CP/CC and dppe π* orbitals. For 7, a further feature around 275 nm (36363 cm⁻¹) is again dominated by LLCT transitions but also involves some Intraligand transitions (ILCT) centred on π(C≡P) → π*(C≡P). A weaker feature around 300 nm (33333 cm⁻¹) is again dominated by LLCT. In contrast, while a dominance of LLCT is also apparent for 8, a strong feature around 298 nm (33550 cm⁻¹) involves significant contributions from ILCT, centred on π→π* transitions of the alkylnyl (HOMO→LUMO+11) and C≡P (HOMO→LUMO+18/19) ligands; a smaller contribution from metal→ligand charge transfer (MLCT) is evident between ruthenium and the dppe π* orbitals (HOMO→LUMO+5, 9, 10).

In conclusion, we have described the first organometallic complexes to incorporate the terminal cyaphide ligand as part of an extended π-system; this also represents only the second unequivocal report of a terminal metal-cyaphide complex. Structural and theoretical studies reveal a modestly screened cyaphide moiety with a stabilised, but nonetheless accessible, lone-pair akin to classical phosphaalkynes. The cyaphide contributes significantly to the HOMO and HOMO-1, with an influence that is clearly moderated by the trans-alkynyl ligand. The molecules absorb strongly in the UV region, their electronic spectra being dominated by LLCT transitions to the dppe ligands, though ILCT π→π* transitions within the C≡P moiety also contribute, most significantly so in 8 for which further ILCT occurs within the C≡CC₆H₄OMe ligand. These molecules are the first of a novel class of conjugated, organometallic hetero-ynyl complexes that we continue to explore and develop.

This work was supported by the Royal Society, Leverhulme Trust (F/00 230/AL; studentship to NT) and University of Sussex (studentship to VKG). IRC gratefully acknowledges the award of a Royal Society University Research Fellowship. We thank Dr A. K. Brison (Manchester) for collection of Raman scattering data.

Notes and references

13 CCDC 962350: see ESI for full details and ellipsoid plots.
14 CCDC 962351: see ESI for full details.
18 CCDC 990881: crystals grown by vapour diffusion of hexane into thf solution; see ESI for full details.