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ARTICLE TYPE

The preparation, characterisation and electronic structures of 2,4-pentadiynyl nitrile (cyanobutadiynyl) complexes

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Convenient preparative routes to mononuclear ruthenium complexes containing the 2,4-pentadiynyl nitrile, or cyanobutadiynyl, ligand are described. The electronic properties of the $[C_5N]^-$ ligand are closely related to those of not only the cyanide ($[CN]^-$) and 2-propynyl nitrile or cyanoacetylide ($[C\equiv CC\equiv N]^-$) ligands, but also those of the isoelectronic polyynyl ($[C\equiv C]_nR^-$) ligands.

The unsaturated cyanocarbon 2,4-pentadiynenitrile (cyanobutadiyne, $HC\equiv CC\equiv CC\equiv N$, **1**) and other similarly structured cyanocarbons are thought to occur within interstellar clouds, the circumstellar environment of carbon-rich stars and within the atmosphere of Titan.¹ Although recent synthetic developments have permitted the isolation of tens of milligram quantities of pure **1**,² sufficient for improved spectroscopic investigations,³ the use of **1** directly in subsequent synthetic work is still extremely limited.⁴ Nevertheless, the 2,4-pentadiynyl nitrile anion $[C\equiv CC\equiv CC\equiv N]^-$ is an attractive formal synthetic target that would extend the homologous series of cyanide ($[CN]^-$)⁵ and cyanoacetylide ($[C\equiv CC\equiv N]^-$)⁶ ligands, and complement the larger and isoelectronic families of polyynyl ($[C\equiv C]_nR^-$) and polyynediyl ($[C\equiv C]_n^{2-}$) ligands.⁷

We have recently described convenient methods for the synthesis of metal complexes $M(C\equiv CC\equiv N)L_n$ ($ML_n = Fe(dppe)Cp$,⁸ $Ru(PPh_3)_2Cp$,⁹ $Ru(dppe)Cp^*$)¹⁰ containing the 2-propynyl nitrile (cyanoacetylide) ligand from reactions of phenylcyanate, $PhOCN$, with a metal alkynyl anion^{8,9,10a} or 1-cyano-4-dimethylamino pyridinium tetrafluoroborate ($[CAP]BF_4$) with an alkynyl complex, the latter proceeding through an intermediate cyanovinylidene.^{10b} In a useful refinement to these published procedures, we have found that $Ru(C\equiv CC\equiv N)(PPh_3)_2Cp$ (**3a**) and $Ru(C\equiv CC\equiv N)(dppe)Cp^*$ (**3b**) can be prepared in one-pot reactions from the very easily obtained vinylidenes $[Ru(C=CH_2)(L_2)Cp]PF_6$ with KO^tBu and $[CAP]BF_4$.[†]

The synthesis of complexes featuring the cyanoacetylide ligand has prompted us to consider compounds containing the next member of this family of unsaturated cyanocarbon ligands, 2,4-pentadiynyl nitrile. Reaction of $Ru(C\equiv CC\equiv CSiMe_3)(PPh_3)_2Cp$ ¹¹ with $[CAP]BF_4$ ¹² in CH_2Cl_2 at room temperature gave the desired 2,4-pentadiynyl nitrile complex $Ru(C\equiv CC\equiv CC\equiv N)(PPh_3)_2Cp$ (**4a**) in 44% isolated yield after chromatographic purification and crystallisation.[†]

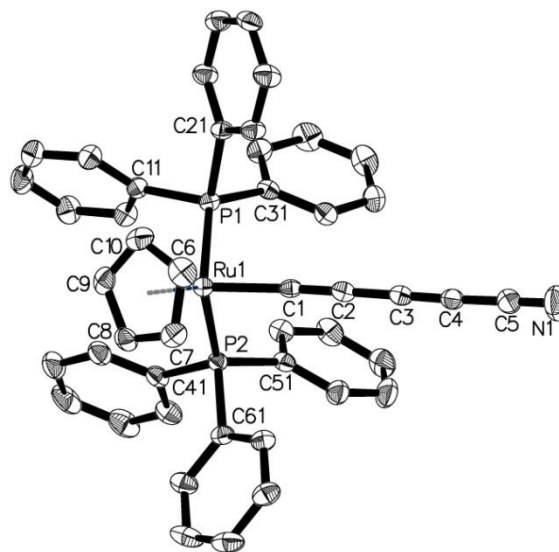


Figure 1. A plot of a molecule of **4a**. Selected bond lengths (Å) and angles (°): Ru1-C1 1.958(3); C1-C2 1.230(4); C2-C3 1.346(5); C3-C4 1.215(5); C4-C5 1.362(5); C5-N1 1.148(5); Ru1-P1 2.2947(8); Ru1-P2 2.3050(9); Ru1-C1-C2 171.9(3); C1-C2-C3 178.9(4); C2-C3-C4 178.7(4); C3-C4-C5 176.6(4); C4-C5-N1 179.8(5).

The isomeric 2-ethynyl-cyanovinylidene, $[Ru\{=C=C(C\equiv CR)(CN)\}(PPh_3)_2Cp]^+$, which could be formed by addition of cyanogen to the C_β carbon of the diyne reagent, was not observed. The ligand structure was established by resonances in the ^{13}C NMR spectrum at 145.5 (t, $J_{CP} = 26$ Hz, C_α), 93.4 (br, C_β), 72.4 (C_γ), 53.4 (C_δ) and 108.4 (C_ϵ), and $\nu(C\equiv CC\equiv N)$ bands at 1977w, 2112m, 2192w cm^{-1} in the IR spectrum, and a single crystal X-ray diffraction study (Figure 1).[‡] The closely related complex $Ru(C\equiv CC\equiv CC\equiv N)(dppe)Cp^*$ (**4b**) was prepared in an entirely analogous fashion, albeit in substantially lower yield (10%) after crystallisation.[‡]

The homologous series $Ru(C\equiv N)(L_2)Cp'$ (**2**),^{10,13} $Ru(C\equiv CC\equiv N)(L_2)Cp'$ (**3**)^{9,10} and $Ru(C\equiv CC\equiv CC\equiv N)(L_2)Cp'$ (**4**) [**a**: $(L_2)Cp' = (PPh_3)_2Cp$; **b**: $(L_2)Cp' = (dppe)Cp^*$] permits a detailed investigation of the characteristics of these cyanocarbon ligands.¹⁴ The key metric parameters of the $Ru-C\equiv CC\equiv CC\equiv N$ chain in **4a** and **4b** are essentially independent of the nature of the auxiliary ligands within the limits of precision. Nevertheless, the

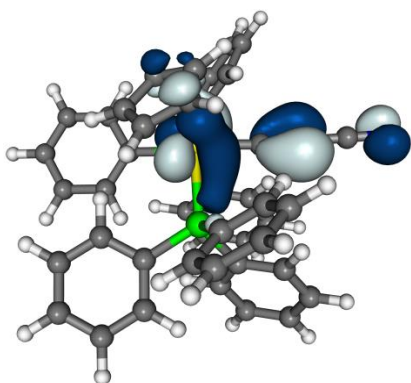


Figure 2. Isosurface plot (± 0.04 (e/bohr^3)^{1/2}) of the HOMO of **3a'**.

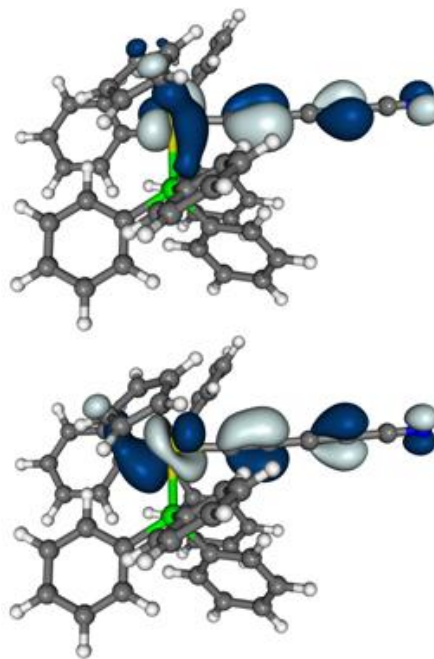


Figure 3. Isosurface plots (± 0.04 (e/bohr^3)^{1/2}) of the HOMO (top) and HOMO-1 (bottom) of **4a'**.

alternation in the bond lengths along the chain clearly supports description of the C_5N ligand in terms of a 2,4-pentadiynyl nitrile moiety. Structural comparisons across the series **2**, **3** and **4** are most readily made within the $Ru(\text{dppe})\text{Cp}^*$ series, with the structures of **2b** and **3b** having been reported earlier.^{10a} The Ru-C(1) bond lengths in **3b** and **4b** are shorter than in the cyano derivative **2b**, and also shorter than in alkynyl and diynyl complexes $Ru(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ (2.015(2) Å)¹⁵ and $Ru(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ (2.015(4) Å).¹¹ The elongation of the average Ru-P bond length on moving from **3b** to **4b** is consistent with trends observed in related polyynyl series and reflects decreasing C→Ru σ -donation, rather than any pronounced increase in the Ru→ C_nN π -back-bonding.^{10b,14,16} The seven atom $Ru\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$ chain in **4a** is linear, with individual angles along the chain varying between 176.6 - 179.8°. In contrast the $Ru\text{C}_5N$ chain in **4b** is substantially bowed, likely a consequence of packing effects,[‡] with individual angles falling between 166.1 - 178.1°.¹⁷

There has been considerable interest in the development of synthetic routes to metal complexes containing polyynyl ($\{\text{C}\equiv\text{C}\}_n\text{R}\}$) ligands, and in the molecular and electronic structures of these long carbon-strings.^{7,14,17} The cyanocarbon ligands contained in **2** - **4** are isoelectronic with ethynyl ($[\text{C}\equiv\text{CH}]^-$), 1,3-butadiynyl ($[\text{C}\equiv\text{CC}\equiv\text{CH}]^-$) and 1,3,5-hexatriynyl ($[\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CH}]^-$) moieties. When this isoelectronic analogy is considered alongside the simple synthetic routes available for **2** - **4**, and the almost ubiquitous nature of the cyanide ligand in inorganic chemistry,⁵ the cyanocarbon complexes make a clear case for further investigation.

Electronic structure calculations (BLYP35/def2-SVP/COSMO)[†] have been undertaken on the representative series **2a'** - **4a'** (the prime notation being used to indicate the computational systems), which complement earlier DFT studies.¹⁴ The optimised structures were in good agreement with the available crystallographic data, with Ru-C(1) bond lengths decreasing with increasing chain length, and bond length alternation clearly apparent in the cyanocarbon ligand. The calculated $\nu(\text{C}_n\text{N})$ vibrational frequencies are in fairly good agreement with experimental values in condensed phases (**2a'** 2131 cm^{-1} , **2a** 2070 cm^{-1} ; **3a'** 2039, 2248 cm^{-1} , **3a** 2000, 2180 cm^{-1} ; **4a'** 1998, 2144, 2259 cm^{-1} , **4a** 1977, 2112, 2192 cm^{-1}).

The character and distribution of the frontier orbitals over the $Ru\text{C}_n\text{N}$ chain is sensitive to the nature of the cyanocarbon fragment. In the case of the parent cyano complex **2a'** the HOMO

is essentially metal centred (55 %), with only a small contribution from the cyano ligand (4 %), whilst the HOMO-1, which lies only 0.1 eV lower in energy, has modestly more mixed Ru d - / CN π -character (52/14 %; Figure S1). The LUMO also has appreciable metal character, and is of δ -symmetry with respect to the CN π -systems.

The general characteristics of these orbitals are preserved in **3a'** although the ordering of the metal d - and $d\pi$ -orbitals are reversed, with the HOMO now being extensively delocalised over the five atom $Ru\text{C}\equiv\text{CC}\equiv\text{N}$ chain (Ru/ C_3N : 42/32 %) (Figure 2). In the case of the 2,4-pentadiynyl nitrile complex **4a'**, the HOMO (Ru/ C_5N : 35/43 %) and HOMO-1 (Ru/ C_5N : 47/40 %) are essentially derived from the anti-bonding combination of the orthogonal ligand π -systems with metal d -orbitals and are hence delocalised over the seven atom $Ru\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$ chain (Figure 3), whilst the LUMO has appreciable cyanocarbon π^* -character (Ru/ C_5N : 8/64 %). These general descriptions are very similar to those derived for closely related polyynyl complexes,^{14,16} and highlight the electronic similarity in these ligand families.

Given this close electronic relationship between metal polyynyl complexes $Ru(\{\text{C}\equiv\text{C}\}_n\text{H})(\text{PR}_3)_2\text{Cp}$ and $Ru(\{\text{C}\equiv\text{C}\}_n\text{C}\equiv\text{N})(\text{PR}_3)_2\text{Cp}$, it is somewhat surprising that calculations with the model radical cations [**2a**]⁺ ($\nu(\text{C}\equiv\text{N})$ 2180 cm^{-1}), [**3a**]⁺ ($\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ 2091, 2288 cm^{-1}) and [**4a**]⁺ ($\nu(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})$ 2055, 2183, 2288 cm^{-1}) reveal a significant degree of electronic and orbital relaxation in both [**3a**]⁺ and [**4a**]⁺ leading to heavily metal localised spin densities (SDs) in all cases (Figure 4, see also Mulliken atomic SDs in Table S5). The localised SDs contrast with the appreciable delocalisation of the α -SOMO over the C_3N - and C_5N -ligands, respectively. Such a localisation of the SD due to spin polarisation of the doubly occupied valence MO manifold is not uncommon for situations in which the SOMO is metal-ligand antibonding (cf. Figure S3[†]).¹⁸ The spin density and orbital composition, together with the calculated vibrational frequencies and key bond parameters,

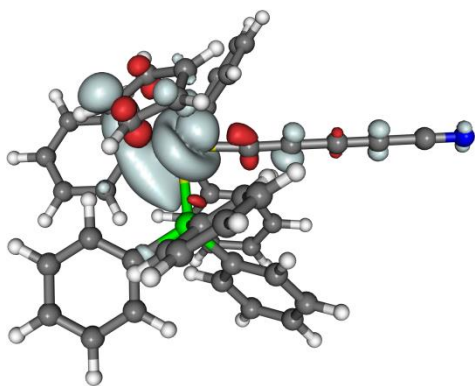


Figure 4. Spin density isosurface plot (± 0.002 e/bohr³) of $[4a']^+$.

support the description of $[2a' - 4a']^+$ in terms of a formal Ru^{III} oxidation state. This observation contrasts the more ligand-based oxidation associated with polyyne chain complexes based on the same metal auxiliary.¹⁶

Conclusions

A simple synthetic route to the first examples of complexes bearing the 2,4-pentadiynyl nitrile ligand is reported. It appears that despite the electronic similarities of closed shell / 18-electron polyyne and cyanocarbon complexes, the cyanocarbon ligands in these ruthenium complexes are less able to support the unpaired electron than their all-carbon cousins. These electronic characteristics provide further opportunities to fine-tune the electronic properties of bimetallic ruthenium 'mixed-valence' complexes in a manner not available to the better known redox non-innocent all-carbon and carbon-rich systems.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: full synthetic details, spectroscopic characterisation, electrochemical data and computational details. Plots of **4a** and **4b** and tables of crystallographic details, bond lengths and angles. Plots of selected frontier orbitals, tables of orbital energies, Mulliken population analyses and Cartesian coordinates from $[2a' - 4a']^{n+}$ ($n = 0, 1$). See DOI: 10.1039/b000000x/

[‡] Crystal Data for **4a**. C₄₆H₃₅NP₂Ru×(1.5 CH₂Cl₂)×(0.125 C₆H₁₄), M=902.92, triclinic, a = 8.8477(3), b = 13.5114(5), c = 18.6418(7) Å, α = 87.912(10), β = 81.897(10), γ = 72.388(10)°, V = 2102.82(13) Å³, T = 120K, space group P-1 (no. 2), Z = 2, μ(MoKα) = 0.675, 25093 reflections measured, 10610 unique (R_{int} = 0.0467) which were used in all calculations. The final wR₂ was 0.1293 (all data) and R₁ was 0.0473 (7910 > 2σ(I)). Crystal Data for **4b**. C₄₁H₃₉NP₂Ru, M=708.74, monoclinic, a = 10.2903(2), b = 22.7951(5), c = 14.8498(3) Å, β = 108.363(10)°, V = 3305.92(12) Å³, T = 120K, space group P2₁/n (no. 14), Z = 4, μ(MoKα) = 0.602, 52188 reflections measured, 8382 unique (R_{int} = 0.0530) which were used in all calculations. The final wR₂ was 0.1075 (all data) and R₁ was 0.0421 (6925 > 2σ(I)).

- (a) R.L. Snell, F.P. Schloerb, J.S. Young, A. Hjalmarson and P. Friberg, *Astrophys. J.*, 1981, **244**, 45. (b) M.A. Cordiner, S.B. Charnley, J.V. Buckle, C. Walsh and T.J. Millar, *Astrophys. J.*, 2011, **730**, L18. (c) V. Vuitton, R.V. Yelle and M.J. McEwan, *Icarus*, 2007, **191**, 722. S.J. Edwards, C.G. Freeman and M.J. McEwan, *Int. J. Mass Spectrom.*, 2009, **279**, 82.
- Y. Trolez and J.-C. Guillemin, *Angew. Chem. Int. Ed.*, 2005, **44**, 7224.
- (a) I. Couturier-Tamburelli, B. Sessouma, A. Coupeaud, J.-P. Aycard and N. Pietri, *Chem. Phys.*, 2009, **358**, 13. (b) Y. Benilan, T. Ferraday, N. Fray, A. Jolly, F. Roulin and J.-C. Guillemin, *Bull. Am. Astron. Soc.*, 2005, **37**, 717. (c) A. Coupeaud, M. Turowski, M. Gronowski, N. Pietri, I. Couturier-Tamburelli, R. Kolos and J.-P. Aycard, *J. Chem. Phys.*, 2007, **126**, 164301. (d) Y. Benilan, A. Jolly, Y. Trolez, F. Raulin and J.-C. Guillemin, *J. Mol. Spectrosc.*, 2007, **245**, 109.
- M. Turowski, M. Gronowski, J.-C. Guillemin and R. Kolos, *J. Mol. Struct.*, 2012, **1025**, 140.
- (a) G.J. Baird, S.G. Davies, S.D. Moon and S.J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1985, 1479. (b) K.R. Dunbar and R.A. Heintz, *Prog. Inorg. Chem.*, 1996, **45**, 283. (c) H. Vahrenkamp, A. Geiss and G.N. Richardson, *J. Chem. Soc., Dalton Trans.*, 1997, 3643. (d) W. Kaim, A. Klein and M. Glockle, *Acc. Chem. Res.*, 2000, **33**, 755. (e) S. Wang, X.H. Ding, Y.H. Li and W. Huang, *Coord. Chem. Rev.*, 2012, **256**, 439.
- (a) W.H. Baddley, C. Panattoni, G. Bandoli, D.A. Clemente and U. Belluco, *J. Am. Chem. Soc.*, 1971, **93**, 5590. (b) R. Kergoat, M.M. Kubicki, L.C. Gomes de Lima, H. Scordia, J.E. Guerschais and P. L'Haridon, *J. Organomet. Chem.*, 1989, **367**, 143. (c) R. Kergoat, L.C. Gomes de Lima, C. Jégat, N. Le Barre, M.M. Kubicki, J.E. Guerschais and P. L'Haridon, *J. Organomet. Chem.*, 1990, **389**, 71. (d) Y. Zhou, A.M. Arif and J.S. Miller, *Chem. Commun.*, 1996, 1881.
- (a) M.I. Bruce and P.J. Low, *Adv. Organomet. Chem.*, 2004, **50**, 179. (b) P.J. Low and M.I. Bruce, *Adv. Organomet. Chem.*, 2001, **48**, 71.
- M.E. Smith, R.L. Cordiner, D. Albesa-Jové, D.S. Yufit, J.A.K. Howard and P.J. Low, *Can. J. Chem.*, 2006, **84**, 154.
- R.L. Cordiner, D. Corcoran, D.S. Yufit, A.E. Goeta, J.A.K. Howard and P.J. Low, *Dalton Trans.*, 2003, 3541.
- (a) R.L. Cordiner, M.E. Smith, A.S. Batsanov, D. Albesa-Jové, F. Hartl, J.A.K. Howard, P.J. Low, *Inorg. Chim. Acta*, 2006, **359**, 946. (b) N.J. Brown, P.K. Eckert, M.A. Fox, D.S. Yufit, J.A.K. Howard and P.J. Low, *Dalton Trans.*, 2008, 433.
- M.I. Bruce, B.G. Ellis, M. Gaudio, C. Lapinte, G. Melino, F. Paul, B.W. Skelton, M.E. Smith, L. Toupet and A.H. White, *Dalton Trans.*, 2004, 1601.
- E.M. Long, N.J. Brown, W.Y. Man, M.A. Fox, D.S. Yufit, J.A.K. Howard and P.J. Low, *Inorg. Chim. Acta*, 2012, **380**, 358.
- (a) R.J. Haines and A.L. duPreez, *J. Organomet. Chem.*, 1975, **84**, 357. (b) M.I. Bruce and R.C. Wallis, *Aust. J. Chem.*, 1981, **34**, 209.
- O.F. Koentjoro, R. Rousseau and P.J. Low, *Organometallics*, 2001, **20**, 4502.
- M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton and A.H. White, *Organometallics*, 2003, **22**, 3184.
- (a) F. Gendron, A. Burgun, B. Skelton, A.H. White, T. Roisnel, M.I. Bruce, J.-F. Halet, C. Lapinte and K. Costuas, *Organometallics*, 2012, **31**, 6796. (b) Direct comparisons between the computational results reported here with the work of Costuas et al. in 16(a) are not possible given the different functionals employed, but trends in the data sets are indicative.
- S. Szafert and J.A. Gladysz, *Chem. Rev.*, 2006, **106**, PR1.
- C. Remenyi and M. Kaupp, *J. Am. Chem. Soc.*, 2005, **127**, 11399.